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Applied Plastics Engineering Handbook

Processing and Materials

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Preface

To be sure, there are a great many plastics books on the market. Some have been written by a single author, while others are edited works with multiple contributors. Some are single-volume textbooks or references, others are multivolume works. They vary widely in scope and coverage. Some sweep over a broad swath of the sprawling plastics industry. Others drill deep down into a segment of the industry—a class of materials, for example, or a process. They vary in level and emphasis as well. Some are addressed primarily to students, others to professionals. Some are designed to meet the needs of researchers, others the needs of practitioners in industry. No single source, no matter how extensive, can meet every need in every setting. The industry, in both its academic and business components is just too massive. In any case, most plastics books are idiosyncratic—their coverage conforms to the predilections or biases of their authors and editors, again not a surprise given the breadth not only of the plastics industry, but also of current and future applications.

Moreover, in trying economic times, with severe pressures on everyone with a demanding job, from professors to engineers, it is difficult to identify potential contributors who can find enough space in their busy professional lives to put together cogent and comprehensive articles or chapters on topics of interest to broad audiences. Nevertheless, it's still possible to assemble a coherent collection of writings from a diverse group of industrial practitioners and experienced academics, who are willing to impart their hard-won knowledge and expertise to an audience of professionals. As a result of the efforts of the contributors to this volume, I have been able to construct a useful reference for a wide audience, including plastics engineers, polymer scientists, materials engineers and scientists, and mechanical and civil engineers. (As a mechanical engineer myself, of a certain vintage, I would have particularly appreciated a reference such as this one, inasmuch as my materials training focused on metallic materials, which have been supplanted in numerous application by lighter plastics and composites.)

Reviewers of the handbook manuscript agreed with my estimation. Here are summaries of their comments. Reviewer #1 asserted that project engineers for devices using or requiring polymeric materials, as well as researchers in basic polymer chemistry modification, in biomaterials device development, and in applying composite metal/polymer materials for structural applications should find information in the handbook to be useful. Chemical engineers and scientists in related disciplines (chemistry, biology) will also find much useful information in this handbook and turn to it as a first choice, particularly if the user has limited experience in the polymer field.

This reviewer wrote of the handbook that "it appears to be the kind of text to which I would refer to refresh my memory on some subject or to create an understanding for myself of a particular polymer sub-field. I would also believe that the text would be invaluable to managers in the field of materials invention or device application who would wish to have the handbook available as a ready, in-depth, reference relative for basic engineering science or manufacturing techniques for polymeric materials. I similarly would think, especially, that applications engineers and managers in consumer products and more complex engineering situations would wish to consult the handbook for initial materials selection and to verify their own understanding of specific polymeric materials' technology and its applicability to a desired technical result.

"The handbook should also be interesting to those students studying or planning a career in chemical processing industries, including those in the medical device and/or applications field. The handbook could be used as a course text though the scope of the book would require two terms for completion."

Reviewer #2 asserted that the encyclopedic approach of this handbook targets a very wide audience—from students (graduate and undergraduate level) to professionals—chemists, designers, technologists, scientists, and engineers and marketing/sales managers in consumer products (appliances, decorative, food and beverage processing); automotive, construction, aeronautics, chemical, electronics industries; and medical device and biopharmaceutical industries.

This handbook, the reviewer continued, could also be helpful for audiences not very familiar with polymer basics looking to find basic introductory articles for plastics processing and applications. More advanced readers will find the book a useful review of more complicated topics, and in this way the handbook will help promote a theoretical basis for plastics industry advancement. This handbook could be recommended as a reference to graduate and undergraduate students with variety of specialties in chemical and polymer engineering—paper and textile chemistry, materials, plastics processing, corrosion protection, coatings, etc., and polymer courses focusing on polymer processing, formulation, and characterization.

According to reviewer #3, the *Applied Plastics Engineering Handbook* can be used by all professionals who have anything to do with plastics. The handbook has a breadth of coverage that allows it to be useful to those new to the plastics industry as well as to experts. This handbook can be used by a practitioner to learn more about how a polymer can make a product better, to determine how a process can be made faster and more efficient, or just to gain a better understanding of what a polymer or process is all about. One purpose of the handbook is to provide experts with information about materials and processes they may already have had experience with as well as with new insights and additional information that may be useful. This handbook can be used in a wide variety of libraries, from universities to companies that process polymers or make plastic products. It would be very useful for small and start-up companies where they cannot hire experts in every different field of endeavor. This handbook supplies information that can give a well prepared practitioner the ability to venture into a new or parallel market. This handbook can also be useful to government agencies and legislators who need to learn more about a hot topic. This handbook can be a must-have reference in any serious polymer library.

The *Applied Plastics Engineering Handbook* opens with a brief introductory chapter on the plastics industry. Then the handbook is divided into five sections. The first section presents in-depth discussions of important polymeric materials and is divided into three parts. The first part, on plastics, begins with a brief survey chapter, and then deals with engineering thermoplastics, polyolefins, fluoropolymers, and poly (vinyl chloride); the second part covers thermoplastic and thermoset elastomers; and the third part focuses on nanocomposites.

The handbook's second major section, Biobased Polymers and Recycling has three chapters, Biodegradable and Biobased Polymers, Polymeric Biomaterials, and Recycling of Plastics.

The book's third major section presents descriptions of key processes, including blow molding, chaotic advection, and its application to extruding micro and nano-structured plastic materials, chemical mechanical polishing: role of polymeric additives and composite particles in slurries, compression molding, extrusion, injection molding, microcellular injection molding, rotational molding, and thermoforming. The section closes with an overview of process monitoring and process control.

The book's fourth major section covers additives, including adhesion promoters, silane coupling agents, coating and colorants, dispersants and coupling agents, functional fillers for plastics, flame retardants, plasticizers, and stabilizers.

The fifth and final section opens with a chapter on design of plastic parts then presents applications: plastics in buildings and construction, infrastructure applications of fiber-reinforced polymer composites, the plastic piping industry in North America, and PET use in blow-molded rigid packaging.

As noted earlier, an editor can develop a handbook like this one only because contributors are willing to participate in the first place and to diligently complete their chapters. Their participation and diligence are tested by the circumstance that I rarely meet them face-to-face. We correspond mainly through email, with occasional telephone calls. That's how things work in today's world. I'm able, in all of the projects I work on, to engage with experts around the world. For this handbook, a handful of contributors are based in Europe (Chris DeArmitt, who contributed two additives chapters himself, was instrumental in finding them), although most are located throughout the United States. In total, I was able to secure the participation of several dozen contributors, the majority of whom are employed in, or consult to, industry, while the remainder are professors at a number of diverse institutions. I cannot say often enough how grateful I am for their time and hard work. My thanks also to my wife, Arlene, whose constant support is vital.

Myer Kutz
Delmar, NY
December 2010

About the Editor

Myer Kutz has headed his own firm, Myer Kutz Associates, Inc., since 1990. For the past several years, he has focused on developing engineering handbooks on a wide range of technical topics, such as mechanical, materials, biomedical, transportation, and environmentally conscious engineering, for a number of publishers, including Wiley, McGraw-Hill, and Elsevier. Earlier, his firm supplied consulting services to a large client roster, including Fortune 500 companies, scientific societies, and large and small publishers. The firm published two major multi-client studies, "The Changing Landscape for College Publishing" and "The Developing Worlds of Personalized Information." Before starting his independent consultancy, Kutz held a number of positions at Wiley, including acquisitions editor, director of electronic publishing, and vice president for scientific and technical publishing. He has been a trustee of the Online Computer Library Center (OCLC) and chaired committees of the American Society of Mechanical Engineers and the Association of American Publishers. He holds engineering degrees from MIT and RPI and has worked in the aerospace industry. In addition to his edited reference works, he is the author of eight books, including *Temperature Control*, published by Wiley, *Rockefeller Power*, published by Simon & Schuster, and *Midtown North*, published under the name Mike Curtis. He lives in Delmar, NY, with his wife, Arlene.

Contributors

Sushant Agarwal
Department of Chemical Engineering, West Virginia University, Morgantown, WV 26506, USA

Ruth K. Arisman
Akagaha, Inc., Lenox, MA 01240, USA
rarisman@akagaha.com

Jamil Baghdachi
Eastern Michigan University, Ypsilanti, MI 48197, USA

Roberto Benson
Department of Materials Science and Engineering, University of Tennessee, Knoxville, TN 37996, USA
rbenson1@utk.edu

S.L. Belcher
Deceased

Mark Berry
PPD Tech, 10 Buttonwood Rd, Bedford, NH 03110, USA
m.berry@ppdtech-usa.com

Kirk M. Cantor
Plastics and Polymer Engineering Technology, Pennsylvania College of Technology, Williamsport, PA 17701, USA

William F. Carroll, Jr.
The Vinyl Institute, 1737 King Street, Suite 390, Alexandria, VA 22314, USA

Ernest A. Coleman
C P Technology, H-211 Willow Street, PA 17584, USA
eccpt@aol.com

Cecil Coutinho
Department of Chemical & Biomedical Engineering, University of South Florida, ENB 118, 4202 E Fowler Avenue, Tampa, FL 33620, USA

Chris DeArmitt
Applied Minerals, Inc., 110 Greene St., New York, NY 10012, USA

Sina Ebnesajjad
FluoroConsultants Group, LLC, 16 Orchard View Drive, Chadds Ford, PA 19317, USA www.FluoroConsultants.com
sina@fluoroconsultants.com

William G. Frizelle
Consutant, 15707 Old Jamestown Road, St Louis, MO 63034, USA

Hota GangaRao
Constructed Facilities Center, College of Engineering and Mineral Resources, West Virginia University, Morgantown, WV 26506, USA

Pieter Gijsman
DSM Research, P.O. Box 18, 6160 MD Geleen, The Netherlands
E-mail: pieter.gijsman@dsm.com

Allen D. Godwin
ExxonMobil Chemical Company, 4500 Bayway Drive, Baytown, TX 77520, USA

Rakesh K. Gupta
Department of Chemical Engineering, West Virginia University, Morgantown, WV 26506, USA
Rakesh.Gupta@mail.wvu.edu

Vinay K. Gupta
Department of Chemical & Biomedical Engineering, University of South Florida, Tampa, FL 33620, USA
vkgupta@eng.usf.edu

József Hári
Laboratory of Plastics and Rubber Technology, Department of Physical Chemistry and Materials Science, Budapest University of Technology and Economics, Budapest, Hungary; Institute of Materials and Environmental Chemistry, Chemical Research Center, Hungarian Academy of Sciences, Budapest, Hungary
jhari@mail.bme.hu

Wei He
Department of Materials Science and Engineering and Department of Mechanical, Aerospace, and Biomedical Engineering University of Tennessee, Knoxville, TN 37996, USA
whe5@utk.edu

Geoffrey Holden
Holden Polymer Consulting, Incorporated, PMB 473, 1042 Willow Creek Road, A101 Prescott, AZ 86305, USA
gbholden@yahoo.com

Ann Innes
Flame Retardants Associates, Inc., PO Box 597, Concrete
WA 98237, USA

Jim Innes
Flame Retardants Associates, Inc., PO Box 597, Concrete
WA 98237, USA

Long Jiang
Composite Materials and Engineering Center, Washington
State University, WA 99164, USA
Jianglong@wsu.edu

Richard W. Johnson
The Vinyl Institute, 1737 King Street, Suite 390, Alexandria,
VA 22314, USA

David Kazmer
Plastics Engineering, University of Massachusetts Lowell,
Lowell, MA 01854, USA

J.E. Mark
Department of Chemistry and the Polymer Research
Center, University of Cincinnati, Cincinnati, OH 45221,
USA

George H. Melton
University of Rhode Island, Kinston, RI 02881, USA
george_melton@mail.uri.edu

Adrian Merrington
Michigan Molecular Institute, 1910 West Saint Andrews
Road, Midland, MI 48640, USA

Sylvia S. Moore
The Vinyl Institute, 1737 King Street, Suite 390, Alexandria,
VA 22314, USA

Eldridge M. Mount, III
EMMOUNT Technologies, LLC, 4329 Emerald Hill Circle,
Canandaigua, NY 14424, USA

Bruce Muller
Plastics Consulting, Inc., 682 S. W. Falcon St. Palm City,
FL 34990, USA

Paul Nugent
www.paulnugent.com

Peter G. Pape
Peter G Pape Consulting, 3575 E. Marcus Drive, Saginaw,
MI 48603, USA
pgpape@yahoo.com

Robert A. Paradis
The Vinyl Institute, 1737 King Street, Suite 390, Alexandria,
VA 22314, USA

Edward N. Peters
Sabic Innovative Plastics, Selkirk, NY 12158, USA
ed.peters@sabic-ip.com

Werner Posch
Plastics Engineering, Upper Austria University of Applied
Sciences, Wels, Austria

Béla Pukánszky
Laboratory of Plastics and Rubber Technology, Department
of Physical Chemistry and Materials Science, Budapest
University of Technology and Economics, Budapest,
Hungary; Institute of Materials and Environmental
Chemistry, Chemical Research Center, Hungarian Academy
of Sciences, Budapest, Hungary
bpukanszky@mail.bme.hu

Roger Rothon
Rothon Consultants/Manchester Metropolitan University,
3 Orchard Croft, Guilden Sutton, Chester
CH3 7SL, UK
rogerrothon@btinternet.com

Nick Schott
University of Massachusetts Lowell, Lowell, MA 01854,
USA

Robert A. Tatara
Department of Technology, Northern Illinois University,
DeKalb, IL 60115, USA

Jim Throne
Consultant, Dunedin, FL 34698, USA
jthrone@tampabay.rr.com

Thomas Walsh
Walsh Consulting Services, 11406 Lakeside Place Drive,
Houston, TX 77077, USA

Patrick Watts
Medcomp Inc., Harleysville, PA 19438, USA

Dan Weissmann
DW & Associates, 16 Windham Dr., Simsbury, CT 06070, USA

Jinwen Zhang
Composite Materials and Engineering Center, Washington State University, WA 99164, USA
jwzhang@wsu.edu

David A. Zumbrunnen
Laboratory for Advanced Plastic Materials & Technology, Department of Mechanical Engineering, Clemson University, Clemson, SC 29634, USA
zdavid@clemson.edu

Introduction to the Plastics Industry

Kirk M. Cantor [1] ***and Patrick Watts*** [2]
[1] Plastics and Polymer Engineering Technology, Pennsylvania College of Technology, Williamsport, PA 17701, USA
[2] Medcomp Inc, Harleysville, PA 19438, USA

The plastics industry encompasses a wide spectrum of the manufacturing world, both geographically and in terms of products produced. Companies all across the world have found profitability within the plastics industry with very little limitation to the applications able to be used. These companies continue to expand the industry each and every day as new applications are discovered and implemented.

Within every industry, there are three main branches which include its markets, materials, and methods. The plastics industry is mainly marketed to supplement other industries. Although the plastics industry is, in fact, a separate industry, its main role is as a support industry to the others. The automotive, medical, packaging, electronics, aerospace, construction, and many other industries have an incredible dependence on the plastics industry. From a medical catheter to the handle of a screwdriver, a wide range of parts and applications are created through the use of plastic, within the industries previously stated.

No industry can function without producing some sort of material for profit. The plastics industry produces parts that contain a high percentage of polymer within the final product. Polymers are made synthetically and contain many properties not found in natural materials. There are many different types of polymers being used today and more are yet to be discovered. Polymers will be discussed in greater detail later on in this book.

Some industries are constrained by the method by which they must create their product. The plastics industry is able to avoid these constraints through the utilization of many different processing methods. The methods used in the formation of plastic products are molding, extrusion, blow molding, thermoforming, rotational molding, and composites fabrication. Each of these processes has its own unique benefits and techniques for shaping the plastic. Of these processes, molding is most widely practiced and extrusion is used second most. Within each of these processes, there are sub-processes which are slightly different from the others, but follow the same basic processing pattern. Each of these will be discussed in greater detail within this book.

1. Statistics of the Plastics Industry

The plastics industry ranks third amongst all other industries in the world. The role of this industry in the global economy is vital since other industries rely on plastic parts in order to generate profits. Also, the size of the industry covers countless markets that depend on the plastics industry to thrive.

The Society of the Plastics Industry (SPI) reports that, in the United States alone, the plastics industry accounts for almost $400 billion in annual sales. A workforce of over 1.1 million people is employed by plastics companies in the United States. The number of facilities in the United States exceeds 17,600, which includes a presence in each of the 50 states.

Many industries are rather expensive to maintain. Although annual sales are so high, the investment will often be nearly as great. However, in 2007, the United States plastics industry nearly had an $11 billion trade surplus.

SPI also states that plastics industry shipments in the United States have grown 3.1% each year since 1980. During the same time, productivity in plastics manufacturing has shown a growth rate of 2.2% annually. This is a faster rate than manufacturing as a whole has shown since 1980.

Plastics manufacturing has a huge economic impact worldwide. The magnitude of the plastics industry is not reserved for only North America. The plastics industry's presence in Europe has continued to strengthen over the past years. Asia's economy, although not as strong as it has been, remains among the world leaders in almost every industry.

Clearly, plastics companies have an influence on the economy and community in almost every area of the United States and also the world. Most people, however, do not realize the magnitude of the impact of the plastics industry in their everyday lives. Even fewer have a basic understanding of the polymer world and the mechanics that are used to create the plastic products we use each and every day.

2. The Future of the Plastics Industry

The plastics industry is currently booming in the industrial world. There seems to be a constant search for more products to be produced using plastic as opposed to the various traditionally used materials. As consumers cry out for more plastic products to simplify their lives, environmentalists continue to raise concern about potential destruction that plastics may bring upon our natural world.

Therefore, the future of the plastics industry should combat these claims and attempt to reduce harmful effects on the environment. Surprisingly enough, this is exactly what the plastics industry is doing.

Over the past years, there has been a push toward the development and implementation of biopolymers. These are polymers that are created using natural monomers such as starches from plants. These polymers are able to biodegrade completely.

The most widely used polymers in industry today are petroleum based. Supposedly, thousands of years will pass before these polymers fully decompose. However, TheRecord.com reported in a May 2008 article that a 16-year-old Canadian high school student was able to decompose a petroleum-based plastic bag in 3 months.

Daniel Burd won the Canada-wide science fair competition by mixing landfill dirt with yeast and tap water in order to isolate bacteria that would decompose a plastic bag. The only byproducts of the reaction are water and carbon dioxide.

It doesn't matter how the waste is dealt with, as long as it can be minimized. The future of the industry needs to find a way to eliminate as high of a percentage of the waste produced as possible. The simplest way to do so is through the use of recycling, but perhaps there is a better method that is not yet functional. Biopolymers may be the wave of the future, or perhaps a simple solution such as Daniel Burd's will be adopted at an industrial scale. Either is a possible solution, but a resolution is needed.

3. Summary

It is easy to realize the importance of the plastics industry when one looks around to see all of the plastic products used in our everyday lives. The world of plastic parts may seem complex, but this is mostly due to the fact that the plastics industry is diverse and not reduced to only a few processing techniques.

Plastics can complete many applications largely in part to the ability of being able to form many different polymers. These polymers are similar in that they contain many repetitions of one or more repeat units, but contain different properties depending on the monomers used.

The main polymers used in industry today are polyethylene, polypropylene, and polystyrene, but there are dozens of polymers used within the industry. Each provides distinct advantages for various applications.

Plastics can either be completely amorphous or may contain a percentage of crystals. Crystals provide structural integrity for the plastic parts. Additives can also be added to the polymers in order to gain strength characteristics.

Many times the desired product can only be produced through using a specific process. There are six main processes by which plastic products are produced. Each of these contains a few sub-processes which are slightly different, but still encompass the main idea of the overall process.

Molding is the most widely used forming process for plastics with injection molding easily being the largest subprocess. Extrusion is a close second to molding and may become the most used process in the future. Other processes that are prevalently used include blow molding, thermoforming, rotational molding, and composites fabrication. Each is used within specific applications and requires a thorough knowledge in order to master the different forming techniques.

Many companies choose to specialize in one or two of the six main processes. This allows for these companies to focus their ability on a small region of the industry as opposed to trying to have a presence in many different fields.

4. Conclusion

As manufacturing continues on in the current state of the world's economy, the plastics industry will continue to be a leader. There is such a large percentage of products in today's consumer market that it is virtually impossible to avoid plastics completely. Also, more and more applications are being found for the plastics industry to support.

The flexibility of the industry is a key factor in its success. The ability to use and develop a multitude of polymers and processes is critical for the survival and growth of the plastics industry.

Overall, the plastics industry is continuously growing and shows almost no sign of slowing. As world powers continue to rely on each other in the manufacturing world, the plastics industry can provide a stable environment for international trade.

Consumers must simply look past the fear of harming the environment and begin to realize that plastics provide a simpler and safer way to produce many products. Even though there are some environmental issues with polymers, there are also ways to reduce and even eliminate these problems. All we must do is learn about the building blocks that are contained within the products which surround us and come to the realization that we can do more with plastics.

Part I: Plastics, Elastomeric and Nanocomposite Materials

1 Plastics Materials

***Kirk M. Cantor*[1] *and Patrick Watts*[2]**
[1] Plastics and Polymer Engineering Technology, Pennsylvania College of Technology, Williamsport, PA 17701, USA
[2] Medcomp Inc., Harleysville, PA 19438, USA

1.1 Polymeric Materials

1.1.1 Long-Chain Molecules

All polymers used within the plastics industry have the same long-chain molecular structure. The only difference between the polymers is the repeat unit along the chain.

Most of the time, the words “plastic” and “polymer” are used interchangeably in conversation. In actuality, these two terms refer to two separate states of the product. The term “plastic” comes from the Greek word “plastikos,” meaning “moldable.” The term caught on since the plastic products are molded into their final shape.

The word “polymer” literally means “many parts.” Polymers are long, chain-like molecules comprised of a main base unit that repeats throughout the structure. Hundreds and even thousands of these units are repeated to form just one polymer chain. Plastic is made up of mostly polymer, but also contains such things as colorant and many other additives.

Polymers can be classified as either being a thermoplastic polymer or a thermoset polymer (Figure 1.1). Thermoplastic polymers are composed of individual polymer chains. Thermosetting polymers crosslink and create a chemical bond between two separate polymer chains. These polymers are generally stronger than thermoplastic polymers after processing but cannot be reground and fed back into the process.

Thermoplastics are more widely used in the plastics industry today due to their lower cost and relatively easy processing capabilities. However, thermosets are mostly utilized when a desired application requires very high strength and/or high heat resistance.

Polymers are also classified by their semi-crystalline or amorphous state. Within a semi-crystalline polymer, there are ordered regions known as crystals. The polymer chains align themselves into layers in some sections and remain amorphous (disordered) elsewhere. All polymers are completely amorphous in the melt state. Crystals form during cooling of the polymer. At present there are no polymers that are entirely comprised of crystals.

Amorphous polymers do not contain any crystalline regions. The polymer chains remain in the random pattern that is created during processing. About half of the major polymers used today are amorphous and the others are semi-crystalline. Figure 1.2 shows what crystalline regions look like compared to amorphous regions.

There are two key transition temperatures for polymers. Amorphous regions of a polymer are frozen in place below the glass transition temperature (T_g). This is the critical temperature needed in order for the brittle, amorphous regions of the polymer to be able to flow.

The second important temperature is the melt temperature (T_m). This is the point above which crystalline regions of a polymer are able to flow. Therefore, amorphous polymers only have a T_g and semi-crystalline polymers have both a T_g and a T_m. It is also important to know that the T_m of a semi-crystalline polymer will be higher than its T_g. Thus, there may be flow (movement) present in the amorphous regions without flow occurring amongst the crystals.

All types of molecules can be characterized by their molecular weight. Since polymers are molecules, we can also characterize them by their molecular weight. Polymers are formed by addition of repeat units. This allows for the molecular weight of a polymer to be an excellent indication of chain length as well. Since we know the molecular weight of the repeat unit, the chain length or total molecular weight

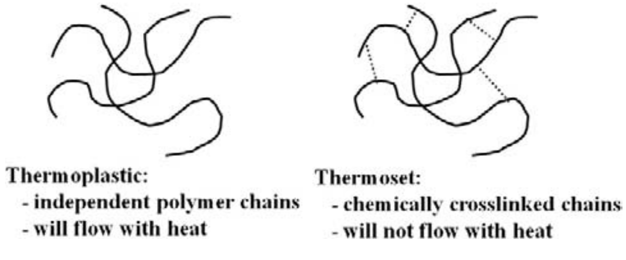

Figure 1.1 Thermoplastic vs. thermoset.

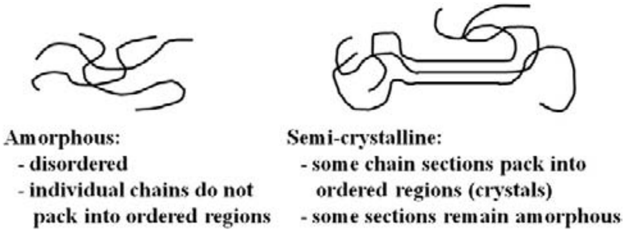

Figure 1.2 Amorphous vs. semi-crystalline.

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can be easily calculated by knowing one of these values. This is important in the polymerization process for the polymers.

The long chains created within the polymerization process and through the use of repeat units provide some very important properties. Long-chain molecules create entanglements with each other. This provides needed strength for products and also a sense of elasticity to return to its original shape. Entanglements also promote a polymer with a high melt viscosity. Viscosity is the resistance to flow.

The chains can be aligned directionally, or oriented, in order to establish desired characteristics. Equal, biaxial orientation allows for excellent strength for films created in industry. Anisotropic, or imbalanced, orientation is important within the creation of fibers. The large majority of the molecules in fibers are oriented in the same direction and create a strong tensile strength in that same direction.

Long chains also promote crystallization in semi-crystalline polymers. Crystal regions provide an added stiffness and increased toughness to the finished product. However, increased crystallization also reduces clarity of the polymer.

1.1.2 Polymer Chemistry

Everything has a molecular structure. In the case of polymers, this structure is comprised of a series of a repeating unit. Prior to becoming a repeat unit in a polymer chain, these small molecules were known as "monomers." Many of these monomers include a double bond between two carbon atoms and four pendant groups attached to these two carbons. The term "polymerization" refers to the process of combining these monomers into very long chains which we know as "polymers." Most of the time, this is accomplished using heat and pressure (Figure 1.3).

The two primary processes available today are addition polymerization and condensation polymerization. Addition polymerization occurs by the monomers simply being hooked on to one another with no by-products produced. Similarly, monomers attach to one another in condensation polymerization, but a by-product, such as H_2O or HCl, is given off.

There are three stages to addition polymerization. First, the polymer chain is initiated by a catalyst of some sort and the chain begins to grow. The second step is the propagation phase. During this stage, the monomers continue to attach to one another until the final stage occurs. Lastly, the termination stage closes the polymer chain. This usually occurs by two growing chains combining to form one finished polymer chain.

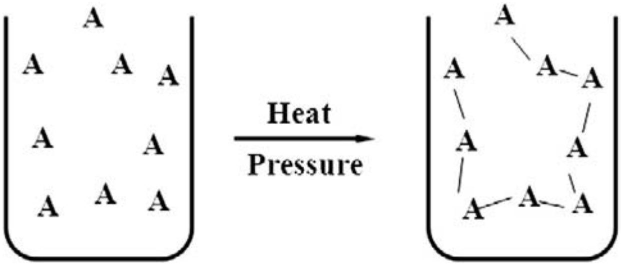


Figure 1.3 Polymerization.

Condensation polymerization takes place as reactions occur within functional end groups. A by-product of the reaction is condensed and released as the reaction occurs. The reactions terminate by consuming all available monomer.

1.1.2.1 Polyethylene

Of the common polymers, polyethylene (PE) is one of the better known and most used. It is formed through addition polymerization of the ethylene monomer (Figure 1.4). PE displays a wide range of properties that largely depends on its molecular weight. PE is also able to be extrusion-processed. However, low-density polyethylene (LDPE) is more easily able to be extruded than high-density polyethylene (HDPE). PE is a semi-crystalline polymer. Most grocery bags are produced from PE.

1.1.2.2 Polypropylene

Another common and relatively inexpensive polymer is polypropylene (PP). It is also formed using addition polymerization, but the propylene molecule is the monomer present (Figure 1.5). PP generally has a lower percentage of crystallinity than PE but displays better strength and stiffness characteristics. It is also able to be extrusion-processed. Trading card collectors use polypropylene sheets to preserve the condition of their cards while showing them off.

1.1.2.3 Polystyrene

Polystyrene (PS) is polymerized through addition polymerization of styrene monomer (Figure 1.6). In its pure state,

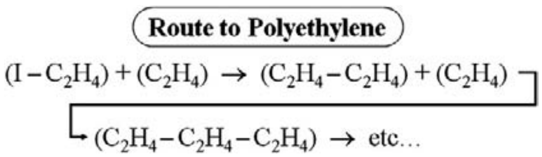
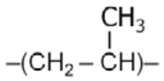
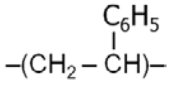


Figure 1.4 Polyethylene chemistry.



$$-(CH_2-\overset{\overset{\displaystyle CH_3}{|}}{C}H)-$$

Figure 1.5 Polypropylene repeat unit.



$$-(CH_2-\overset{\overset{\displaystyle C_6H_5}{|}}{C}H)-$$

Figure 1.6 Polystyrene repeat unit.

PS is stiff, brittle, and clear. It is widely recognizable by its use in CD cases. It is also used to make the white foam found in packaging products and cups. PS is amorphous and thermoplastic. It is sometimes modified with rubber to provide improved impact toughness. This modification produces high-impact polystyrene, or HIPS.

1.1.2.4 Polyvinyl chloride

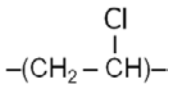
Polyvinyl chloride (PVC) is another extremely common amorphous polymer and is made from vinyl chloride (Figure 1.7). It is addition polymerized. PVC is generally a rigid polymer but can be made flexible by adding plasticizer. It is also fairly easy to use in extrusion processing, but it is thermally unstable which means it can degrade and release hazardous HCl gas. It has a relatively low flammability warning though.

1.1.2.5 Polyamide

Polyamide (PA) is a typical example of a condensation polymerized polymer in which H_2O is released (Figure 1.8). In the case of polyamide, an amine group and an alcohol group of two monomers join to form an amide group. PA, generically known as Nylon, is hygroscopic, meaning it absorbs moisture and must be dried prior to processing. There are many different grades of Nylon, which is highly crystalline. PA has low melt strength, but it is still able to be extruded.

1.1.2.6 Polyethylene terephthalate

Polyethylene terephthalate (PET) is another hygroscopic polymer (Figure 1.9). It is also semi-crystalline but can be quenched to form amorphous PET (APET). PET exhibits excellent strength properties, especially when chains are oriented. Due to its great barrier properties, PET is widely used in the bottling industry.



$$-(CH_2-\underset{}{\overset{\overset{\textstyle Cl}{|}}{CH}})-$$

Figure 1.7 Polyvinyl chloride repeat unit.

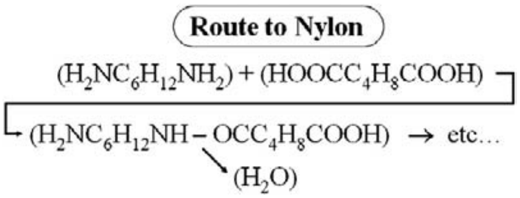


Figure 1.8 Nylon chemistry.

$-(CO\text{-}C_6H_6\text{-}CO\text{-}O\text{-}CH_2\text{-}CH_2\text{-}O)-$

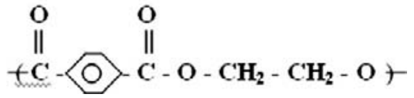


Figure 1.9 Polyethylene terephthalate repeat unit.

1.1.2.7 Acrylonitrile butadiene styrene

Acrylonitrile butadiene styrene (ABS) is a block, addition polymerization polymer. The three monomers that form the structure are present in the name (Figure 1.10). It is amorphous and hygroscopic. ABS is lightweight yet exhibits excellent strength properties. It is most recognizable in computer housings.

1.1.2.8 Polycarbonate

Polycarbonate (PC) is an amorphous polymer (Figure 1.11). It is polymerized through condensation polymerization with NaCl and H_2O being released. It is also hygroscopic. PC has excellent strength, toughness, and optical properties. It is often used in manufacturing bulletproof windows and even lenses for eyeglasses.

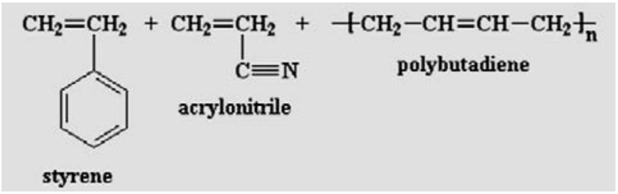


Figure 1.10 Acrylonitrile butadiene styrene chemistry.

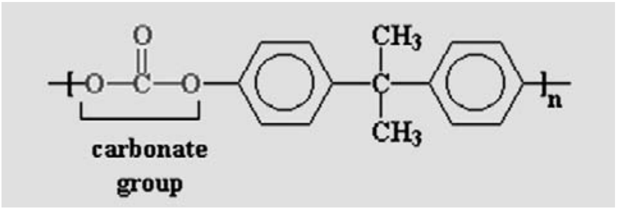


Figure 1.11 Polycarbonate repeat unit.

2 Engineering Thermoplastics

George H. Melton[1], Edward N. Peters[2] and Ruth K. Arisman[3]
[1] University of Rhode Island, Kinston, Rhode Island 02881, USA
[2] Sabic Innovative Plastics, Selkirk, New York 12158, USA
[3] Akagaha, Inc., Lenox, Massachusetts 01240, USA

2.1 Introduction

Engineering polymers comprise a special, high-performance segment of synthetic plastic materials that offer premium properties. When properly formulated, they may be shaped into mechanically functional, semiprecision parts, or structural components. The term "mechanically functional" implies that the parts will continue to function even if they are subjected to factors such as mechanical stress, impact, flexure, vibration, sliding friction, temperature extremes, and hostile environments [1].

As substitutes for metal in the construction of mechanical apparatus, engineering plastics offer advantages such as corrosion resistance, transparency, lightness, self-lubrication, and economy in fabrication and decorating. Replacement of metals by plastics is favored as the physical properties and operating temperature ranges of plastics improve and the cost of metals and their fabrication increases [2]. Plastic applications in transportation, a major growth opportunity, have been greatly accelerated by the current awareness of the interplay of vehicle weight and fuel requirements. The ability to replace metals in many areas has resulted in tremendous growth in engineering thermoplastics.

A significant driving force behind the growth in engineering thermoplastics is the continuing expansion of electrical/electronic markets, which demands smaller, lighter components that operate at higher speeds. In addition, the same requirements are driving the automotive market segment. Original equipment manufacturers strive toward lower production cost, style flexibility, lower maintenance, and more efficient, lower polluting vehicles that utilize better performing materials under the hood and in exterior components. The consumption of engineering plastics increased from 10 million to more than 40 billion pounds from 1953 to 2009. Engineering polymers are the fastest growing segment of the plastics industry with an anticipated growth rate from 8% to 10%. This chapter focuses on the development of engineering thermoplastics during the past 70 years.

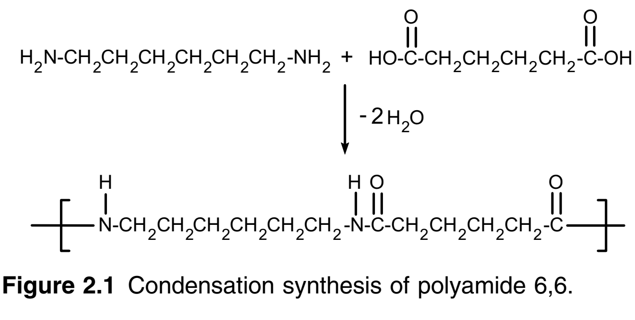
2.1.1 Polyamides

Polyamides, commonly called nylons, were the first commercial thermoplastic engineering polymers and are the prototype for the whole family of polyamides. Nylon 6,6 began at DuPont with the polymer experiments of Wallace Carothers in 1928, and made its commercial debut as a fiber in 1938 and as a molding compound in 1941. By 1953, 10 million pounds of nylon 6,6 molding resin represented the entire annual engineering plastic sales [3,4].

Nylon was a new concept in plastics for several reasons. Because it was semicrystalline, nylon underwent a sharp transition from solid to melt; thus it had a relatively high service temperature. A combination of toughness, rigidity, and "lubrication-free" performance peculiarly suited for mechanical bearing and gear applications. Nylon acquired the reputation of a quality material by showing that a thermoplastic could be tough, as well as stiff, and perform better than metals in some cases. This performance gave nylon the label "an engineering thermoplastic."

Nylon 6,6, PA66, is prepared from condensation reaction of hexamethylene diamine (HMDA) and adipic acid as shown in Figure 2.1.

PA66 exhibits a glass transition temperature, T_g, of 78 °C and a crystalline melting point, T_m, of 269 °C. The crystallinity and polarity of the molecule permit dipole association that conveyed to relatively low molecular weight polymers the properties normally associated with much higher molecular weight amorphous polymers. At its T_m, the



$$H_2N\text{-}CH_2CH_2CH_2CH_2CH_2CH_2\text{-}NH_2 + HO\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_2CH_2CH_2CH_2\text{-}\overset{O}{\overset{\|}{C}}\text{-}OH \xrightarrow{-2H_2O} \left[\overset{H}{\overset{|}{N}}\text{-}CH_2CH_2CH_2CH_2CH_2CH_2\text{-}\overset{H}{\overset{|}{N}}\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_2CH_2CH_2CH_2\text{-}\overset{O}{\overset{\|}{C}}\right]$$

Figure 2.1 Condensation synthesis of polyamide 6,6.

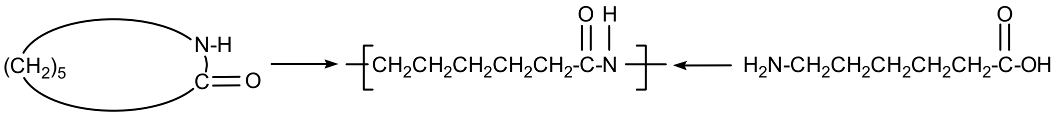


Figure 2.2 Synthetic routes to polyamide 6.

polymer collapsed into a rather low-viscosity fluid in a manner resembling the melting of paraffin wax. It lacked the typical familiar broad thermal plastic range that is normally encountered in going from a glassy solid to a softer solid to a very viscous taffy stage. This factor led to some complications in molding because very close tolerances were required in mold construction, and very precise temperature and pressure monitoring was necessary to prevent flash or inadvertent leaking of the mobile melt. Early molders of nylon were highly skilled—they had to be because the industry was young.

Nylon based on ω-aminocarboxylic acids, although briefly investigated by Carothers, was commercialized first in Germany around 1939 [4]. Of particular interest to the plastic industry is nylon 6, PA6, based on caprolactam, which became available in 1946 in Europe. Allied Chemical Company initially introduced PA6 to the United States for fiber purposes in 1954. Polycaprolactam is semicrystalline. Its T_m of 228 °C is lower than PA66 and has been successfully applied as a molding compound. The synthesis of PA6 from caprolactam appears in Figure 2.2. Nylon 4,6 was developed and commercialized in 1990 by DSM (Dutch State Mines) to address the need for a polyamide with higher heat and chemical resistance for use in automotive and electrical/electronic applications. PA46 is prepared from 1,4-diaminobutane and adipic acid.

Nylon 4,6 has a T_m of 295 °C and has higher crystallinity than nylon 6 or 6,6 [3]. In general, the key features of polyamides are fast crystallization, which means fast molding cycling; high degree of solvent/chemical resistance; toughness; lubricity; fatigue resistance; and excellent flexural-mechanical properties that vary with degree of water plasticization. Deficiencies include a tendency to creep under applied load and very high moisture absorption, which will plasticize the polyamide and lower some properties.

Varying the monomer composition has produced many different varieties of polyamides. Variations include nylon 6,9; nylon 6,10; and nylon 6,12 (made from HMDA and the 9-, 10-, and 12-carbon dicarboxylic acids, respectively); and nylon 11 and nylon 12 (via the self-condensation of 11-aminoundecanoic acid and lauryl lactam, respectively). These specialty nylons exhibit lower T_ms and a decrease in moisture absorption—only one-third or one-fourth that of nylon 6 or nylon 6,6.

When unsymmetrical monomers are used, the normal ability of the polymer to crystallize can be disrupted; amorphous (transparent) nylons can then be formed. These amorphous nylons are not as tough as nylon 6 or 6,6 but they do offer transparency, good chemical resistance in some environments, and lower moisture absorption.

For example, the polyamide prepared from the condensation of terephthalic acid with a mixture of 2,2,4- and 2,4,4-trimethylhexamethylenediamines (PA6-3-T) was developed at W. R. Grace and Company, later produced under license by Dynamit Nobel AG, and currently available from Evonik Industries under the trade name Trogamid TR. This amorphous polyamide exhibits a T_g of 148 °C, high clarity, stiffness, toughness, resistance to chemicals, and very good resistance to UV damage. It is used in water filter housings, flow meters, grease containers, and spectacle frames.

Another amorphous nylon was developed at Emser Werke AG and is based on aliphatic, as well as cycloaliphatic amines and terephthalic acid. It is marketed under the Grilamid trade name by EMS-Chemie. This amorphous nylon exhibits a T_g of 155 °C, high transparency, stiffness, and resistance to chemicals. It is used in viewing glasses, transparent housings, and high-quality spectacle frames.

2.2 Aromatic Polyamides, Aramids

Nylons prepared from aromatic diamines and aromatic dicarboxylic acids can lead to very high-heat aromatic nylons (aramids). Poly(*m*-phenyleneisophthalamide), MPIA, is made from *m*-phenylenediamine and isophthalic acid and has a T_g of 280 °C. Its structure is shown in Figure 2.3 and available from DuPont under the Nomex trade name. MPIA is used in fibers to make heat-resistant and flame-retardant apparel, electrical insulation, and composites.

Poly(*p*-phenyleneterephthalamide), PPTA, is made from *p*-phenylenediamine and terephthalic acid and has a T_g of 425 °C and a T_m of >500 °C. Its structure is shown in Figure 2.4 and is available from DuPont under the Kevlar

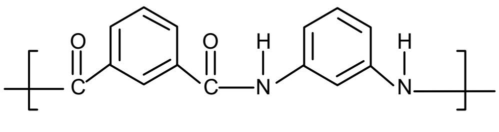


Figure 2.3 Structure of MPIA.

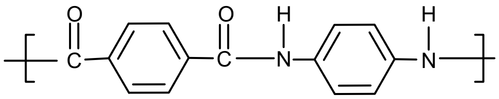


Figure 2.4 Structure of PPTA.

trade name. PPTA is used to make highly oriented crystalline fibers derived from liquid-crystalline technology. PPTA fibers exhibit a very high modulus and its uses include composites for sporting goods, bullet-resistant apparel, automotive transmission parts, and tires.

2.3 Semiaromatic Polyamides

Several semiaromatic polyamides are based on the reaction of HMDA and terephthalic acid. The preparation of poly(hexamethylene terephthalate), polyamide 6,T, appears in Figure 2.5. However, pure nylon 6,T exhibits a very high T_m of 370 °C and a T_g of 180 °C. The high T_m results in expensive polymerization processes and difficulty in molding. Therefore, modified copolymers based on nylon 6, T have been examined extensively because of use of inexpensive monomers and enhanced properties over aliphatic polyamides. For example, terpolymers using an inexpensive, third monomer such as isophthalic acid, adipic acid, caprolactam, or 1,5-hexyl diamine have led to the commercialization of semiaromatic polyamides by Amoco, BASF, and DuPont under the trademarks Amodel R, Ultramid T, and Zytel HTN, respectively. These terpolymers exhibit T_ms from 290 °C to 320 °C and T_gs from 100 °C to 125 °C and offer enhanced performance over nylon 6,6 or 6—such as, higher stiffness, increased strength, greater thermal and dimensional stability.

2.4 Polyacetals

After nylon, the next engineering polymers to be commercially introduced were polyacetals [3]. Polyacetals are polymerized from formaldehyde and are called polyoxymethylenes (POM). Staudinger explored the basic polyformaldehyde structure rather thoroughly in the late 1920s and early 1930s, but he failed to produce a sufficiently high molecular weight polymer with requisite thermal stability to permit melt processing [4]. Pure formaldehyde could be readily polymerized, but the polymer equally, readily, spontaneously depolymerized, that is, the polymer unzips.

In 1947, DuPont began a development program on the polymerization and stabilization of formaldehyde and its polymer. Twelve years later, DuPont brought the unzipping tendency under control with proprietary stabilization technology and commercially announced polyacetal polymer under the Delrin trade name. The key to the stabilization of polyformaldehyde resins appears to be a blocking of the terminal hydroxyl groups that participate in, or trigger an, unzipping action. Postetherification or esterification apparently may block/cap the hydroxyl groups. This material has a T_g of −75 °C and a T_m of 181 °C. The synthesis of POM appears in Figure 2.6.

Celanese joined DuPont in the market with their proprietary polyacetal polymer under the Celcon trademark within a year. Celanese managed to obtain basic patent coverage, despite DuPont's prior filing, on the basis of a copolymer variation that led to an enhanced stabilization against thermal depolymerization. The preparation appears in Figure 2.7. This copolymer has a T_m of 170 °C.

Both Celanese and DuPont aimed their products directly at metal replacement. Items such as plumbing hardware, pumps, gears, and bearings were immediate targets. In many respects, the acetals resemble nylons. They are highly crystalline, rigid, cold-flow resistant, solvent resistant, fatigue resistant, mechanically tough and strong, and self-lubricating. They also tend to absorb less water and are not plasticized by water to the same degree as the polyamides.

Rapid crystallization of acetals from the melt contributes to fast mold cycles. Crystallization also causes a significant

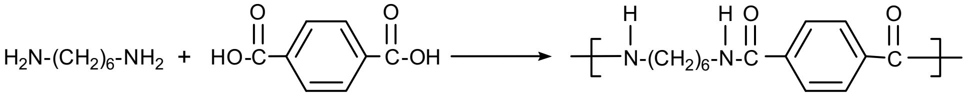


Figure 2.5 Preparation of polyamide 6, T.

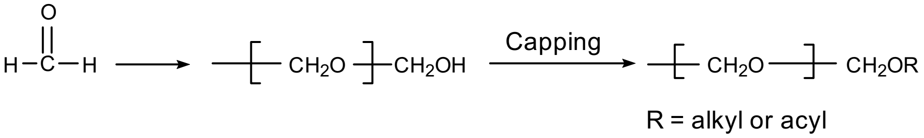


Figure 2.6 Preparation of capped POM.

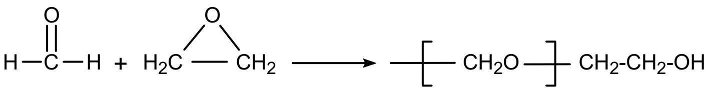


Figure 2.7 Synthesis of POM copolymer.

amount of mold shrinkage. Thus, it is necessary to compensate in mold design for dimensional changes that occur during the transformation from a hot, low-density, amorphous melt to a denser, crystalline solid.

Key areas of use for POMs are industrial and mechanical products that include molded or machined rollers, bearing, gear, conveyor chains, and housings. POMs are widely used in plumbing and irrigation because they resist scale build up and have excellent thread strength, creep resistance, and torque retention. A deficiency of polyacetals is a tendency to thermally unzip and an essentially unmodifiable flammability.

2.5 Polycarbonates

The aromatic polycarbonates (PC) were the next engineering polymers to be introduced. D.W. Fox at General Electric Company (GE) (now Sabic Innovative Plastics) and H. Schnell at Bayer AG (Germany) independently discovered the same unique super tough, heat-resistant, transparent, and amorphous polymer in 1953 [5—7]. When the companies became aware of each other's activities, agreements were reached that enabled both parties to continue independent commercialization activities without concern for possible subsequent adverse patent findings. GE's PC was introduced into the United States under the Lexan trademark in 1959 at about the same time as the polyacetals, and a commercial plant was brought on stream in 1960.

PCs of numerous bisphenols have been extensively studied. However, most commercial PCs are derived from bisphenol A (BPA). Both solution- and solvent-free, melt-transesterification processes are used to manufacture PCs.

In the solvent processes, phosgene reacts with BPA to produce a polymer in a solution. PC is produced by an interfacial adaptation of the reaction in Figure 2.8 [8]. The bisphenol plus 1—3 mol% monofunctional phenol, which controls molecular weight, are dissolved or slurried in aqueous sodium hydroxide, methylene chloride is added as a polymer solvent, a tertiary amine is added as a catalyst, and phosgene gas is dispersed in the rapidly stirred mixture. Additional caustic solution is added as needed to maintain basicity. The growing polymer dissolves in the methylene chloride, and the phenolic content of the aqueous phase diminishes.

In the solvent free, melt-transesterification, diphenyl carbonate reacts with BPA to regenerate phenol for recycle and molten, solvent-free polymer as shown in Figure 2.9. Transesterification is reported to be the least expensive route.

BPA-based PC is an amorphous polymer with a T_g of 150 °C. It offers outstanding impact strength, glass-like transparency, heat resistance, excellent electrical properties, intrinsic flame retardancy, and high dimensional stability up to just below its T_g. This outstanding combination of properties and processing versatility has made PCs the ideal resin for many applications. In addition, transparency gave PCs another dimension and has led to applications in safety glazing, light covers, automotive headlamp lenses, water bottles, compact disc, and ophthalmic applications.

The PCs, such as the nylons and acetals, were directed toward metal replacement applications. Glass fiber filled versions of PCs are available, and this combination is particularly well suited to compete with metal parts. As in the case of other amorphous polymers, glass fibers act as stiffening and strengthening agents but do not raise operating temperatures significantly. In semicrystalline polymers, fillers tend to act as a crutch to bridge the soft, amorphous regions that have T_g-dependent properties, thereby permitting the plastic to maintain structural integrity up to its crystalline melting point. Without filler, crystalline polymers tend to creep under static load at relatively low temperatures because their T_g values are generally comparatively low.

PCs are readily modified via copolymerization with long-chain aliphatic dicarboxylic acids to give a resin with improved flow; other bisphenols or phthalates to increase T_g and give PCs with higher heat resistance; and trisphenols to give a branched PC with improved melt strength for blow

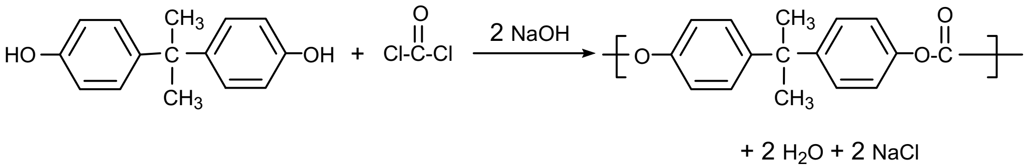


Figure 2.8 Interfacial synthesis of BPA polycarbonate.

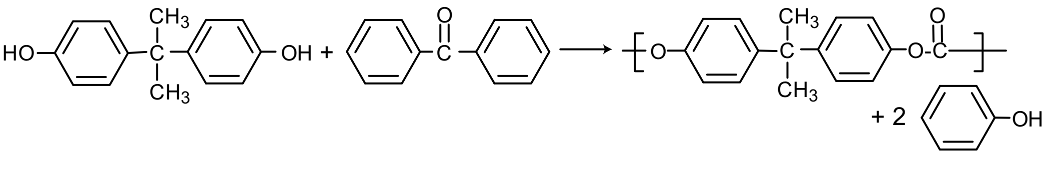


Figure 2.9 Transesterification route to BPA polycarbonate.

molding/extrusion. In addition, PC is amenable for the development of many different commercial polyblends [5,9]. Blending PCs with other thermoplastics widens the performance window and will be discussed later in this chapter.

2.6 Poly(Phenylene Ether)

In 1956, A. Hay of the GE discovered a convenient catalytic oxidative coupling route to high molecular weight aromatic ethers [10,11]. Polymers were made by bubbling oxygen through a copper—amine-catalyzed solution of phenolic monomer at room temperature. A wide variety of phenolic compounds were explored, but the cleanest reactions resulted from those that contained small, electron-donor substituents in the two ortho positions. Hence, research quickly focused on 2,6-dimethylphenol and poly(2,6-dimethyl-1,4-phenylene ether) or PPE. The synthesis is shown in Figure 2.10.

In 1964 GE introduced the PPE homopolymer under the PPO trademark. PPE had excellent hydrolytic resistance and an extremely high T_g of 215 °C. However, the very high melt viscosity and a pronounced tendency to oxidize at processing temperatures made PPE very difficult to process. However, in 1965 Westlake Plastics Company started production of extruded rods, sheets, and tubing of PPE under the Alphalux trademark. Also in 1965 Richardson Co. put a miscible blend of PPE with crystal polystyrene, PS, on the market. In spite of the PPE/PS miscibility, the single-phase blend was not a commercial success.

In the mid-1966 GE introduced a family of PPE blends with high impact polystyrene (HIPS), under the Noryl trademark. This combination of total compatibility with PS and the added toughness from HIPS was the key to commercial success. Varying the PPE/HIPS ratio results in a wide range of high temperature, easy to process, tough, dimensionally stable plastics [12].

Noryl resins became the world's most successful and best-known polymer blends because combinations of PPE resins and styrene polymers tend to assume the best features of each:

- PPE resins with very high heat distortion temperatures (HDTs) can readily raise the HDT of styrenics to over 100 °C, which is a significant temperature because this qualifies the product for all boiling water applications.
- HIPS, with ease of processing and well-established impact modification, balances the refractory nature of PPE resins.
- PPE resins bring fire retardance to the system.
- Both PPE resins and styrene polymers have excellent water resistance and outstanding electrical properties.
- In addition, PPE/PS blends exhibit lower specific gravity than other engineering thermoplastics.

The first applications were those requiring autoclaving (medical equipment) and outstanding electrical properties at elevated temperatures. As compounding, stabilization, and processing skills improved, markets for PPE blends expanded to include office equipment, electronic components, automotive parts, water distribution systems, and general metal replacement.

PPE-based resins are relatively resistant to burning, and judicious compounding can increase their burn resistance without the use of halogenated flame retardants. They may be modified with glass and other mineral fillers. Because of low moisture absorption, dimensional stability, and ability to be used over a wide temperature range, PPE-based resins are especially adaptable to metallization.

After expiration of the original patent on PPE, several manufacturers (e.g., BASF, Huls, Borg-Warner, Asahi, Engineering Plastics Ltd., Mitsubishi) began sales of their own blends based on PPE or its copolymers.

2.7 Polysulfones

Polyarylsulfones are a class of high use-temperature thermoplastics that characteristically exhibit excellent thermo-oxidative resistance, good solvent resistance, hydrolytic stability, and creep resistance [13]. Routes to polysulfones were discovered independently and almost simultaneously in the laboratories of Union Carbide Corporation, ICI, and 3M Corporation.

In 1965 A.G. Farnham and R.N. Johnson of Union Carbide (this business was acquired by Amoco Polymers in 1986 and is currently part of Solvay Advanced Polymers, LLC) announced the preparation of thermoplastic polysulfones (PSF) [14]. The first commercially available polysulfone was prepared by the aromatic nucleophilic displacement of the chlorides on 4,4′-dichlorodiphenyl sulfone by the anhydrous disodium salt of BPA as shown in

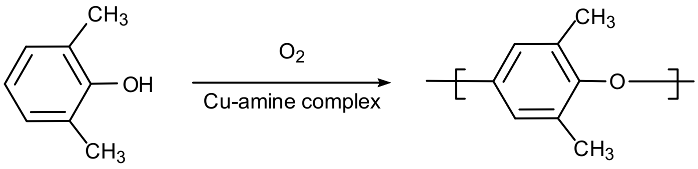


Figure 2.10 Oxidation coupling preparation of PPE.

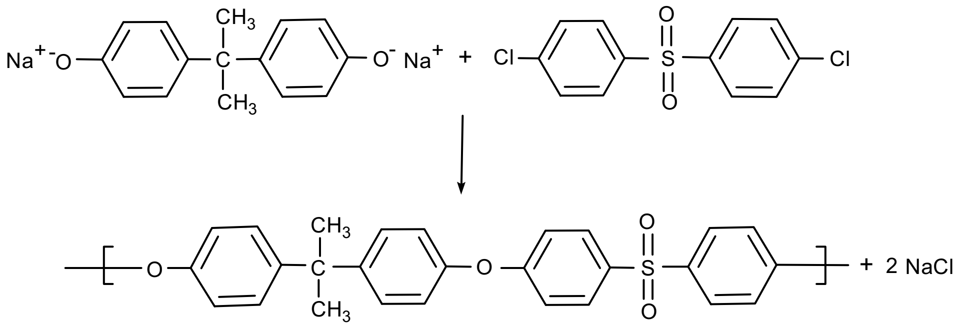


Figure 2.11 Aromatic nucleophilic displacement to form PSF.

Figure 2.11. The reaction is conducted in a dipolar aprotic solvent, such as dimethyl sulfoxide. This polysulfone became commercially available in 1966 under the Udel trademark. This amorphous polymer exhibits a T_g of 186 °C. Polysulfones are somewhat polar, aromatic ethers with outstanding oxidation resistance, hydrolytic stability, and high HDT.

In 1967 3M introduced their polyarylsulfones under the Astrel 360 trade name. This polymer was made by the Friedel–Crafts reaction of biphenyl with 4,4′-dichlorodiphenylether and exhibited a very high T_g of 277 °C. The structure is shown in Figure 2.12. The price was very high, it was difficult to melt process, and had limited availability. This resin is no longer commercially available.

In 1972 ICI started market development of polyethersulfone (PES). PES offers high heat (T_g of 225 °C) and thermal stability, better chemical/solvent resistance, and improved toughness over PSF [15]. The structure appears in Figure 2.13.

In 1976 Union Carbide introduced a second-generation polysulfone resin under the Radel R polyphenylsulfone (PPSU) trade name. This higher performing PPSU is prepared from 4,4′-biphenol and bis(*p*-chlorophenyl) sulfone. Its structure is shown in Figure 2.14 [16]. The biphenyl moiety imparts enhanced chemical/solvent resistance, outstanding toughness, greater resistance to combustion, a T_g of 225 °C, and greater thermo-oxidative stability.

Aromatic polysulfones offer hydrolytic stability and very high thermal endurance in conjunction with a good balance of mechanical properties which are suitable for hot water and food-handling equipment, range components, TV applications, alkaline battery cases, and film for hot transparencies. The unmodified products are transparent with a slightly yellow tint. Low flammability and low smoke suit it for aircraft and transportation applications. In addition, it can withstand rigorous handling and repeated steam sterilization cycles and is used in medical application. Thus, polyarylsulfones are used in surgical equipment, laboratory equipment, life support parts, and autoclavable tray systems. Blow molding polyarylsulfones produce suction bottles, tissue culture bottles, and surgical hollow shapes.

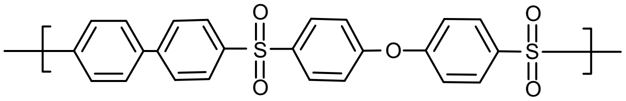


Figure 2.12 Structure of polyarylsulfone.

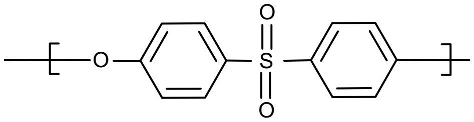


Figure 2.13 Structure of PES.

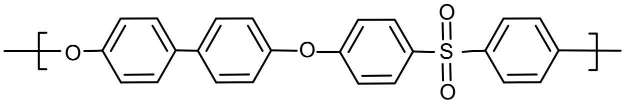


Figure 2.14 Structure of PPSU.

2.8 Polybiphenyldisulfones

In the mid-1970s and again in the mid-1980s, ICI had unsuccessful marketing efforts for polyetherbiphenyldisufones [17]. These higher performance polysulfones are high-temperature, amorphous polymers which are prepared by the aromatic nucleophilic displacement of the chlorides on 4,4-bis(4-chlorophenylsulfonyl) biphenyl with bisphenols under basic conditions in a dipolar aprotic solvent. The more rigid biphenyldisufone unit results in polymers with noticeably higher T_gs than other sulfone polymers. Indeed, the BPA and hydroquinone based polymers exhibit T_gs of 245 and 265 °C, respectively [18,19]. Their structures appear in Figure 2.15.

In 2004 Solvay Advanced Polymers introduced these high-temperature sulfone polymers under the Supradel trademark. In 2007 the trademark was changed to EpiSpire.

These higher temperature sulfone polymers are transparent and completely amorphous and can be melt processed by injection molding and extrusion. They exhibit high thermal

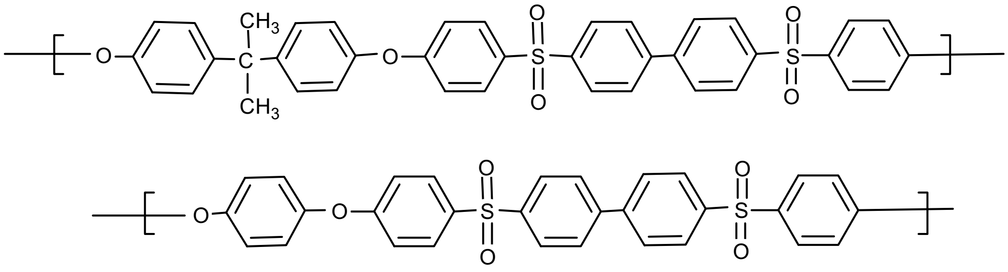


Figure 2.15 Structures of polybiphenyldisulfones.

performance capabilities, good strength, stiffness, and dielectric properties over a wide temperature range; resistance to hydrolysis by hot water and steam; excellent resistance to acids and bases; and inherent flammability resistance.

The material's thermal performance combined with its good strength and stiffness, dimensional stability, and creep resistance suggests opportunities in high-temperature injection molding applications that traditionally have been limited to filled, semicrystalline polymers.

Applications for polybiphenyldisulfones include opportunities in metal replacement as well as high-performance thermoset resins in a wide range of engineering applications. This included automotive, aerospace, electrical, electronic, and industrial product applications.

2.9 Thermoplastic Polyesters

In the late 1920s W. Carothers and his research group at DuPont investigated the formation of polyester from the reaction of aliphatic dicarboxylic with diols. These aliphatic polyesters were found to be inadequate as fiber precursors because of their low melting points. The aliphatic polyesters were bypassed for polyamides with much higher T_ms. Thermoplastic polyesters had their beginning in 1941 when J.R. Whinfield and J.T. Dickson at DuPont, in a reinvestigation of polyesters as fiber precursors, substituted terephthalic acid for the previously investigated aliphatic dibasic acids and discovered high melting crystalline polymers [20,21]. ICI, DuPont, and others developed these polymers into the familiar polyester fibers and films.

Whinfield and Dickson quickly realized that the polymer poly(ethylene terephthalate) (PET) based on ethylene glycol and terephthalic acid was the best suited for fibers. PET exhibits a T_g of 70 °C and a T_m of 265 °C. The synthesis appears in Figure 2.16.

In addition, they made and described several other polyesters including poly(butanediol terephthalate) (PBT). PBT exhibits a T_g of 45 °C and a T_m of 225 °C. The synthesis of PBT from the transesterification reaction of dimethyl terephthalate and butanediol is shown in Figure 2.17. Many years later a number of polyester fiber producers became interested in PBT. One producer explained that they were interested in PBT because it resembled nylon, which was becoming popular as a carpet yarn, and they were not in the nylon business. Hence, they considered PBT as means of competing in carpet yarns.

While the fiber producers were busily expanding their fiber activities, a number of companies were simultaneously trying to adapt PET as a molding compound. In 1966, the first injection molding grades of PET were introduced; however, these early materials were not very successful. The primary problem was that PET does not crystallize very rapidly; a molded object composed of a crystallizable polymer caught in an amorphous or partially crystallized state would be rather useless. In service, such a part could crystallize, shrink, distort, crack, or fail. The obvious solution was to use hot molds and hold the parts in the mold until the crystallization process was completed. Postannealing also permits continued crystallization. These approaches, especially with glass fiber incorporation, led to acceptable parts at economically unacceptable molding cycles. Alternately, some developers tried to use very low molecular weight PET glass

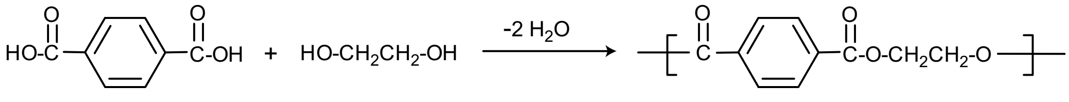


Figure 2.16 Condensation polymerization to form PET.

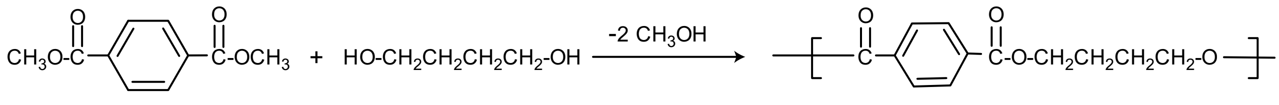


Figure 2.17 Transesterification route to PBT.

products that crystallized more rapidly; however, because of their low molecular weights, these products lacked essential properties. A very broad search has been conducted for such things as nucleating agents and crystallization accelerators. An improved PET injection-molding compound was introduced by DuPont in 1978 under the trade name Rynite. A number of other companies have followed DuPont into the market. The PET-based molding compounds are gaining acceptance at a substantial rate, but actual volume is relatively small. While other companies sought means of increasing the rate of crystallization of PET, Celanese chemists turned their attention to PBT and found that it met all the requirements for a molding compound.

The basic composition of matter patents had long since expired on PBT when Celanese sampled the market in 1970 with a glass-fiber reinforced PBT product designated X-917. This PBT molding compound was subsequently available under the Celanex trade name. Eastman Kodak followed Celanese early in 1971, and GE followed Eastman Kodak later in the same year with a PBT polyester resin under the Valox trade name. Since that time a dozen or more additional companies around the world have entered (and some have subsequently exited) the business.

Basically, PBT seems to have a unique and favorable balance of properties between nylons and acetal resins. It has relatively low moisture absorption, extremely good self-lubrication, fatigue resistance, solvent resistance, and good maintenance of mechanical properties at elevated temperatures. Maintenance of properties up to its crystal melting point is excellent if it is reinforced with glass fiber. Very fast molding cycles with cold to moderately heated molds complete the picture. Key markets include under-the-hood automotive applications, which require thermal and solvent resistance; electrical and electronic applications; power tools, small and large appliance components; and athletic goods.

2.10 Liquid Crystalline Polymers (Polyesters)

Most commercially important polyester liquid crystalline polymers (LCPs) are based on *p*-hydroxybenzoic acid (HBA). In the 1970s J. Economy of Carborundum Company developed poly(1,4-benzoate), which could be compression-sintered and was marketed under the Ekanol trade name [22,23]. The structure appears in Figure 2.18. This material was not easy to melt process and probably did not form liquid crystalline melt. It is reported that it could be compression molded around 440 °C.

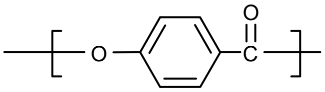


Figure 2.18 Structure of poly(1,4-benzoate).

However, copolymerizing HBA with 4,4′-biphenol and terephthalic acid (TTA) resulted in melt-processible LCPs which were commercialized under the Ekkcel trade name; properties are a function of the monomer ratios. Typically the T_g is around 180 °C and the T_m 340−400 °C. Its structure appears in Figure 2.19. These polymers were difficult to manufacture and process. In 1979 Carborundum sold the Ekkcel business to Sumitomo Chemical and the technology sold to Dartco. Dartco introduced their Xydar product line in the fall of 1984 for use in dual ovenable cookware. Their LCP was based on an improved *p*-HBA, biphenol, and terephthalic acid-based resin. This technology was later sold to Amoco Polymers (now Solvay Advanced Polymers).

In the 1970s G.W. Calundann of Celanese (now Ticona) was developing LCPs based on copolymers of HBA with 6-hydroxy-2-naphthoic acid or with 2,6-dihydroxynaphthalene and 2,6-naphthalene dicarboxylic acid. Structures of these naphthalene-based LCPs are depicted in Figure 2.20. In the fall of 1985 their LCP was commercialized under the Vectra trade name.

Principal U.S. and European suppliers of polyester LCPs are Ticona, Amoco, and DuPont with products under the Vectra, Xydar, and Zenite trademarks, respectively.

LCPs have a rod-like aromatic structure. The rod-like molecules arrange themselves in parallel domains in both the melt and solid states. In the molten state the molecules readily slide over one another giving the resin very high flow under shear. Thus, melt viscosities decrease significantly as shear rates increase. Molders lower the melt viscosity of LCPs by increasing injection velocity rather than temperature.

Highly crystalline LCPs offer high strength and rigidity in the direction of flow, dimensional stability, excellent solvent/chemical resistance, high heat resistance, and inherent flame retardancy. LCPs have anisotropic properties, that is, properties are different in the direction of flow and perpendicular to the flow direction.

Polyester LCPs are used in electronic connectors, surgical devices, and other parts where thin walls are essential.

2.11 Poly(Phenylene Sulfide)

The first poly(phenylene sulfide), PPS, was made in 1897 by the Friedel−Crafts reaction of sulfur and benzene [24]. Various other early attempts have been reported, all of which resulted in amorphous resinous materials that decomposed

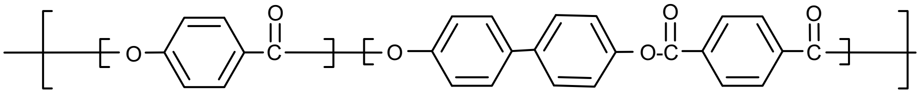


Figure 2.19 Structure of HBA/biphenol/TTA based LCP.

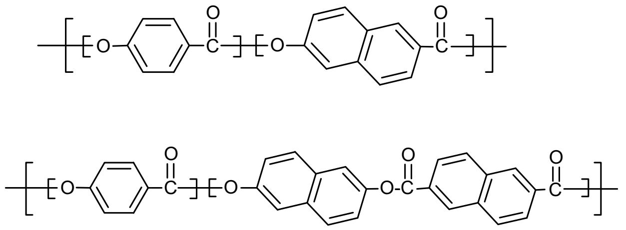


Figure 2.20 Structures of naphthalene based LCPs.

between 200 and 300 °C. These materials were probably highly branched and even partially cross-linked.

In 1967, J.T. Edmonds and H.W. Hill at Phillips Petroleum (now Chevron Phillips Chemical Co., LP) developed the first commercially viable process for the synthesis of PPS by reacting 1,4-dichlorobenzene with sodium sulfide in a dipolar aprotic solvent [25]. The synthesis appears in Figure 2.21. The polymer precipitates out of solution as a crystalline powder. However, this limited the molecular weight of the PPS. Hence, thermal treatment under an oxygen atmosphere was used to advance the molecular weight. This could result in branching or slight crosslinking which would lower the ultimate performance.

The polymer exhibits a T_g of 85 °C and melts at 280 °C. In 1973, Phillips Petroleum introduced linear and branched products under the Ryton trade name [26].

Branched PPS exhibits high heat resistance, excellent chemical resistance, low friction coefficient, good abrasion resistance, and good electrical properties. Physical characteristics include high flexural modulus, very low elongation, and generally poor impact strength. Moreover, branched or slightly crosslinked PPS is reported to be somewhat difficult to process because of its very high melting temperatures, relatively poor flow characteristics, and because some chemistry appears to continue during the fabrication step. Molded pieces have limited regrindability. Annealing of molded parts enhances mechanical properties but leads to almost total loss of thermoplastic character.

In 1986 a linear, high molecular weight PPS was developed. Linear PPS overcomes the weak points of branched or crosslinked PPS and exhibited several performance advantages over branched PPS products. These include faster cycle times, higher elongation and impact strength, more consistent melt viscosity, higher weld line strength, and lighter color. Linear PPS is available under the Fortron trade name (Ticona).

Glass, glass-mineral, and carbon fiber reinforced grades that have high strength and rigidity are available. The unreinforced resin is used only in coatings. The reinforced materials are finding applications in aerospace technology, pump systems, electrical and electronic equipment, appliances, and automotive vehicles and machines.

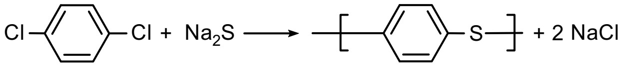


Figure 2.21 Synthesis of PPS.

2.12 Polyetherimide

Polyetherimide (PEI) was formally announced by GE in 1982 [27]. This amorphous polymer with the Ultem trade name resulted from the research work of a team headed by J.G. Wirth in the early 1970s. The early laboratory process involved a costly and difficult synthesis. Further development resulted in a number of breakthroughs that led to a simplified, cost-effective production process. The final step of the process involves the imidization of a diacid anhydride with *m*-phenylene diamine as shown in Figure 2.22. PEI has a T_g of 217 °C.

Polyetherimide offers an impressive collection of attributes such as high heat resistance, stiffness, impact strength, transparency, high mechanical strength, good electrical properties, high flame resistance, low smoke generation, and broad chemical resistance. In addition to its unique combination of properties matching those of high-priced specialty plastics, PEI exhibits the processability of traditional engineering thermoplastics, although higher melt temperatures are required. The excellent thermal stability is demonstrated by the maintenance of stable melt viscosity after multiple regrinds and remolding. The processing window is nearly 100 °C, and PEI can be processed on most existing equipment. Furthermore, this excellent flow resin can be used for the molding of complicated parts and thin sections (as thin as 0.005 inches). PEI is suitable for use in internal components of microwave ovens, electrical and electronic products, and automotive, appliance, and aerospace, and transportation applications.

2.13 Polyimides

Polyimides are a class of polymers prepared from the condensation reaction of a dicarboxylic acid anhydride with a diamine [28]. Aromatic, ultrahigh heat-resistant polymers exhibit useful mechanical characteristics through a wide temperature range, high tensile strength and modulus, outstanding electric properties, flame resistance, creep resistance, high toughness, and excellent wear resistance, and outstanding long-term heat resistance in air or inert atmosphere. Another advantage inherent in polyimides is high resistance to hydrolysis. Polyimides have excellent resistance to a broad range of chemicals. However, it will be attacked by 10% and stronger solutions of sodium hydroxide.

Poly(pyromellitimide-1,4-diphenyl ether), PDMA–ODA, is prepared from pyromellitic anhydride (PMDA) and 4,4′-oxydianiline (ODA) as shown in Figure 2.23. PMDA–ODA has a T_g around 360–400 °C. This very high T_g does not lend itself to standard melt-processing techniques.

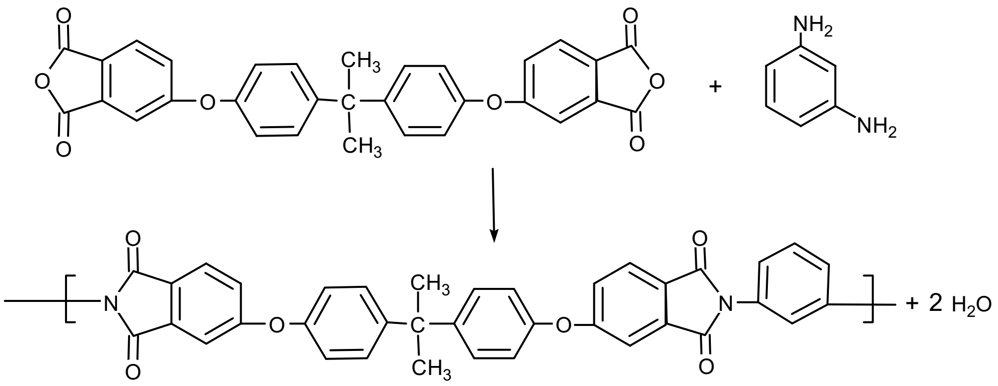


Figure 2.22 Preparation of PEI.

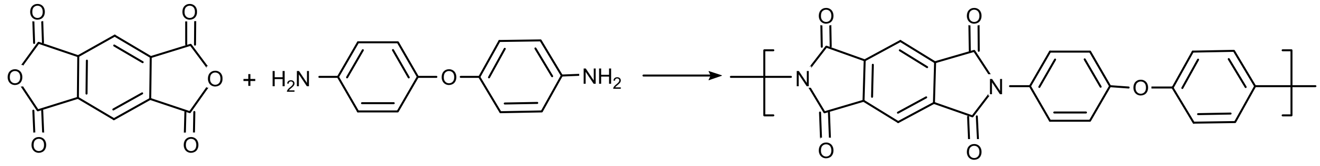


Figure 2.23 Preparation of PMDS–ODA.

PMDA–ODA resins are available as films and direct-formed parts from formulated resin. Films and molded parts are available from DuPont under the Kapton and Vespel trade names, respectively.

Another family of aromatic polyimides is produced from the condensation reaction between biphenyltetracarboxylic dianhydride (BPDA) and aromatic diamines such as ODA and *p*-phenylene diamine, PDA. The polyimides BPDA–ODA and BPDA–PDA are available from Ube Industries under the Upilex R and S trademarks, respectively. Their T_gs are reported to be >400 °C. Structures appear in Figure 2.24.

Aromatic polyimides have been the subject of much attention as a material for use in the electronics and other leading-edge industries. Films are used in flexible printed circuit boards, as wire and cable wrap, motor-slot liners, transformers, and capacitors. Molded parts are used in applications requiring resistance to thermally harsh environments such as automotive transmission parts, thermal and electrical insulators, valve seats, rotary seal rings, thrust washers and discs, and bushings.

2.14 Polyamide Imides

Polyamide imides (PAIs) were first developed at DuPont in 1955. In the early 1960s they became commercially available from Standard Oil of Indiana (Amoco; now Solvay Advanced Polymers) under the Torlon trade name. PAIs are prepared from trimellitic anhydride chloride and various aromatic diamines such as ODA and methylene dianiline, MDA [28]. Structures are shown in Figure 2.25. PAIs are amorphous thermoplastics that offer T_gs around 275 °C toughness, high continuous use temperatures, inherent flame resistance, high modulus, and very high strength. PAIs contain amide groups and hence will absorb moisture and can

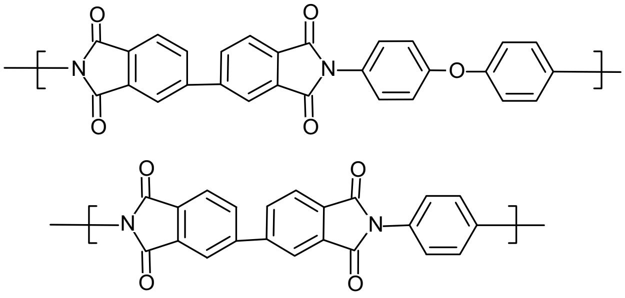


Figure 2.24 Structures of BPDA–ODA and BPDA–PDA.

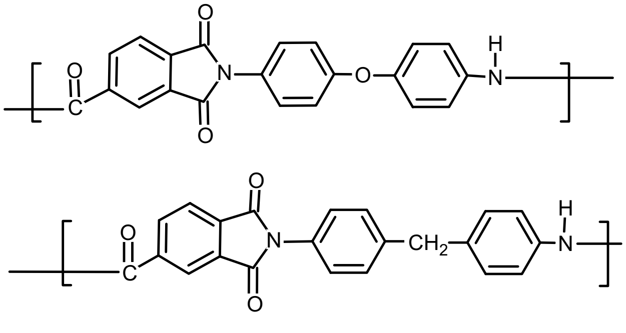


Figure 2.25 Structures of ODA and MDI based PAIs.

affect dimensional stability. PAIs have very broad chemical resistance but are attacked by aqueous caustic and amines. PAIs require very high processing temperatures.

Typical uses include injection-molded automotive parts such as housings, connectors, switches, relays, thrust washers, valve seats, bushings, wear rings, ball bearings, rollers, and thermal insulators.

2.15 Aromatic Polyketones

The aromatic polyketones are a family of semicrystalline engineering thermoplastics in which the combination of ketone, aryl ether, and aromatic moieties imparts outstanding high temperature properties combined with exceptional thermal stability [29]. Indeed, aromatic polyketones are regarded as among the highest performing materials in the world. In addition, aromatic polyketones offer excellent environmental resistance, high mechanical properties, resistance to chemical environments at high temperatures, inherent flame retardancy, excellent friction and wear resistance, and impact resistance. A further property of aromatic polyketones is chemical purity that has led to applications in silicon chip manufacture. Aromatic polyketones were first produced in the 1960s and 1970s but did not become commercially available until the early 1980s.

In the early- to mid-1970s Raychem Corporation commercially introduced a polyetherketone (PEK) under the Stilan trade name. This semicrystalline, aromatic polyether was developed by K. Dahl in the 1970s (p. 277 of Ref. [29]).The rigorous conditions needed to make PEK involved Friedel–Crafts chemistry and required using very strong solvents such as hydrogen fluoride or an excess of aluminum chloride to keep the polymer in solution. PEK was expensive to manufacture and was mostly made for captive use. The synthesis is shown in Figure 2.26. PEK has a T_m of 364 °C and a T_g of 166 °C. In the 1980s Raychem licensed their patents to BASF and discontinued production.

2.15.1 Synthesis of PEK

Polyetheretherketone (PEEK) is a semicrystalline polyether prepared under milder conditions via aromatic nucleophilic substitution reaction of the potassium salt of hydroquinone and 4,4′-difluorobenzophenone as shown in Figure 2.27. Several companies conducted early work on PEEK, which resulted in low molecular weight polymer, owning to crystallization and precipitation from solution. However, Rose and coworkers at ICI (now Victrex Co.) substituted a very high boiling solvent such as diphenylsulfone at temperatures close to the melting point of the polymer and high molecular weight PEEK was obtained. In 1980 PEEK was commercialized under the Victrex PEEK trade name. PEEK has a T_m of 335 °C and a T_g of 145 °C. PEEK is the most widely used member of aromatic polyketones.

Applications are in the chemical process industry (compressor plates, valve seats, pump impellers, thrust washers, bearing cages), aerospace (aircraft fairings, radomes, fuel valves, ducting), and electrical (wire coating, semiconductor wafer carriers) industries.

2.16 Polyarylates

Polyarylates (PARs) are a family of aromatic polyesters derived from aromatic dicarboxylic acids and bisphenols. They have been under investigation since the late 1950s. The PARs that have received the most attention are based on BPA and isophthalic or terephthalic acids. The homopolymers of BPA and isophthalic acid or terephthalic acids are semicrystalline [30]. They have T_ms of 270 and 370 °C and T_gs of 183 and 206 °C. These semicrystalline PARs were not commercialized because of their high crystalline melting points and very slow crystallization rates. However, amorphous PARs are prepared from a mixture of isophthalic and terephthalic acids and BPA and can be melt-processed without difficulty. The structure appears in Figure 2.28. Unitika of Japan (1974), Union Carbide Corporation (now Solvay Advanced Polymers) (1978), Hooker Chemical Company (1979), and DuPont (1986) commercialized PARs under the trade names U-polymer, Ardel, Durel, and Arylon, respectively. PARs exhibit T_gs of 180–185 °C.

These amorphous PARs are transparent, slightly yellow in color, dimensionally stable, resistant to creep, have excellent electrical properties, rigid, and have good impact strength. PARs have poor chemical resistance to ketones, esters, and aromatic and chlorinated hydrocarbons. Typical uses include

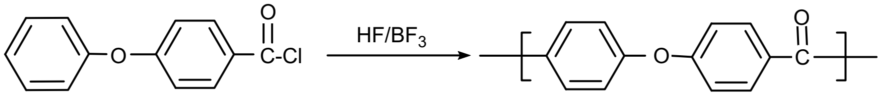


Figure 2.26 PAIs from trimellitic anhydride chloride and ODA and MDA.

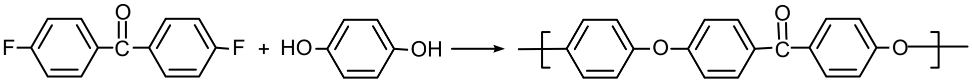


Figure 2.27 Preparation of PEEK.

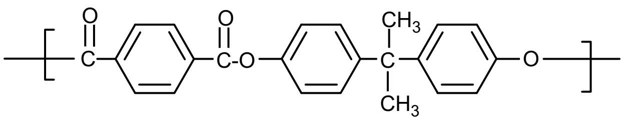


Figure 2.28 Structure of polyarylates.

electrical/electronic and automotive applications, which require higher heat deflection temperature than PC.

2.17 Aliphatic Polyketones

Aliphatic polyketones are produced from olefin monomers and carbon monoxide. Basic patents on catalyst and composition appeared in the early 1970s [31]. However, these early resins were not processible due to residual catalyst. In 1982 J. Dent of Royal Dutch/Shell discovered a new class of catalyst system that was capable of copolymerizing carbon monoxide and ethylene into linear, perfectly alternating polyketone polymers of high molecular weight. In 1996 Shell commercialized a terpolymer of carbon monoxide, ethylene, and a small amount of propylene under the Carilon trade name. The synthesis appears in Figure 2.29.

The semicrystalline, ethylene/propylene/CO terpolymer has a T_m of 200 °C and a T_g of about 15 °C. Aliphatic polyketones offer toughness, chemical resistance, and wear resistance and was competing with polyamides, thermoplastic polyesters, and syndiotactic polystyrene (SPS) in the electrical connector market and POMs in gear and barring applications.

The material had limited success. In 2000, Shell announced that it was withdrawing their polyketones from the marketplace.

2.18 Syndiotactic Polystyrene

New developments in metallocene catalyst have resulted in the production of SPS, a semicrystalline polymer. When the phenyl groups lie on alternating sides of the polymer backbone the configuration is called *syndiotactic*. The structure of SPS appears in Figure 2.30. Amorphous polystyrene (atactic PS) has no stereoregularity and is a relatively brittle, amorphous polymer with poor chemical resistance. In contrast, SPS has high stereoregularity, a T_m of 270 °C, a T_g of 100 °C, and good chemical/solvent resistance [32].

Dow Chemical commercialized SPS in 1997 under the Questra trade name.

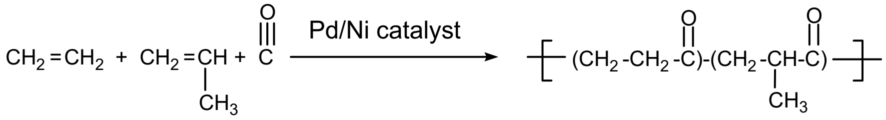
SPS is targeted at automotive under-the-hood and specialty electronic applications. It will complete with polyamides, thermoplastic polyesters, aliphatic polyketones, and PPS.

However, SPS grades suffered from poor mechanical properties relative to other engineering thermoplastics. Glass-reinforced grades were handicapped by no attraction between the sizing on the glass and the nonpolar, nonfunctional SPS. Besides lower strength and stiffness, the weld lines were very poor. In 2005, Dow Chemical discontinued the Questra product line. SPS plastics are available from Indemitsu Kosan, Co. under the Xarec SPS trade name.

2.19 Polyphenylene

Poly(*p*-phenylene) is a highly crystalline, rigid rod polymer that is insoluble and infusible. Modification of poly(*p*-phenylene) can result in an amorphous, transparent, and melt-processible polymer. In 2003 Mississippi Polymer Technologies (MPT) introduced modified poly(*p*-phenylene) under the Parmax trade name. In 2006 Solvay Advanced Polymers acquired MPT and offers amorphous *p*-phenylene copolymers under the PrimoSpire trademark. The structure is based on a string of substituted and unsubstituted benzene rings producing a highly rigid chain structure. The substituted benzene rings have pendant benzoyl groups. These benzoyl-substituted phenylene units along with some *m*-phenylene units are sufficient to prevent crystallization. These polymers are prepared by carbon–carbon coupling polymerization reactions of 1,4-dichlorobenzene,

Figure 2.29 Synthesis of aliphatic polyketones.



$$CH_2{=}CH_2 + \underset{\displaystyle CH_3}{CH_2{=}\underset{|}{C}H} + \overset{\displaystyle O}{\underset{}{\overset{|||}{C}}} \xrightarrow{\text{Pd/Ni catalyst}} \left[(CH_2\text{-}CH_2\text{-}\overset{\displaystyle O}{\overset{||}{C}})\text{-}(CH_2\text{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}\text{-}\overset{\displaystyle O}{\overset{||}{C}}) \right]$$

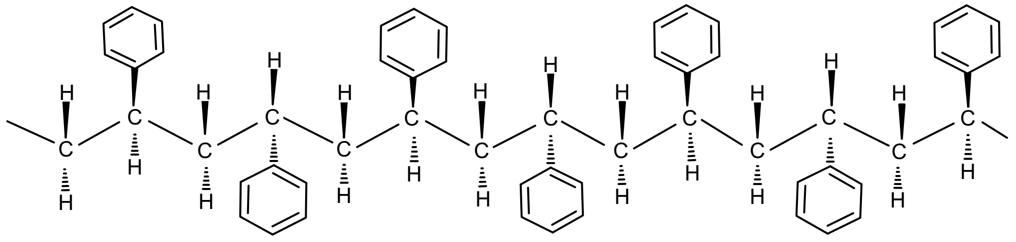


Figure 2.30 Structure of syndiotactic polystyrene.

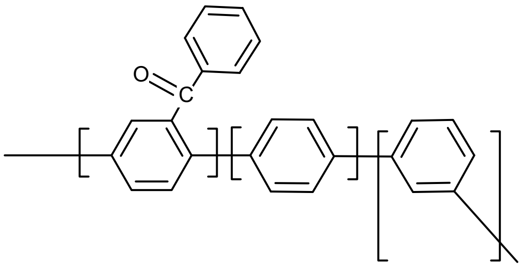


Figure 2.31 Structure of modified polyphenylene.

2,5-dichloroacetophenone, and 1,3-dichlorobenzene. The structure is depicted in Figure 2.31.

The amorphous polymers retain the rigid rod characteristics and are self-reinforcing which results in very high, isotropic mechanical properties. They are the stiffest unreinforced thermoplastics that are commercially available and provide exceptional strength and stiffness without fillers. Indeed, it exhibits 2—4 times the stiffness and 2—3 times the strength of other thermoplastics. In addition, there are no issues in the orientation of glass- or carbon-fibers within the plastic matrix—and the resulting directional differences in strength.

The glass transition temperature is 165 °C. The highly aromatic polymer is inherently flame-resistant. The high surface hardness results in excellent scratch and wear resistance. Coefficient of friction is very low and compressive strength is more than 690 MPa. Mechanical performance is maintained across a wide range of temperatures. For example, mechanical properties are retained all the way down to liquid helium temperatures (4 °K). Other characteristics include broad chemical resistance.

Modified poly(*p*-phenylene) can be processed by using standard melt-processing techniques. The polymer is soluble in common solvents and can be cast into films and coatings. In addition, machinable stock plastic shapes are available.

Self-reinforcing polyphenylene is suitable for applications that have historically relied on ceramic, composites, and metals for superior mechanical performance. Market potential includes: aerospace/defense (inherent flame resistance, lightweight, superior ablation properties, high compressive strength), health care (strength without fibers, autoclavability, X-ray transparency, chemical resistance), semiconductor/electronic (chemical resistance, low moisture absorption, high purity, dimensional stability, low CTE).

2.20 Trends in Engineering Thermoplastics

An interesting trend that appears to presage the wave of the future in engineering thermoplastics is the current focus on polymer blending and alloying. Metals and their alloys have been coeval with the spread of civilization. Early man used available metals in their naturally occurring state. The progress of civilization was literally determined by man's ability to modify natural metals, allowing mankind to induce the properties necessary for increasingly sophisticated tools. Indeed, societies that learned to exploit blends of metals developed distinct advantages over their monometallic neighbors; this was exemplified by the advent of bronze and later steels.

Metal alloying probably made the transition from art to science in the past century. The basic ingredients are essentially known and fixed in number. The plastic age began in 1909 with the discovery by Leo Baekeland of synthetic phenol—formaldehyde resin. As pointed out in the beginning of this chapter, the engineering plastic age began 70 years ago. While metal alloy components are essentially fixed, polymer alloy components are unlimited from a technical standpoint, but somewhat fixed from an economic point of view. It is still possible to make totally new and useful polymers if their value will support the cost of synthesizing new monomers and polymers. However, companies are motivated to produce blends for a number of reasons. For example, using available polymers to produce desirable and novel alloys is much more economically attractive. In addition, properties can be quickly tailored with existing resins to achieve performance required for specific applications. Variables include base polymers (over 50), performance enhancing additives such as impact modifiers, stabilizers, and reinforcing fibers and fillers. The available degrees of freedom make the opportunity challenging and provide almost infinite possibilities. Indeed, there are a plethora of engineering resin blends and alloys available. Some of the more commercially significant materials include blends of PC, polyamides, and PPE. Polymer science is key in developing compatible blends, stable morphology, and effective melt mixing of dissimilar polymers.

The unique family of miscible blends of PPE with PS and HIPS was already presented in this chapter.

PC/ABS blends offer a balance of properties that combines the most desirable properties of both resins [33]. The addition of ABS improves the melt processing of PC/ABS blends, which facilitates filling large, thin-walled parts. Moreover, the ABS enhances the toughness of PC—especially at low temperatures—while maintaining the high strength and rigidity of the PC. In addition, PC/ABS offers good UV stability, high dimensional stability at ambient and elevated temperatures, and the ability for chlorine/bromine-free flame retardance [2,5]. PC/ABS blends were first introduced by Borg—Warner (now Sabic Innovative Plastics) under the Cycoloy trade name in 1971. In 1977 Bayer (now Mobay) with a license from Borg—Warner launched PC/ABS resins under the Bayblend trade name. PC/ABS is used in interior and exterior automotive applications, lap- and desk-top computers, copiers, printers, telecommunications, electrical, and appliances.

Another important PC blend is with PBT. PC/PBT blends offer a balance of performance characteristics unique among engineering thermoplastics with its optimal combination of toughness, chemical resistance, dimensional stability, lubricity, and high HDT. These blends exhibit very good aesthetics, lubricity, UV resistance, and color retention. In 1982 Sabic Innovative Plastics introduced an impact modified PC/PBT polymer blend under the Xenoy trade name.[34] Applications for PC/PBT resins include automotive bumpers/fascia, tractor hoods and panels, components on outdoor recreational vehicles, lawn mower decks, power tool housings, material handling pallets, and large structural parts.

Polyamides have been used as engineering thermoplastics for over 70 years. In that time a substantial effort has gone into PA blends and alloys. Main areas of development were blends to address moisture sensitivity, dimensional stability, and impact modification.

Polyamide/PPE blends were developed for use in exterior automotive parts. It is the first injection moldable thermoplastic with both the strength and rigidity needed for large vertical body-panels, along with the high heat resistance for in-line or on-line painting. PA/PPE alloys can provide a 50% weight savings over traditional materials and hence can provide improved fuel efficiency. Blends were introduced in 1984 under the Noryl GTX trade name (Sabic Innovative Plastics) [35–37].

Compatibilized blends with ABS and polypropylene give PA blends that exhibit reduced water absorption and good dimensional stability. These blends also have good toughness, rigidity, and chemical resistance. In addition, PA/PP blends have low permeability to gases and polar solvents.

Polyamides are generally regarded as tough materials. However, they are susceptible to notches and can exhibit brittle failure. Hence, blends of polyamide with elastomers have been developed. Polyamide blends with 10–25% of reactive or compatibilized elastomers give super tough polyamide alloys.

Clearly, the trend toward alloys and blends is of major importance. In general, blends and alloys of thermoplastics have an annual growth rate of 8–10% and constitute 40–50% of the sales of plastics.

2.21 Conclusions

The future of engineering plastics looks bright. The industries served by these plastics and many others, who use traditional materials such as metals, glass, and ceramics, will look to the benefits of engineering polymers to provide them with cost-effective materials to help overcome the pressures of spiraling costs. The world economy will continue to influence technical trends. The commercialization of any new engineering polymers based on a new monomer, although not impossible, is unlikely. Rather, the major thrust will take place in molecular shuffling with existing monomers, blend activity, and processing improvements. Key examples are the commercialization of aliphatic polyketones and SPS, which use commodity monomers.

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3 Polyolefins

Werner Posch
Wels University of Applied Sciences

3.1 Industrial Processes for Polyolefin Production

A polyolefin is a polymer produced from an olefin or alkene as a monomer. In organic chemistry, an alkene, olefin, or olefine is an unsaturated chemical molecule containing at least one carbon to carbon double bond. The simplest alkene is ethylene. A special family of these olefins are α-olefines, which have a double bond at the primary or α position.

Due to their double bonds olefins represent an interesting synthesis potential for chemical reactions. There have previously been numerous attempts, particularly with the low-molecular representatives, ethene and propene, to manufacture longer hydrocarbons with C−C linkages (Figure 3.1).

This location of a double bond enhances the reactivity of the molecule and makes it useful for a number of applications.

3.1.1 Olefins Source

The most common industrial synthesis path for alkenes is the cracking of crude oil. Cracking is the process whereby complex organic molecules are broken down into simpler molecules (e.g., light hydrocarbons) by the breaking of carbon−carbon bonds in the precursors.

3.1.1.1 Steam cracking

Steam cracking is a petrochemical process in which saturated hydrocarbons are broken down into smaller, often unsaturated, hydrocarbons. It is the principal industrial method for producing lighter alkenes (olefins), including ethene (or ethylene) and propene (or propylene) (Figure 3.2).

In steam cracking, a gaseous or liquid hydrocarbon feed-like naphtha, LPG (low pressure gas) or ethane is diluted with steam and then briefly heated in a furnace, obviously without the presence of oxygen.

Typically, the reaction temperature is very hot (around 850 °C) but the reaction is only allowed to take place very briefly. In modern cracking furnaces, the residence time is even reduced to milliseconds (resulting in gas velocities

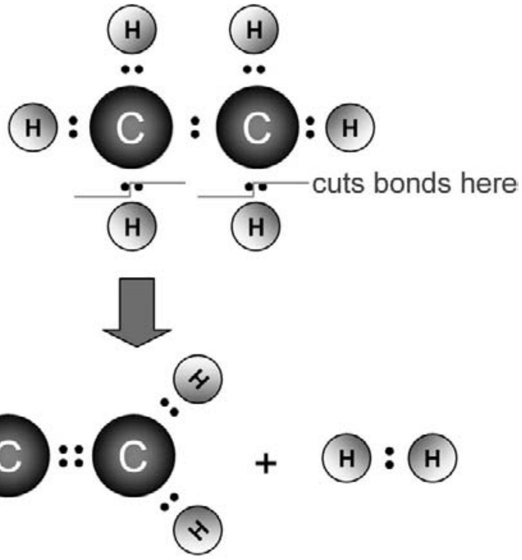


Figure 3.2 Cracking.

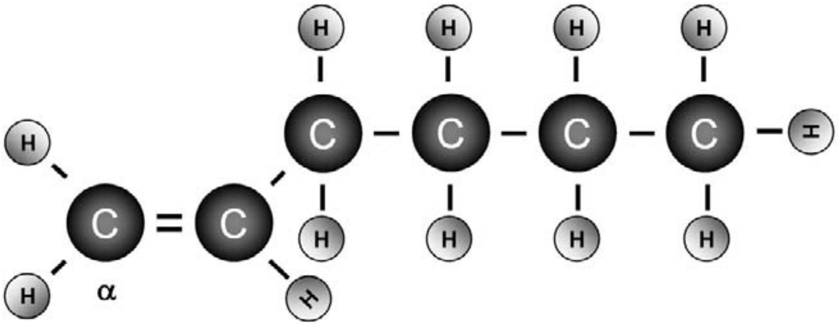


Figure 3.1 C-C double bond.

reaching speeds beyond the speed of sound) in order to improve the yield of desired products.

After the cracking temperature has been reached, the gas is quickly quenched to stop the reaction in a transfer line exchanger. The products produced in the reaction depend on the composition of the feed, on the hydrocarbon to steam ratio and on the cracking temperature and furnace residence time.

Light hydrocarbon feeds (such as ethane, LPG, or light naphthas) give product streams rich in the lighter alkenes, including ethylene, propylene, and butadiene.

Heavier hydrocarbon (full range and heavy naphthas as well as other refinery products) feeds give some of these, but also give products rich in aromatic hydrocarbons and hydrocarbons suitable for inclusion in gasoline or fuel oil.

The higher cracking temperature favors the production of ethene and benzene, whereas lower severity produces relatively higher amounts of propene, C_4-hydrocarbons, and liquid products.

Ethylene is synthesized by steam cracking; however, propylene is merely a by-product. Propylene is synthesized by other methods, such as propane dehydrogenation. FCC LPG (fluid catalytic cracking, liquefied petroleum gas) is an important propylene and butylene source.

3.2 Classes of Polyolefins

Figure 3.3 represents the most important polyolefins such as PE, PP, and PB.

3.2.1 Low-Density Polyethylene

Low-density polyethylene (LDPE) is produced by free radical initiated polymerization in high pressure and high temperature autoclave or tubular reactors, using ethylene under severe polymerization conditions in autoclaves and tubular reactors (Figure 3.4).

- autoclaves (1500−2000 atm, 180−290 °C) or
- tubular reactors (1500−3500 atm, 140−180 °C).

3.2.1.1 Heat control

Heat control is one of the most important process characteristics in polyolefin production. The calculation below illustrates the exothermic heat produced during the polymerization process in comparison to polystyrene.

Example: Production rate: 27.000 kg/h

LDPE: $-\Delta\text{Hp} = 800$ kCal/kg for C_2H_4

PS: $-\Delta\text{Hp} = 160$ kCal/kg for PS

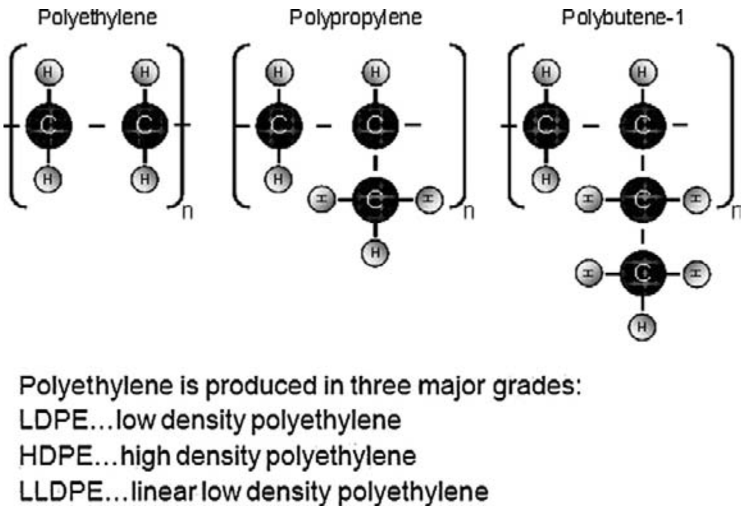
$$800\,\frac{\text{kcal}}{\text{kg}}\ \text{x}\ 27.000\,\frac{\text{kg}}{\text{h}}\ \text{x}\ \frac{1\text{h}}{3600\text{s}}\ \text{x}\ \frac{1000\text{cal}}{\text{kcal}}\ \text{x}\ \frac{4.184\text{J}}{\text{cal}} = 25.1\text{MW}$$

$$160\,\frac{\text{kcal}}{\text{kg}}\ \text{x}\ 27.000\,\frac{\text{kg}}{\text{h}}\ \text{x}\ \frac{1\text{h}}{3600\text{s}}\ \text{x}\ \frac{1000\text{cal}}{\text{kcal}}\ \text{x}\ \frac{4.184\text{J}}{\text{cal}} = 5.0\text{MW}$$

3.2.1.2 Tubular reactor

A tubular reactor is similar to a long heat exchanger. The ethylene is circulated through a compressor—the main pressurization of the feed stream is accomplished by a hyper-compressor to build up the pressure required for free radical polymerization. This free radical polymerization uses peroxide initiators or oxygen to promote polymerization reactions. The commercial tubular reactors are typically between 1000 and 2500 m long. They consist of high pressure tubes each 10−15 m long in a serpentine-like structure within a concrete bay.

The first section of the reactor is used as pre-heater. The ethylene temperature must be sufficiently high to start the



Polyethylene is produced in three major grades:
LDPE...low density polyethylene
HDPE...high density polyethylene
LLDPE...linear low density polyethylene

Figure 3.3 Polyolefins.

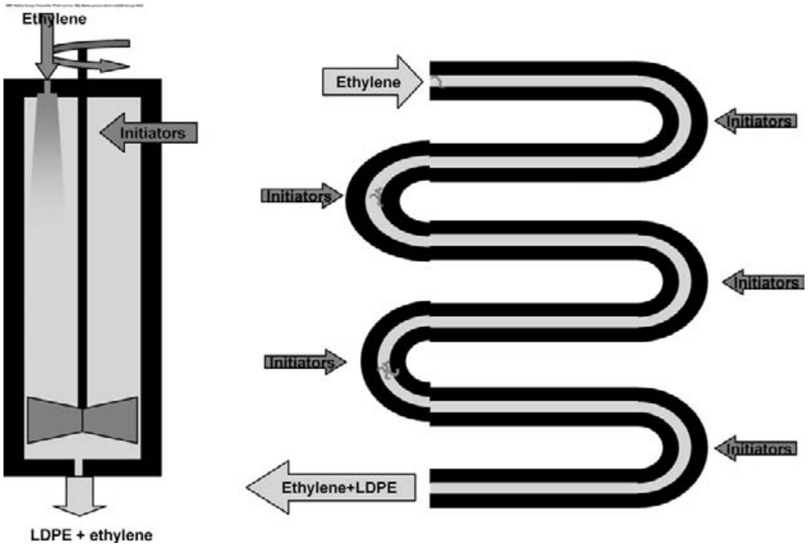


Figure 3.4 Autoclave and tubular reactor.

reaction. While only organic peroxides are used as an initiator for the autoclave reactor, oxygen (air) is also used to generate the free radicals needed to initiate the polymerization reaction in the tubular reactor.

The initiation temperature can, therefore, range from 140 (peroxides) to 180 °C (oxygen). When oxygen is used as the initiator, the air is added to the ethylene gas in the lower pressure zones of the process.

These peroxide initiators are introduced at various points along the length of the tube-zone where temperatures are accurately controlled. The injection of an initiator or a mixture of ethylene/air at different points in the reactor generates a number of zones with higher temperatures (so-called peaks) followed by cooling zones in which the reaction heat is removed from the ethylene/polymer mixture. These temperature peaks/cooling cycles can be repeated several times along the length of the reactor (Figure 3.5).

Because of the heat transfer through the walls of the reactor, the tubular reactor has a higher polymer conversion rate than the autoclave. Conversion rates of up to 36% are achieved, whereas autoclave reactors achieve approximately 20%. The conversion to polymer influences the properties of the product. At higher conversion rates, the degree of branching increases. The exothermic heat can be recuperated from the reactor via the cooling jackets, as no backmixing takes place in the tubular system, and the residence time is limited. The exothermic heat from the reaction is removed via water jackets on the outside walls of the tube.

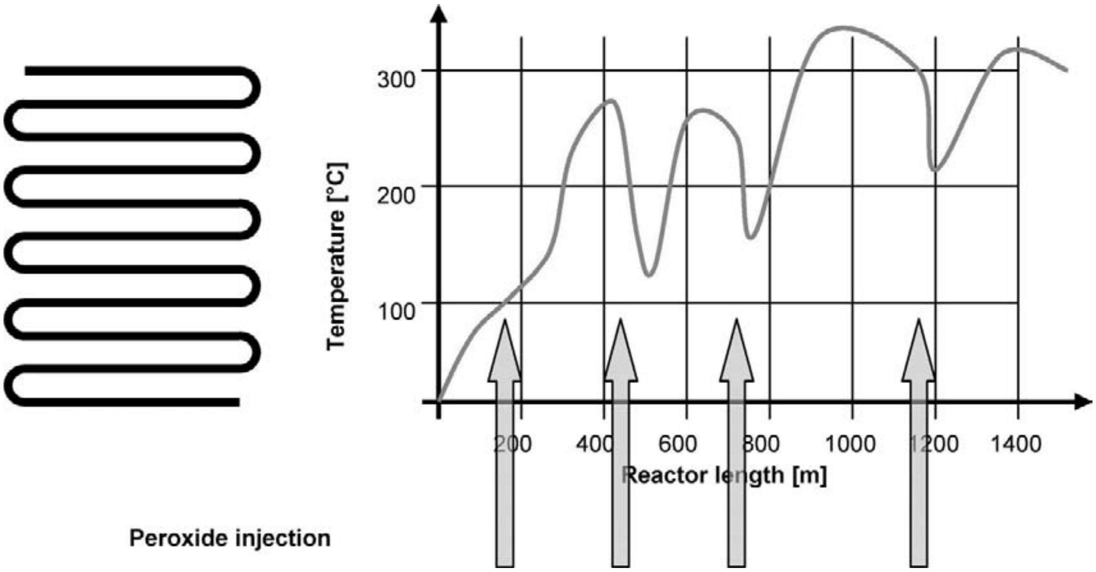


Figure 3.5 Tubular reactor temperature profile.

Upon exiting the reactor the material passes through medium pressure and low pressure separators (separates ethylene from PE), PE moves to the extruder.

3.2.1.3 Autoclave reactor

In the autoclave process polymerization takes place in a series of stirred reactors (2–6). The free radical initiator is introduced in each of the different reactors to optimize productivity and performance, as initiators organic peroxides are used exclusively. The reaction temperature is controlled by the amount of peroxide introduced. Ethylene feed gas and peroxide are introduced to a compressor and then pumped with peroxide initiator into the stirred autoclave cylindrical vessel.

Proprietary designs baffle or partition the reactor into discreet zones enabling control of molecular species and the amount of LCB of polymer in these zones. In contrast to the tubular reactor, backmixing does take place in the autoclave system.

The walls of the autoclave unit are thick to accommodate high pressures which are generated. The heat of reaction is removed by the introduction of fresh feed.

Upon exiting the reactor the material passes through medium pressure and low pressure separators (separates ethylene from LDPE polymer). Afterwards the polymer enters the pelletization process to be pelletized (Figure 3.6).

One or more co-monomers can be polymerized with ethylene and a mixture of initiators used to obtain desired reactor performance and polymer microstructure.

3.2.1.4 Free-radical reaction mechanism

As already mentioned, the polymerization reaction is a free-radical polymerization, with organic peroxides providing the source of the free radicals, which are short-lived reactive intermediates with unpaired electrons. The reaction starts when a free radical reacts with an ethylene molecule, forming a new molecule until the growth of long chain molecules ends.

When high pressures are involved, the polymerization step is very rapid. The polymerization process can be described by the classic kinetic description of free-radical (chain) polymerization.

When simplifying the free radical mechanism, the following steps can be distinguished:

- *Initiation*: Free-radical sites for polymerization are formed by reaction between primary initiator free-radical fragments and vinyl molecules (Figure 3.7).

Free radicals are generated by thermal dissociation of initiators. Free radicals are molecules with unpaired electrons.

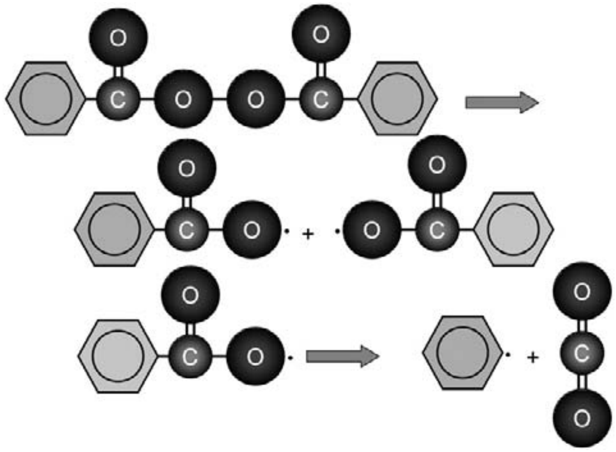


Figure 3.7 Initiation.

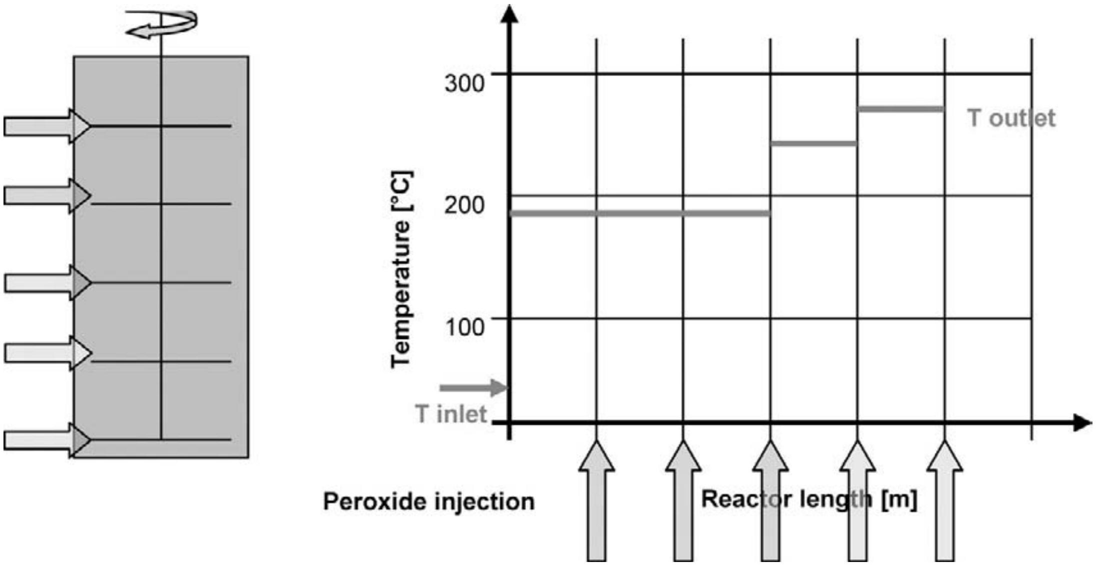


Figure 3.6 Autoclave temperature development.

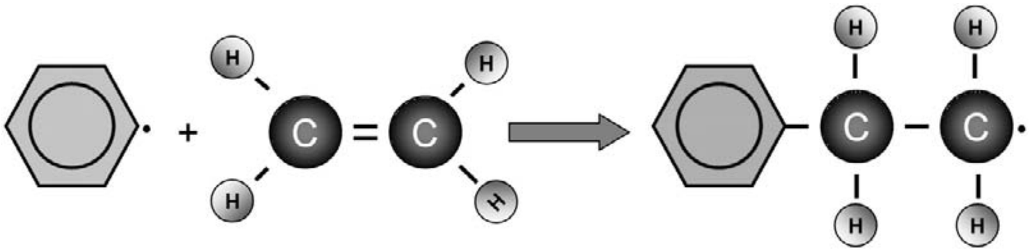


Figure 3.8 Propagation.

- *Propagation*: Polymerization then proceeds through a series of additions of monomer molecules to the growing polymer chain, with the free-radical site jumping to the end of the growing chain after each addition (Figure 3.8).
- *Termination*: Active free radicals are destroyed by either combination (coupling) or, more rarely, disproportionate (Figure 3.9).

A different class of reactions determines the molecular weight and molecular weight distribution of the polymer.

- *Chain transfer reactions*: Active free radical sites at the ends of growing chains jump to another site on the same polymer molecule, a different polymer molecule, a solvent, monomer, or modifier molecule. Chain transfer affects the size, structure, and end groups of the polymers. Chain transfer agents (modifiers) are able to donate hydrogen atoms to this reaction.

3.2.2 High-Density Polyethylene

High-density polyethylene (HDPE) is made with Ziegler—Natta (Z—N) catalyst systems. It has a totally different structure from that obtained by radical polymerization in having a much lower degree of branching (0.5—3 vs. 15—30 side chains per 500 monomer units). Chain transfer to polymer is not possible in coordination polymerization.

LDPE and HDPE are referred to branched and linear polyethylene respectively. The low degree of branching results in high crystallinity (70—90%) compared to (40—60%) in the case of LDPE and a higher crystallization velocity. This increases polymer density (0.94—0.96 g/mL vs. 0.91—0.93 g/mL) and crystalline melting temperature (130—138 °C vs. 105—115 °C).

Compared to LDPE, HDPE has increased:

- tensile strength
- stiffness
- chemical resistance
- upper-used temperature

combined with decreased:

- elongation
- resistance to stress crack
- low-temperature brittleness

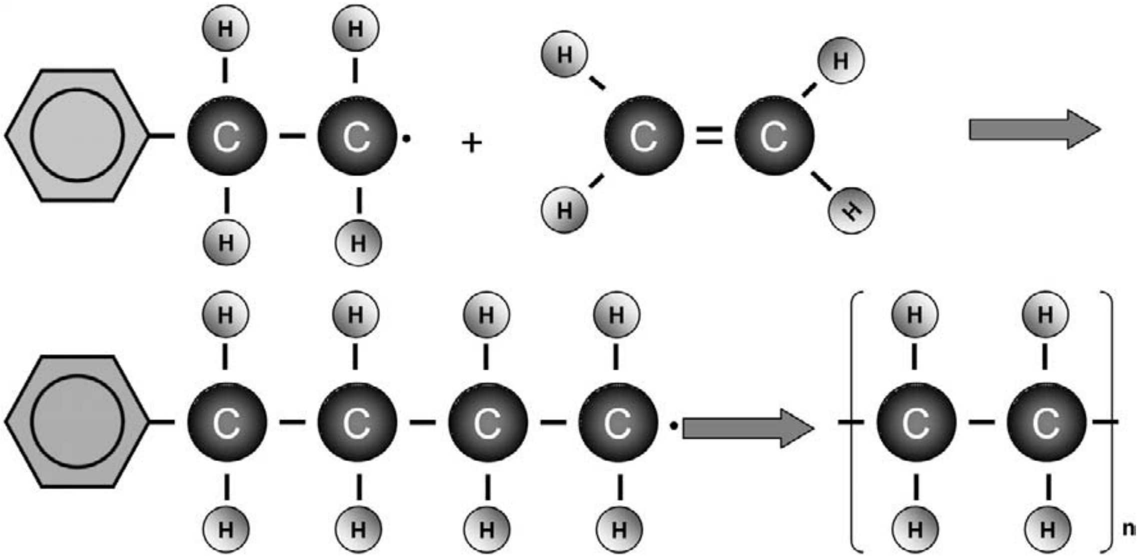


Figure 3.9 Termination.

In summary, HDPE has much greater rigidity than LDPE and can be used in structural applications.

3.2.2.1 Average molecular weight of HDPE

Most HDPEs have average molecular weights in the range of 50×10^3–250×10^3. Various specialty HDPEs are produced by polymerization to higher molecular weights. Increased molecular weights result in increased tensile strength, elongation, and low-temperature impact resistance.

High-molecular weight HDPE (0.25–1.5×10^6 g/mol) as well as ultra high-molecular weight HDPE ($>1.5 \times 10^6$ g/mol) are produced, which has the highest abrasion resistance and impact strength.

3.2.3 Linear Low-Density Polyethylene

Linear low-density polyethylene (LLDPE) is made by the copolymerization of ethylene and a comonomer. Typically, comonomers used for the polymerization of LLDPE are butene, hexene, and octene.

The main polymer chain of LLDPE is composed of long strings of repeating ethylene molecules; the comonomer forms short side chains which are linked to the main chain.

The long-chain branching (LCB) already known from LDPE is not typical for LLDPE. While LDPE has high levels of LCB, there is little LCB in LLDPE; however, there are high levels of short-chain branching (SCB) contributed by the incorporated comonomer. Molecular weight distribution is narrow (LDPE and HDPE tend to be broader).

LLDPE consists of long linear molecules with short side chain branches (SCB). SCB length is a function of the comonomer type employed (Figure 3.10).

3.2.3.1 Commonly used polyethylene comonomers

Butene—A four carbon long molecule (Figure 3.11). Formula: C_4H_8

$H_2C{=}CH{-}CH_2{-}CH_3$

Hexene—A six carbon long molecule (Figure 3.12). Formula: C_6H_{12}

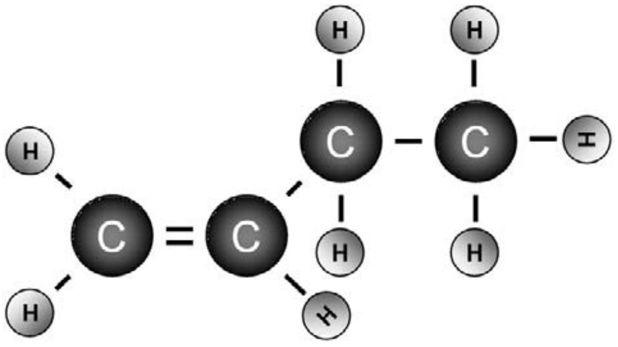


Figure 3.11 Butene.

$H_2C{=}CH{-}CH_2{-}CH_2{-}CH_2{-}CH_3$ (

Octene—An eight carbon long molecule (Figure 3.13). Formula: C_8H_{16}

$H_2C{=}CH{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_3$

3.2.3.2 Comonomer-type product properties

Product toughness will be influenced by short side branching. Longer side chains, like those formed with hexene and octene are longer and result in improved mechanical performance.

Z/N catalysts tend to have more difficulty than single-site catalysts in placing comonomers on the longer chain (higher molecular weight) portion of the polymer; thus, more comonomers end up on the shorter chains. Comonomer addition levels are used to control resin density (see Tables 3.1 and 3.2).

3.2.4 Crosslinked Polyethylene

Crosslinked polyethylene (PEX) can be based upon HDPE as well as MDPE and on LDPE. In the crosslinking process the molecules are linked together by strong chemical bonds, and both chemical and physical crosslinking methods are available. The chemical methods imply the use of crosslinking agents such as peroxide, AZO compounds, or silane, while physical crosslinking is achieved by electron radiation. Figure 3.14 represents various methods for crosslinking of polyethylene.

Figure 3.10 Molecular diagram LLDPE.

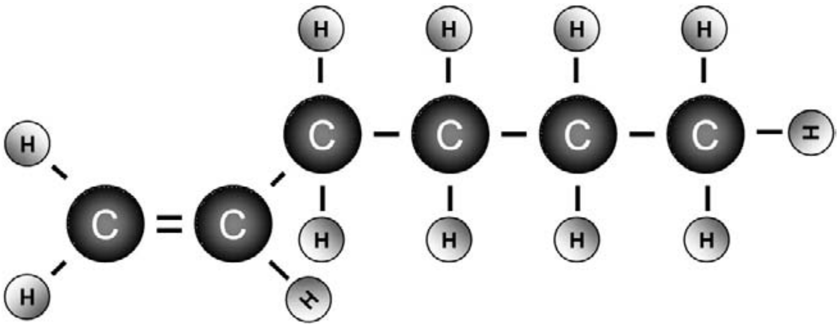


Figure 3.12 Hexene.

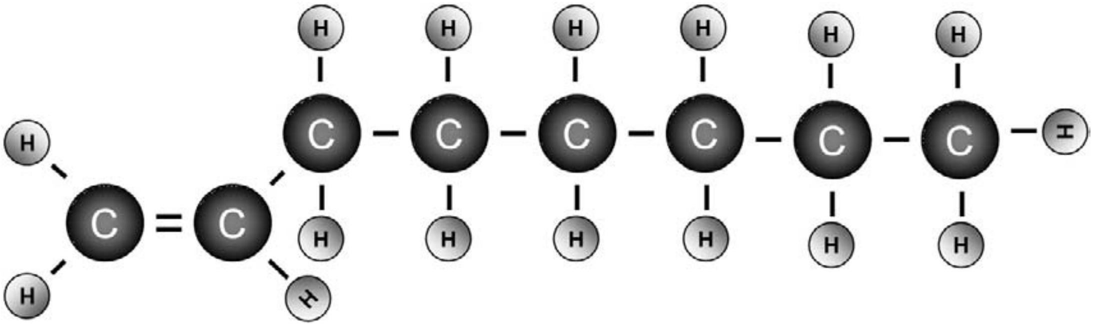


Figure 3.13 Octene.

3.2.4.1 Silane

The "Silane" method of PEX production involves grafting a reactive silane molecule to the backbone of the polyethylene. The tubing is produced by blending this grafted compound with a catalyst which can be done either by using the Sioplas method or by using the Monosil method in which a special extruder is used. After extrusion the tubing is exposed to either steam or hot water to induce the final crosslinking reaction in the tubing.

Table 3.1 Effect of comonomer type on physical properties

Melt Index	1.0	1.0	1.0
Density (g/cm^3)	0.919	0.918	0.920
Comonomer type	Butene	Hexene	Octene
Tensile strength (MPa)	33.1	36.5	46.8

3.2.4.2 Peroxide

The peroxide method (Engel process) employs a special extruder with a plunger action where peroxide is added to the base resin and through a combination of pressure and high temperature the crosslinking takes place as the tubing is produced.

The Azo process is similar in nature to the Engel process, which uses an Azo compound (Azo compounds are chemical compounds with the general formula R—N=N—R', where R and R' can be either aryl (aromatic) or alkyl (aliphatic) functional groups) rather than a peroxide.

The Azo compound decomposes at very high temperatures, normally in downstream catenary tubes, once again

Table 3.2 Molecular structure and properties of various grades of polyethylene

PE Type	Degree of Branching	Degree of Crystallinity (%)	Melting (°C) (crystallization)	Density (g/cm^3)	Strength	Elongation	Max. Use Temperature (°C)
PE-LD	High	40–60	105–115 (80–95)	0.915–0.933	Low	High	90
PE-LLD	Middle	55–65	120–130 (105–115)	0.92–0.94	Middle	Medium	95
PE-HD	Low	70–90	130–138 (115–120)	0.93–0.97	High	Low	100

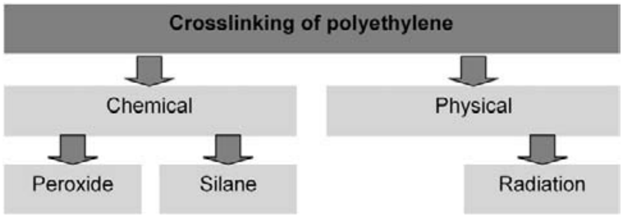


Figure 3.14 Various methods for crosslinking of PE.

forming free radicals to crosslink the polyethylene chains together rather than forming peroxides.

3.2.4.3 Radiation

Electron beam crosslinking takes place when very high energy radiation is used to initiate molecular crosslinking in HDPE. This product is extruded like normal HDPE then taken to an E-beam facility and routed under a beam or ray in the accelerator where it is dosed with a specific amount of radiation to release the hydrogen atoms and cause polymer chains to bond or link to the open carbon sites.

Crosslinking of polyethylene results in the following:

- Improved heat resistance
- Improved pressure resistance at elevated temperatures
- Improved environmental stress–crack resistance
- Improved weathering resistance
- Improved chemical resistance

3.2.5 Polypropylene

Polypropylene is the second most important commercial polyolefin. Isotactic PP has the lowest density (0.90–0.91 g/mL) of the major plastics. It has a high crystalline melting point of 165 °C. The first commercial production of polypropylene was in the 1950s following the discovery of Z–N catalysts.

It was produced initially in a slurry process where propylene is reacted in the presence of a catalyst in solvent to produce a mixture of crystalline and amorphous polymer. The disadvantage of this route was that the catalyst had to be treated with alcohol to deactivate and extract it, while unwanted atactic polymers had to be extracted and removed.

Bulk technologies were then developed in which the solvent was replaced by liquid propylene. In addition, considerable efforts were made in improving the activity of the catalysts. The higher activity catalysts also enabled the introduction of new processes and technology. Industrial production processes are explained within a specific chapter.

There are three main families of polypropylene based on internal structures leading to different properties (Figure 3.15):

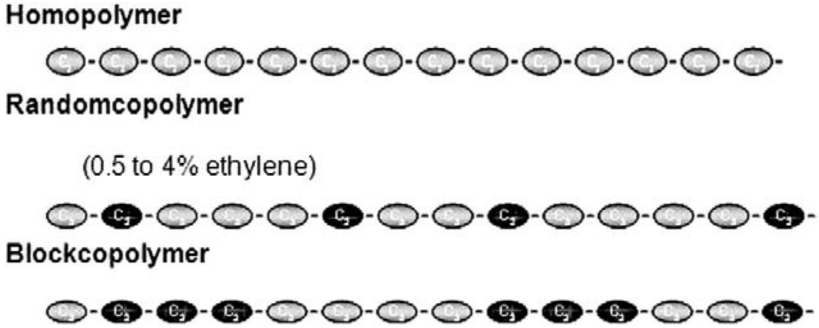


Figure 3.15 Polypropylene product families.

3.2.5.1 Polypropylene homopolymer

The chain characteristics follow directly from the chemistry of the particular polymerization reactions. Stereo regular polypropylene can be obtained by using various catalysts that promote regular insertion of the monomers in the growing chain. Thus, the type of catalyst used, together with the support of the catalyst [Pau1993] has an important influence on the primary chain architecture. The main chain characteristics of linear PP are the molar mass (MM), molar mass distribution (MMD), and chain regularity. Gel permeation chromatography (GPC) is typically used to measure molar mass and molar mass distribution. Polypropylene is a stereoregular polymer. The stereoregular nature is determined by the position of the methyl side–groups along the main chain as illustrated in Figure 3.11. This means that the neighboring methyl groups in a polypropylene chain have two stereoisomeric positions with respect to each other.

The three physical stereo configurations that can be distinguished in polypropylene are isotactic, syndiotactic, and atactic (Figure 3.16).

Polypropylene exists under two main forms:

1. Crystalline, called isotactic PP
2. Amorphous, called atactic PP

Isotactic PP
All methyl groups are on the same side of the chain.

- Polymer can crystallize

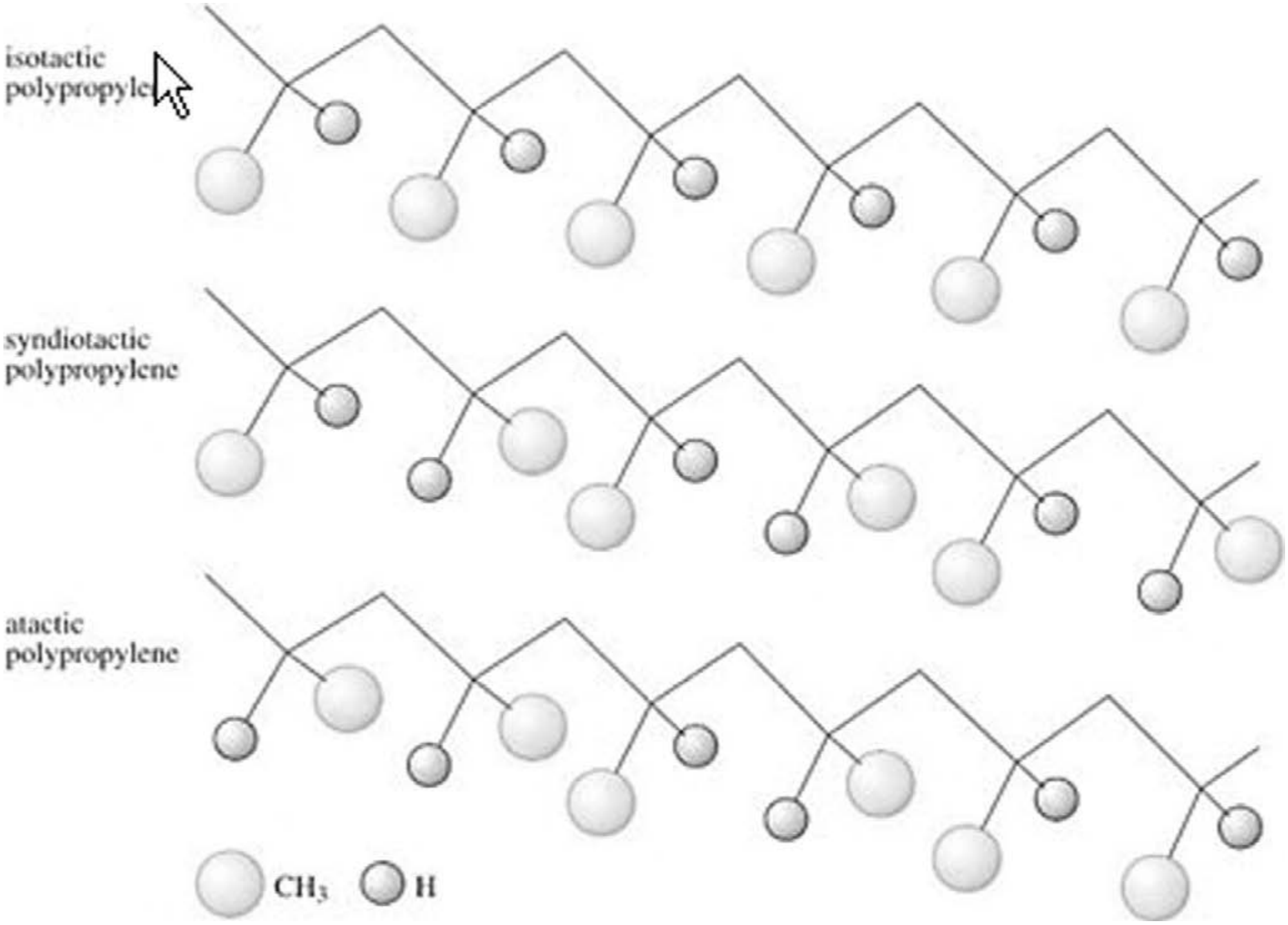


Figure 3.16 PP configuration.

Atactic PP
Methyl groups are randomly distributed along the chain.

- Polymer cannot crystallize

Crystallinity and morphology of polypropylene

The addition of nucleating agents is one of the most important methods employed to modify morphology and is widely applied in the plastics industry. Incorporating finely divided solid particles into semi-crystalline polymers can induce nucleation of fine polymeric crystals. The addition of nucleating agents increases the temperature of crystallization resulting in a decrease in cycle for injection molding [Fil1994]. Nucleating agents increase the number of crystallization sites in polymers and reduce the spherulite size. They cause simultaneous growth and thus evenly sized crystals. Smaller evenly sized crystals improve the physical properties, like transparency and flexural modulus, of the polymer.

An effective nucleating agent provides an active surface for polymer adsorption, providing a higher degree of crystallinity and a more uniform crystalline structure as the melt is cooled. The heterogeneous nuclei influence the crystallization kinetics, the size of spherulites, and, consequently, the resulting properties. In particular, the formation of specific crystalline forms in polymorphic polymers can influence the macroscopic behavior quite dramatically. The most effective solid-particle nucleating agents have a high surface energy as well as a high surface area, generally resulting from a finer particle size. A high surface energy and high specific surface area increases the number of nuclei or spherulites formed and increases polymer chain mobility at higher crystallization temperatures, thus allowing faster crystallization rates.

The advantages in increasing the polymer crystallinity by addition of a nucleating agent include the following:

- Improvement in the stiffness or flexural modulus of the composite
- Increase of crystallization temperature
- Improvement in injection molding cycle times, where parts can be removed more quickly from the mold

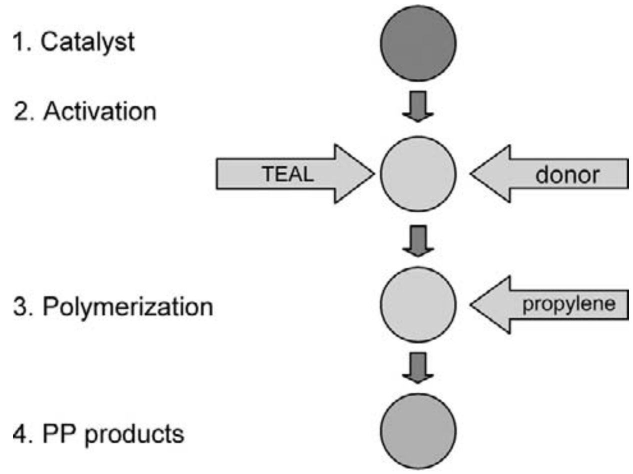


Figure 3.17 Polypropylene production route.

Commonly, PP crystallizes into monoclinic α-phase. However, specific α-nucleating agents are often added into the material primarily to improve the transparency, whilst the shortening of processing time and some improvement of the mechanical properties are added advantages. The second crystalline phase of PP, trigonal β-phase, can become predominant in the presence of a specific β-nucleating agent. Such a β-nucelated material shows significant differences in mechanical properties compared to common α-polypropylene, namely higher toughness and drawability, but lower stiffness and strength. Basically, the addition of nucleating agents significantly decreases a spherulitic size as a number of (heterogeneous) crystallization nuclei rises.

Talc as a nucleating agent: Talc is a commonly used nucleating agent in polypropylene. As little as a few tenths of a percent of an ultrafine talc will provide effective nucleation, with up to 3% by weight of larger talc particles being used for the purpose.

3.2.5.2 Copolymers

Beyond homopolymers, there exist a wide range of copolymers, usually made of two types of ethylene, random or impact.

Random copolymers

Random copolymers typically contain up to 5% (by weight) of ethylene or other comonomers inserted at random within the chain.

Similar to homopolymers, the structural parameters of molecular weight (MW) and molecular weight distribution (MWD) play a similar role for the properties of the random copolymers, while the stereospecificity concept changes its meaning. In fact, the introduction of a comonomer into polymeric chain determines a discontinuity that deeply affects the molecule's crystallization behavior. The crystallization speed slows down, forcing lower total crystallinity and a reduction of the melting temperature related to the less perfect structure of the crystals.

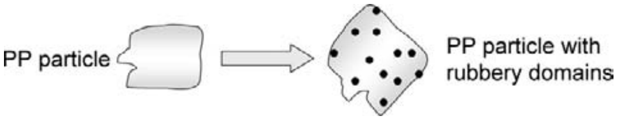


Figure 3.18 Impact PP structure.

Random copolymers are used where clarity, lower melting point, or a lower modulus is desirable.

Impact copolymers

Impact copolymers, also known as heterophasic copolymers or rTPOs, usually contain up to about 40% ethylene-propylene rubber (EPR), distributed inside the semi-crystalline PP homopolymer matrix. This copolymer phase is added to increase the impact strength of the product at low temperatures. As a result of its glass transition temperature the impact strength of polypropylene homopolymer is often unacceptable for use in low temperature applications, such as packaging or automotive applications (Figure 3.18).

These impact properties depend on the EPR rubber dispersion, composition and particle sizes, and on the matrix crystallinity. However, such modifications to improve the impact properties are often detrimental to other desired properties such as high stiffness and HDT. The development of these new systems shows an improved balance between properties and therefore represents one of the major challenges within the PP industry. For instance, an improved balance between impact strength and stiffness, impact strength and transparency as well as impact strength and stress whitening is desired and are therefore areas of continuous research.

Optimizing impact strength usually implies negligible copolymer crystallinity which requires a copolymer of approximately 50 mol% ethylene. By varying the amount of the copolymer phase relative to the homopolymer phase, low-to-high impact strength products can be produced. A polyethylene phase can be added to the impact polypropylene in the third stage, to produce a low blush product that reduces stress whitening (Galli and Ali, 1987).

The improvement of the impact properties while retaining sufficient elastic modulus performance (good stiffness impact strength balance), when coupled with the basic thermal, physical and chemical properties of the PP, has opened a wide area of applications. Key issues are found mainly in the production of structural items in the automotive and durable goods, and also in the packing industries.

Determination of morphology. The shape, content, size, and size distribution of dispersed rubber particles are

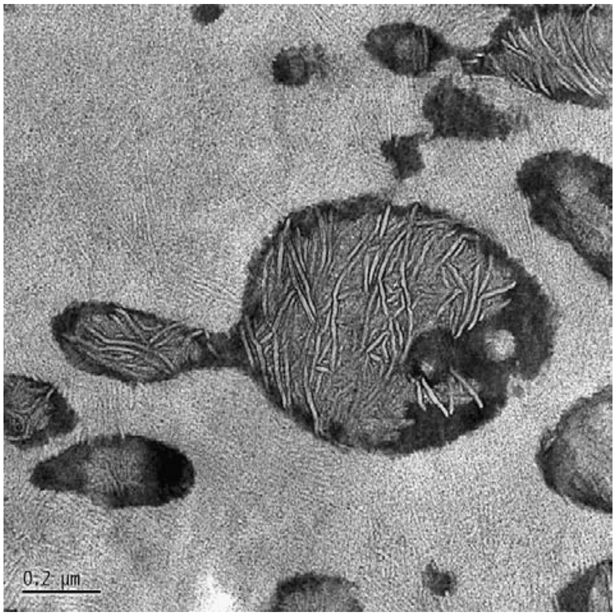


Figure 3.19 Heterophasic PP; Institute for Electron Microscopy, Technical University Graz.

important factors affecting the toughening effect of PP impact-modified copolymer, which relate to the micromorphological structure of the material. A wide range of characterization methods has been applied to study these rTPOs. A number of these techniques are suited to providing information on the morphology of PP copolymers where the EPR domains typically extend from a few hundred nanometers to a few micrometers in size.

Scanning electron microscopy (SEM) has been applied to study the EPR distribution in PP copolymers. TEM is another technique that has been widely applied to study the morphology in PP copolymers. The prepared TEM samples show a clear contrast between matrix and rubber inclusions. This technique has the advantage that the lamellae structure of the PP matrix as well as the rubber part can be studied (Figure 3.19).

Since the amount of elastomer phase in the reactor material cannot be controlled directly, only a qualitative measure is possibly illustrated by the amount of the xylene soluble fraction (XS) in wt%. The XS is measured in boiling xylene according to ASTM D5492.

Mechanical properties. The improvement in toughness (impact strength) when EPR is added to PP matrix normally results in a reduction of its stiffness, which is usually related to a decrease in flexural modulus, yield stress, and an increase in the yield strain. A balance between toughness and stiffness is always required for optimum performance of the rubber-toughened polymer. The mechanical performance, shrinkage, and processing behavior of heterophasic polypropylene is influenced by rubber particle size, rubber composition, and rubber content.

Influence of rubber particle size. The rubber particle size of heterophasic polypropylene can be described by molecular weight. The molecular weight of an ethylene propylene copolymer can be described by its intrinsic viscosity, as measured by the XS fraction. The η of an ethylene propylene copolymer is generally determined at 135 °C using decalin as a solvent (Figure 3.20).

Rubber particle size characterized by intrinsic viscosity influences the flow behavior, shrinkage, and mechanics of heterophasic polypropylene. At equal rubber concentrations, a high IV yields a greater decrease in the MFI when compared to low IV materials. The influence on increased impact properties is also higher.

Influence of rubber particle composition. The composition of the rubber phase is important with respect to the mechanical properties. Varying the ethylene/propylene ratio in an EPR can have a large effect on the heterophasic polypropylene properties.

High propylene content in high IV rubber results in better impact resistance, less shrinkage, and reduced stiffness. High propylene content in low IV rubber results in increased shrinkage, increased impact resistance, and reduced stiffness.

Production. Common to all polymerization units is the bulk polymerization section for homo and random copolymers. This bulk polymerization employs tubular loop reactors filled with liquid propylene which is continuously fed the catalyst and hydrogen for molecular weight control. In the case of random copolymers, a comonomer such as ethylene is also added. The resulting polymer is continuously discharged from the reactor, whereas unreacted propylene is recovered and pumped back into the loop reactor.

The production of impact copolymers also requires a gas phase reactor into which the polymer from the loop reactor is transferred. In this reactor an elastomer is formed by the introduction of ethylene and propylene at certain ratios with the homopolymer matrix formed in the first reactor. One of the most significant challenges in the production of impact copolymers is to control the morphology of the growing catalyst/polymer particle which can have a pronounced effect on the operation of the process.

Various factors influence the performance of these copolymers, including the amount of elastomer for the polypropylene matrix, as well as the chemical affinity of the elastomer for the polypropylene matrix, and also the distribution of the rubber particles. A homogeneous distribution of the rubber particles provides the best dispersion of energy, giving the best impact stiffness ratio. A homogeneous distribution of the rubber particles is also necessary in order to avoid reactor fouling.

There are different industrial processes available for the rTPO production.

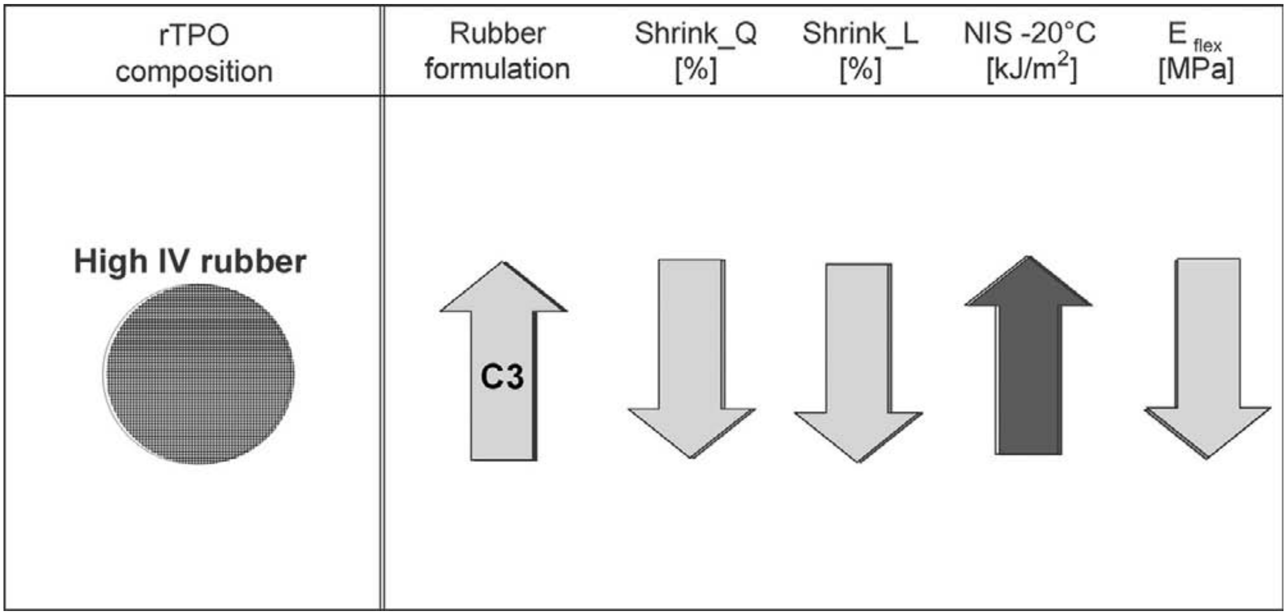


Figure 3.20 Effect of rubber IV on material properties.

3.2.6 Polybutene-1

Polybutene-1 (PB-1) was first synthesized in 1954, one year after polypropylene. It took another 10 years until Chemische Werke HÜLS, Germany, started the first industrial production in 1964 (capacity: ca. 3 kt/a). Vestolen BT was introduced to the market soon afterward.

Polybutene exists in two isomeric forms depending on where the carbon double bond is positioned in the monomer molecule. If it is between the first and second carbon atoms in a linear molecule (butene-1), then the chemically accurate name of the resulting polymer is "polybutene-1" (PB-1). If it is a branched monomer molecule then the resulting polymer is called polyisobutylene (PIB).

The polymer we are concerned with is PB-1. In the past this polymer has been referred to as polybutylene, PB, PB-1, and polybutene, as well as its chemically correct name, PB-1. PB-1 is obtained by polymerization of butene-1 with a stereospecific Z−N catalyst to create a linear, high molecular, isotactic, semi-crystalline polymer. PB-1 combines the typical properties of conventional polyolefins with some characteristics of technical polymers. In chemical structure PB-1 differs from polyethylene and polypropylene only by the number of carbon atoms in the monomer molecule (Figure 3.21).

3.2.6.1 Crystallization behavior

Solid PB-1 can exist in four crystalline states. Three of them are metastable (Forms II, III, and I′). During solidification from the molten state PB-1 mainly crystallizes to tetragonal Form II. In the course of a few days the material passes through a crystalline phase transformation to build the stable Form I (Table 3.3).

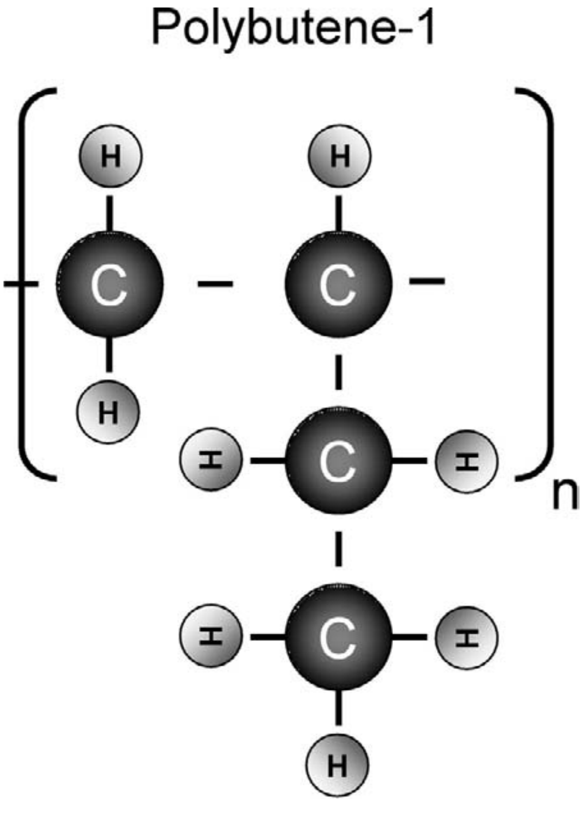


Figure 3.21 Polybutene-1 structure.

Table 3.3 PB1 Crystalline states

Crystalline form	Shape	Melt Temperature (°C)	Density (g/cm^3)
I	Twin hexagonal	121–130	0.915
II	Tetragonal	100–120	0.900
III	Ortho-rhombic	~96	0.897
I'	Hexagonal without twins	95–100	–

The C_2H_5 side groups of PB-1 are long enough to create a free volume between the molecules when the melt solidifies. During the recrystallization phase, the "voids" are filled and the material shrinks approximately 2%.

Hence, crystalline Form I is denser and the product characteristics differ from Form II. The melting temperature, density, hardness, stiffness, and yield stress increase, while the ultimate elongation remains unchanged. Once fully crystallized, PB-1 obtains its best mechanical performance.

The recrystallization continues over a long period but most of it is completed after 7–10 days (Figure 3.15). The speed of phase transformation depends on the temperature, hydrostatic pressure, structure, orientation, and nucleation. Re-crystallization occurs fastest at room temperature. At 23 °C and atmospheric pressure the phase transformation of PB-1 homopolymers takes about 1 week; however, at a pressure of 2000 bar it happens in only 10 minutes (Figure 3.22).

Due to its similar structure, PB-1 is very compatible with PP. It can be used in blends to improve certain characteristics of PP. On the other hand, PB-1 is not compatible with PE. PB-1 copolymers are blended in PE film grades for use in peelable packaging.

3.2.6.2 Strain resistance

In comparison with other polyolefin materials, PB-1 has a higher level of resistance to strain under continually applied stress over long periods of time. This is known as creep behavior and the graph illustrates the increasingly superior performance of PB-1—at times in excess of 100 hours (Figure 3.23).

3.2.6.3 Melt properties

The molecular weight of PB-1 is typically around 750,000. Unexpectedly, the processability is not affected by the high molecular weight. PB-1 can be processed with conventional plastics manufacturing equipment. The melt strength is approximately twice as high as for PP, which results in better drawability and less sagging of the melt during extrusion (Figure 3.24).

Having a tensile modulus of ca. 400 MPa, PB-1 homopolymers are more flexible than PP-R (min. 850 MPa) and PEX (min. 600 MPa). Their flexibility remains high even at low temperatures and allows easier handling during cold seasons.

In addition to its superior mechanical and thermal properties, PB-1 provides a high level of resistance to chemical attack and also meets a level of flammability resistance which satisfies most application demands.

3.2.6.4 Property overview

Physical properties	
Tensile strength	0.5–2.4 N/mm^2
Thermal coefficient of expansion	130×10^{-6}
Max. continuous use temperature	up to 95 °C
Density	0.91 g/cm^3

3.3 Catalysts for Olefin Polymerization

Industrially, many different catalysts have been and are currently used for olefin polymerization. The most significant groups include supported or unsupported Z–N, chromium oxide, and, more recently, metallocene-based systems. The kinetics that control the polymerization process are quite complex and may involve multiple sites on the catalyst surface, reactions between co-catalyst and donor, poisoning, and site transformation effects. In addition, the polymerization may involve chain transfer agents such as hydrogen for molecular weight control and several monomers may be simultaneously polymerized. Further complicating this process is the fact that diffusion resistances may be present during the growth of the polymer particle.

3.3.1 Ziegler–Natta Catalysts

A Z–N catalyst can be defined as a transition metal compound bearing a metal–carbon bond able to carry out

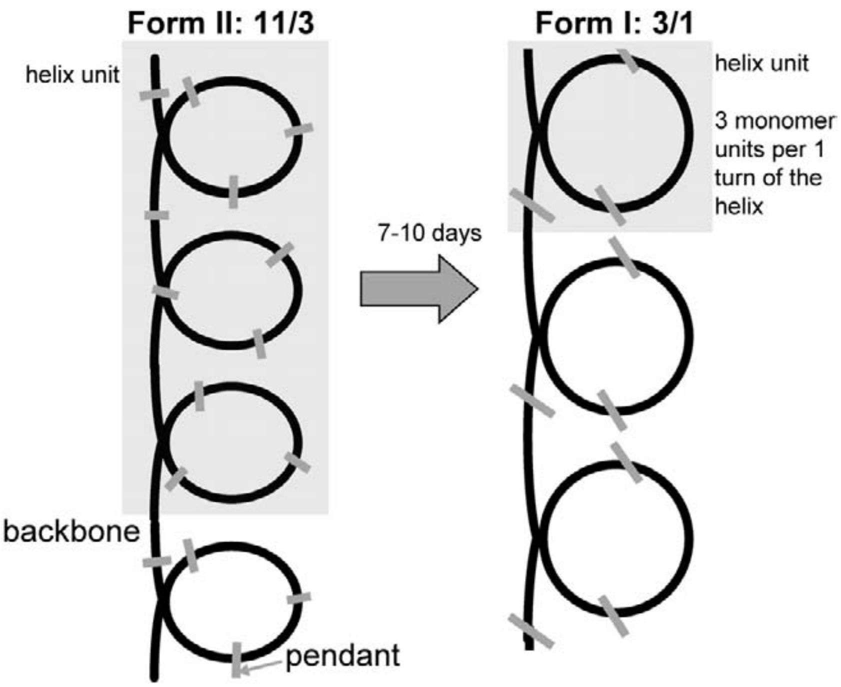


Figure 3.22 Polybutene-1; polymorphic structures.

a repeated insertion of olefin units. Usually, though not necessarily, the catalyst consists of two components:

- a transition metal salt, as $TiCl_4$
- a main-group metal alkyl (activator) which serves the purpose of generating the active metal−carbon bond

The highly active heterogeneous Z−N catalyst, which is used extensively nowadays, has active sites, $TiCl_4$, for polymerization. These active sites are located at the surface and edges of the crystalline structure of titanium chloride. This support has high surface area and pore volume; thus, it significantly increases catalyst activity.

The co-catalysts (activators) used with $MgCl_2$-supported catalysts are invariably altrialkyls, triethyl-aluminum (TEAL),

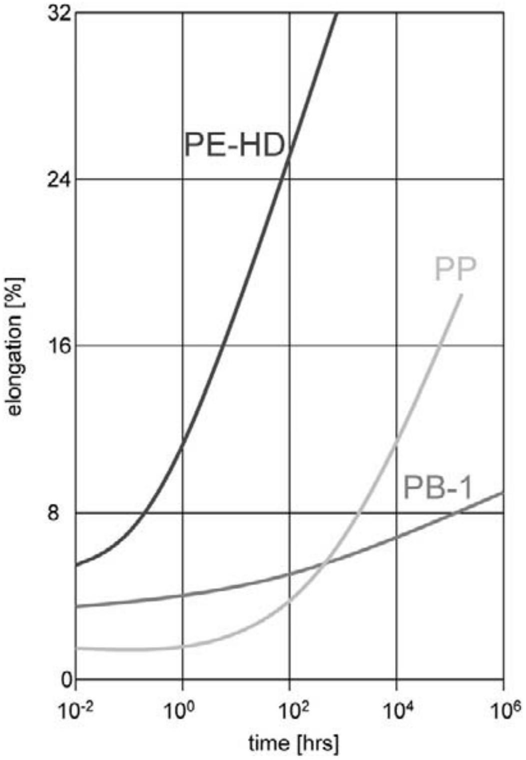


Figure 3.23 Creep behavior.

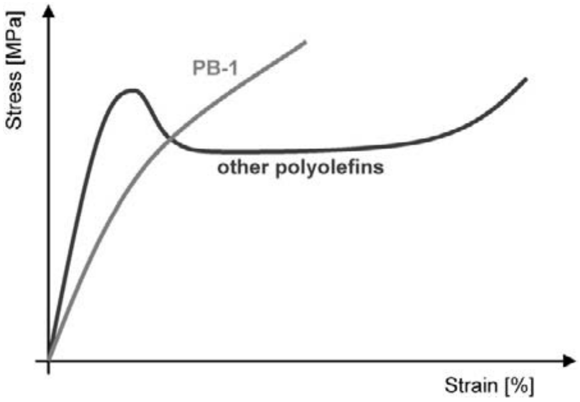


Figure 3.24 Tensile behavior of PB-1 vs. other polyolefins.

and triisobutyl-aluminum (TIBA) being the most preferred ones. For these catalyst systems, active sites are generated through the interaction of the transition metal atoms on the catalyst surface and the organoaluminum compound (cocatalyst).

Because the co-catalysts work as a Lewis acid (electron acceptor), it is also used to scavenge polar impurities from the reactor. These impurities are electron donors, such as oxygen, sulfur, and nitrogen compounds, and moisture that poison the cationic active sites.

A major advance in heterogeneous Z−N catalysts was the use of internal and external donors, which improve the properties of the produced polymer (i.e., crystallinity) as well as increase catalyst activity.

3.3.1.1 Performance of different Ziegler−Natta catalysts

Table 3.4 shows an updated comparison of the performance achievable with the different catalyst generations. The comparison based on data obtained under bulk polymerization conditions at 70 °C and for a 2-hours; run.

For the first two generations, the polymerization rate was very low as well as the isotacticity. Thus, two successive steps, after polymerization, were required:

- polymer purification from catalyst traces
- atactic polymer removal

For the third generation, the polymerization reaction became more steroeselective; however, the activity was not really high. However, this changes a lot when Lewis base, benzoate, is used.

Both catalyst activity and polymerization stereoselectivity increases and PDI decreases while we are moving from the 3rd to the 5th generation. However, this is not the case for succinate-based systems.

3.3.2 Phillips Catalyst

Phillips catalysts are based on Cr(IV) supported on silica and alumina. The true structure of the Phillips catalyst has not to date been well understood. A mixture of chromium oxide and silicon oxide (CrO_3/SiO_2) is used to create the active sites. The catalyst does not require additional chemical activators before the polymerization can occur, since the active site is produced prior to the polymerization by thermal activation at high temperatures (600 °C, for instance). Phillips catalysts are used in both gas-phase and slurry processes. Polyethylene made with Phillips catalysts has a very broad molecular weight distribution, with polydispersities ranging from 12 to 24.

Table 3.4 Evolution of Ziegler−Natta catalyst systems

Year	Catalyst System	Productivity (kg PP/g cat)	I.I (%)	Mmmm (%)	M_w/M_n	Hydrogen Response	Generation
1954	$\delta-TiCl_3 * 0.33AlCl_3 + AlEt_2Cl$	2−4	90−94			Low	1st
1970	$\delta-TiCl_3 + AlEt_2Cl$	10−15	94−97			Low	2nd
1968	$MgCl_2/TiCl_4 + AlR_3$	15	40	50−60		Low	3rd
1971	$MgCl_2/TiCl_4/$Benzonate + $AlR_3/$Benzonate	15−30	95−97	90−94	8−10	Medium	
1980	$MgCl_2/TiCl_4/$Phthalate + $AlR_3/$Silane	40−70	95−99	94−99	6.5−8	Very high	4th
1988	$MgCl_2/TiCl_4/$diether + AlR_3 $MgCl_2/TiCl_4/$diether + $AlR_3/$Silane	100−130 70−100	95−98 98−99	95−97 97−99	5−5.5 4.5−5	High	5th
1999	$MgCl_2/TiCl_4/$succinate + $AlR_3/$Silane	40−70	95−99	95−99	10−15	Medium	6th

Notes: I.I: (isotactic index) is a measure of the isotactic content of a polymer. It is the percentage of insoluble polymer sample in a hydrocarbon solvent such as boiling n-heptane.

Mmmm: measures the isotactic sequence in a polymer chain; in this case, five stereocenters are considered.

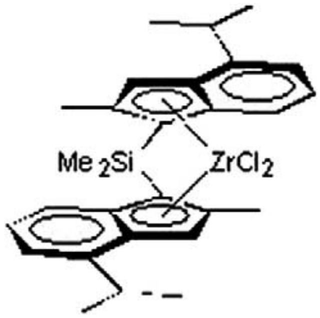


Figure 3.25 Metallocene catalyst structure.

Interestingly, hydrogen is not an effective chain-transfer agent and generally decreases catalyst activity.

3.3.3 Metallocene Catalysts (Single Site Catalyst)

A large variety of metallocene catalysts can be obtained by altering the simple structure of Cp_2ZrCl_2. The nature of the transition metal and the structure of the ligand have a large effect on catalyst behavior (Figure 3.25).

The shape, geometry, and chemical structure of the ligand can affect the activity and selectivity of the catalyst. The symmetry imposed by ligands around the active site determines the geometry for monomer coordination and insertion, and consequently the relative orientation of the catalyst and the growing polymer chain.

There is a difference between polyolefins made by Z−N catalysts and those made by metallocenes.

Metallocene catalysts offer a narrow molecular weight distribution and a significantly reduced low molecular weight fraction. Metallocenes are more sensitive to hydrogen than Z−N catalysts, which results in the ability to produce very high melt flow rate polymers directly in the reactor (Table 3.5).

Table 3.5 Ziegler−Natta vs. metallocene catalysts

	Ziegler−Natta	**Metallocene**
Catalyst	$TiCl_4$	Zr-{Cp}x
Metal	Titanium	Zirconium
Chemistry	Inorganic	Organometallic
Co-Catalyst	TEAl	MAO or Boron Activators
Support	$MgCl_2$	SiO_2
Donor	Various	None
Active sites	Multiple	Single

Figure 3.26 illustrates the effect of a Z−N system and a Metallocene catalyst on the polymer structure. A Z−N system consists of different active centers−every center creates a macromolecule which results in a broader molecular weight distribution in comparison to Metallocene catalysts.

3.3.3.1 Effect of catalyst on melting point

Figure 3.27 provides an explanation for the lower melting point of metallocene polypropylene in comparison to Z−N polypropylene. The melting point of metallocene polypropylene is in the range of 150 °C in comparison to Z−N polypropylene which has a melting point of approximately 162 °C.

Polypropylene produced according to the Z−N process contains a number of chains, which are not isotactic; these are mixed with the wholly isotactic chains and depress the melting point slightly. With the metallocene catalyst the number of irregularities is much smaller, but they are randomly distributed over all chains. They, therefore,

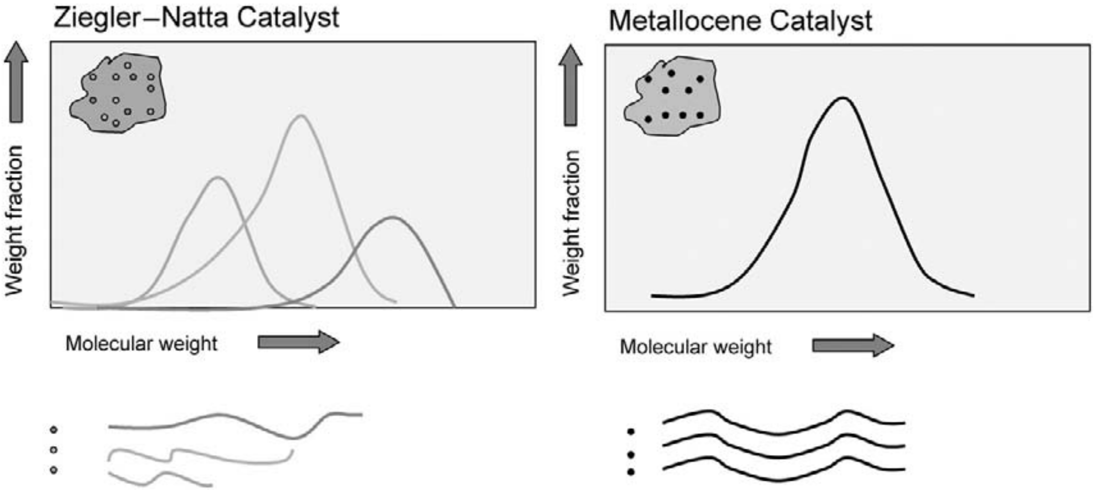


Figure 3.26 Effect of catalyst on polymer structure.

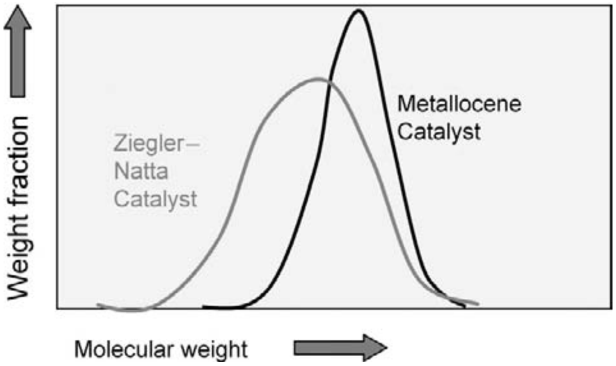


Figure 3.27 Molecular weight distribution by GPC Z/N vs. SSC.

hinder the crystallization process much more than in the old process.

3.3.4 Effect of Operating Conditions on Kinetics and MWD

3.3.4.1 Hydrogen effect

Propylene

Hydrogen effect depends on two factors:

- nature of catalyst system
- monomer type

For propylene polymerization, a remarkable activating effect of hydrogen was observed for almost all Z—N catalyst types. Different hypotheses have been proposed to account for the enhancement of the polymerization rate caused by hydrogen.

Among these theories, the most widely used by different authors are the following:

- Increase in the number of active sites
- Change in oxidation states
- Dormant sites theory

Ethylene

For ethylene polymerization, the effect of hydrogen on the polymerization rate is highly dependent on the catalyst type. Z—N catalysts usually show a decrease in polymerization rate, while different metallocene catalysts show either an increase or an increase followed by a decrease in the rate of polymerization. These are the general dependencies, resulting in different effects. The decrease in catalytic activity results from different reasons:

- It is well known that the main termination mechanism in the absence of hydrogen is b-hydrogen elimination, yielding intermediate metal hydride complexes. These intermediate hydride complexes can be reactivated for propagation by insertion of a monomer unit. Hydrogen may combine with the metal atom and make more metal hydride complexes resulting in a lower propagation rate.
- Hydrogen can cause a reduction of ethylene concentration around active sites because of its characteristics (hydrogenation of olefinic monomer).

3.3.4.2 Effect of polymerization temperature

Propylene

For propylene, a different dependence between the polymerization rate and temperature was noticed for the various catalytic systems. For $TiCl_3$ catalysts the rate increases with increasing temperatures. For the slurry polymerization of propylene with a δ-$TiCl_3$1 3$AlCl_3$ AlEt2Cl catalyst, both polymerization yield and average reaction rate increase in the temperature range 30—90 °C.

For $MgCl_2$-supported catalysts, the polymerization rate shows a distinct maximum in the range 60—70 °C and then decreases with increasing temperature. This decreasing rate at high temperatures points to catalyst deactivation either by over-reduction of the catalyst sites or through sorption theory. The rate of reaction is proportional to the monomer concentration sorped by the amorphous regions of the polymer. The monomer concentration in amorphous polymer decreases by temperature and, consequently, the reaction rate decreases.

Ethylene

Similarly, temperature effect depends on catalyst type. For some metallocene catalysts it was found that there is an increase in catalytic activity with temperature followed by a decrease when the temperature exceeds certain value. The value of this temperature depends on metallocene catalyst type.

3.4 Industrial Reactors

Many processes have been developed for the polymerization of olefins. They differ in both the physical state of the reactor media and in the mechanical operation of the unit. The choice of process is determined by economics, feedstock availability, catalyst, and the desired range of products to be produced. Significant improvements in catalyst design over the past years have led to improvements in process design and simplification. Modern supported catalysts are able to produce polymer with high yields and stereospecificity (for polypropylene) such that the removal of catalyst residue and atactic polymer from the resin is no longer required (Table 6).

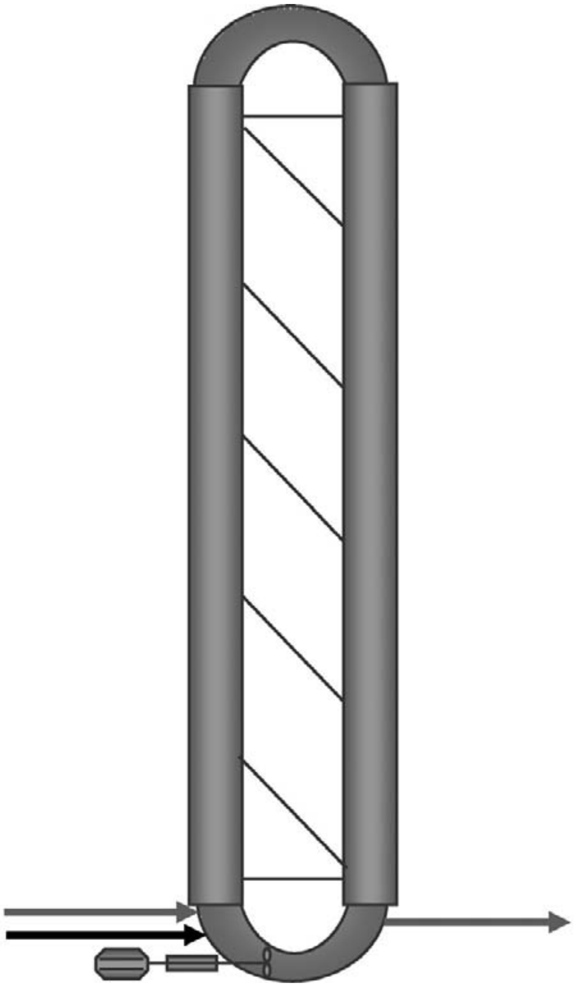


Figure 3.28 Loop reactor.

3.4.1 Slurry Reactors

Slurry-phase processes may involve either an inert diluent such as iso-butane or heptane or a condensed monomer such as propylene. In either case the catalyst particles are suspended and well mixed in the liquid medium. Monomer concentrations are high and the liquid provides good removal of the heat produced by the polymerization of the polymer particles. The two main reactors for slurry-phase olefin polymerization are the loop reactor and continuous-stirred tank. Slurry-phase processes are very attractive for high crystalline homopolymer products such as polypropylene and polyethylene.

The resistance time of slurry process is relatively short in combination with short transitions. The reaction medium is homogenous, especially in loop reactors so it is rare to find hot spots.

Fouling may result if there is a poor control of MFR and/or density due to solubility of polymer (more in C6 than with C3/C4). The recovery of unreacted materials is sometimes complicated, especially in the case of a high-boiling diluent. MFR range can be limited by the solubility of the hydrogen in the solvent (more in C6 than with C3/C4).

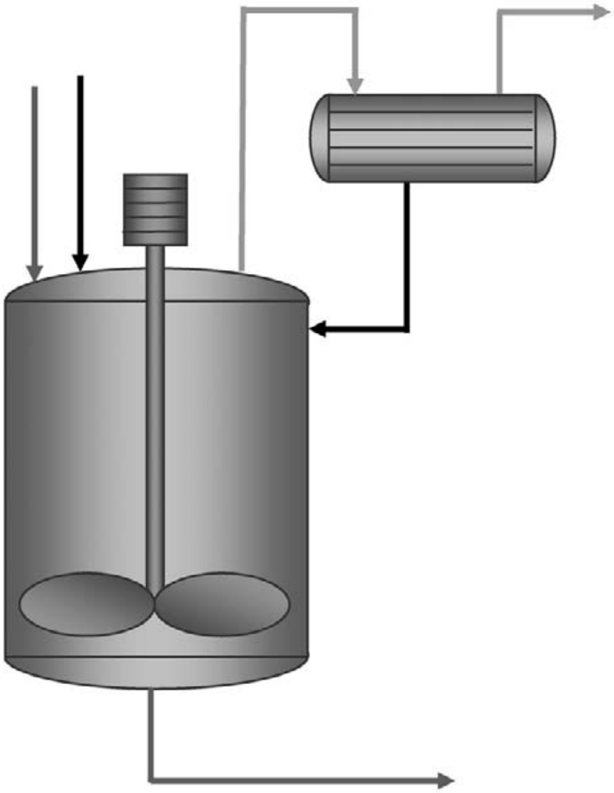


Figure 3.29 Continuous stirred tank reactor (CSTR).

In modern PP suspension processes the polymerization of homopolymers and random copolymers takes place in liquid propylene (bulk polymerization). The polymerization can be continued in one or several gas phase reactors, especially when impact copolymer is produced.

The following are the examples of these types of processes:

- The Spheripol process
- The Borstar process

These processes will be described in more detail in the following sections.

3.4.2 Gas Phase Reactors

Gas phase processes are an economical and energy-efficient alternative to liquid phase polymerization. The separation of the polymer from the monomer is easy since there is no need to flash off liquid monomer or diluent.

Today a full range of polymer products, ranging from polyethylene and polypropylene (homopolymer and impact polypropylene) to random copolymer products, are produced in gas-phase processes. This extended product range is possible with gas phase reactors as there is no solubility limit for hydrogen and comonomer in the reaction medium; this

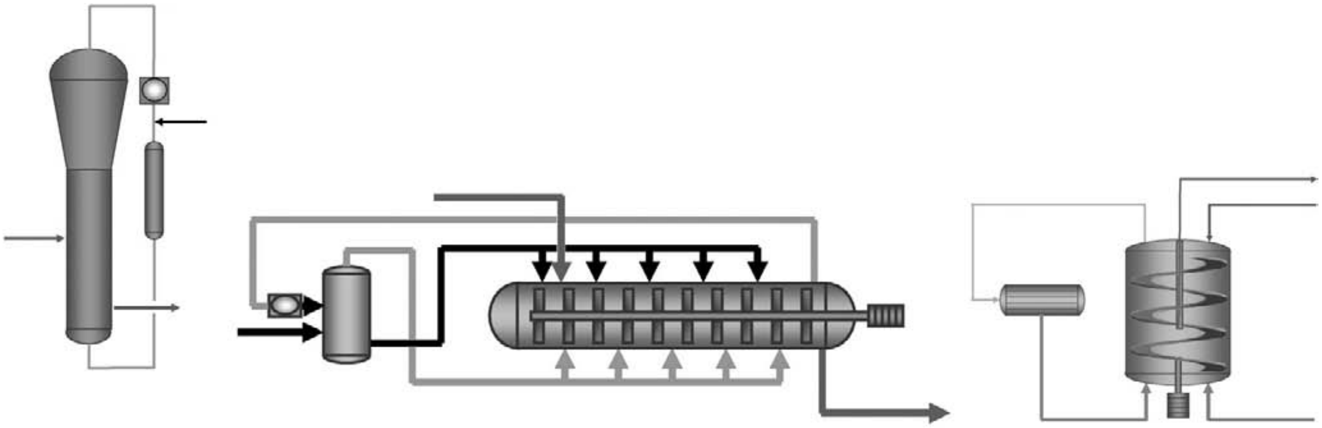


Figure 3.30 Gas phase reactors.

results in products with a higher melt flow index and increased comonomer content. Theoretically, the MFR range in a gas phase reactor is unlimited, although heat removal is a bigger problem than in the slurry process (Figure 3.30).

In slurry and gas phase processes, the polypropylene leaving the reactor is in a fine powder form. This powder is then mixed with various chemical stabilizing and performance additives, fed to an extrusion compounding machine which melt mixes the materials and forces the melt through dies where the resin is cut into pellets, cooled using water, and then packaged for sale.

3.4.3 Industrial Polypropylene Production

The higher activity catalysts also enabled the introduction of gas phase technology. Although the gas phase route was first commercialized in 1967 by BASF (this process is called Novolen), it did not come into wide-scale use until Union Carbide, and later others, offered gas phase technology for licensing in 1983. Advantages of the gas phase route include operating with lower purity propylene and low production costs.

Much development work is presently directed at introducing metallocene catalysts into the PP process to improve the properties of the resins with commercial quantities now becoming available from a number of producers. However, the commercialization of such resins has been slow.

3.4.3.1 Borstar process

Developed in Finland (Porvoo), this process has a similar structure to Borstar PE where in the loop reactor is (supercritical) propylene instead of propane. Loop reactor is operated at 80−100 °C, and pressure is adjusted accordingly from 50 to 60 bar.

High pressure in loop can result in relatively high hydrogen concentrations and a wide range of MFR (wider than others) especially important for thin wall applications within the packaging industry. Obtaining good utilization of propylene since unreacted propylene from the loop is apparently fed to gas phase reactor.

The Borstar PP process is based on the Borstar PE process. When homopolymers and random copolymers are produced, the reactor configuration consists of a propylene bulk loop reactor and a fluidized bed gas phase reactor operated in series. During heterophasic copolymer production, the polymer from the first gas phase reactor is transferred into a second smaller gas phase reactor where the rubbery copolymer is made. For bimodal rubber production a further gas phase reactor is necessary. Such a configuration allows for the production of polypropylenes with outstanding product properties.

The catalyst is continuously pre-polymerized before entering the main loop reactor, which is designed for supercritical conditions and typically operated in the temperature range of 80−100 °C and 5−6 MPa pressure with propylene as the diluent (bulk polymerization). The slurry from the loop

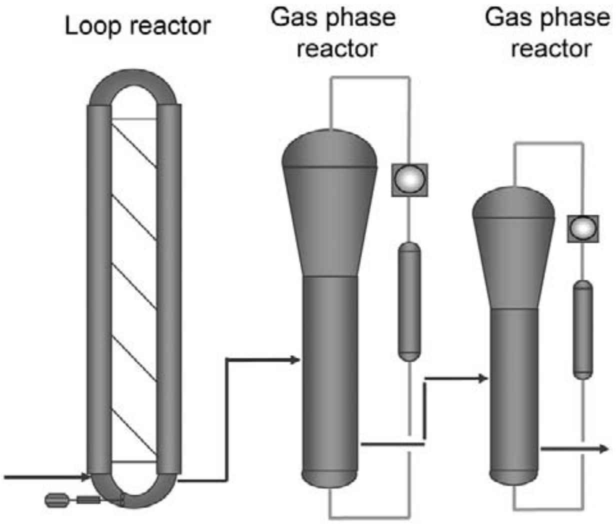


Figure 3.31 Borstar process.

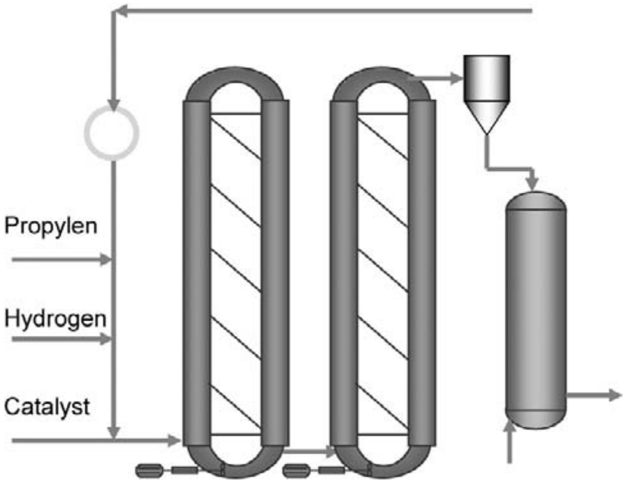


Figure 3.32 Spheripol process.

reactor is fed directly into the gas phase reactor without any flash separation step.

The gas phase reactor is typically operated at 80–100 °C and 2.2–3 MPa. The powder withdrawn from the gas phase reactor is separated from the associated gas and purged with nitrogen to remove residual hydrocarbon before it is transferred for extrusion. The recovered gas is compressed and returned to the gas phase reactor.

A second gas phase reactor is used to produce the rubber phase of a heterophasic copolymer. Here, the powder is withdrawn, purged with nitrogen, and sent for extrusion, as in the homopolymer case. The gas associated with the powder is recovered and recycled back to the gas phase reactor.

The Borstar PP process concept combined with a special nucleation technology broadens the product flexibility in terms of MFI, molecular weight distribution, comonomer distribution, softness, and rigidity.

The number of gas phase reactors depends on the type of product to be made (e.g., 25% total rubber with one, ~45% with two). With two gas phase reactors, production of bimodal rubber is possible (Figure 3.31).

With the Borstar process technology it is possible to produce a portfolio for use in economic manufacture of a full range of polypropylene applications from low melt flow to high flow applications, as well as high impact copolymers.

Borstar polypropylene homopolymers range from grades with a melt flow rate for pipe and sheet extrusion applications to very high flow specialty grades for melt blown applications. In conjunction with BNT it is possible to realize extremely stiff materials.

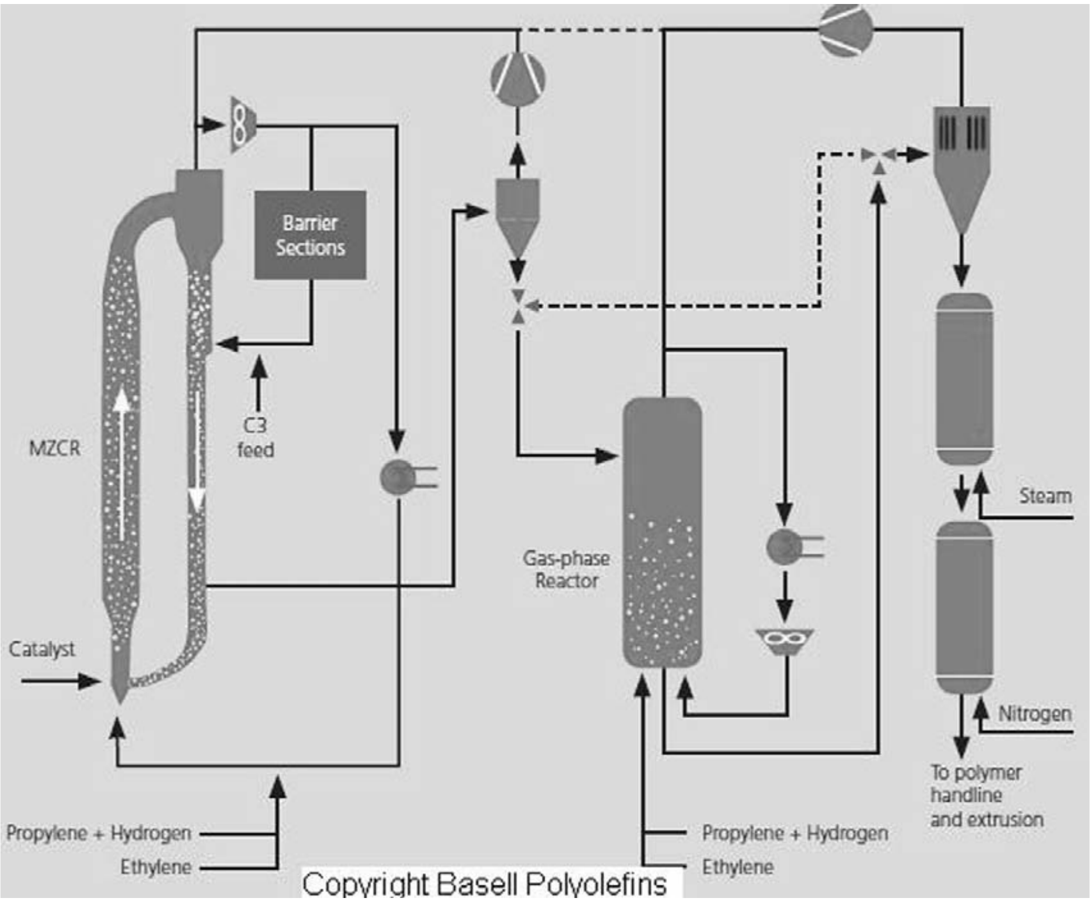


Figure 3.33 Spherizone process.

Table 3.6 Industrial polyolefin processes

Industrial processes				
High pressure processes		**Low pressure catalytic processes**		
Autoclave reactors	**Tubular reactors**	**Gas Phase**	**Slurry**	**Solution**
PE	PE	PE, PP, EPR/ hiPP	PE and PP in hydrocarbon slurries PP in its own liquid monomer Supercritical → both PE and PP in isobutane, isopentane	essentially PE in diluent
No catalyst is necessary		Low pressure processes, require use of catalyst		

Borstar polypropylene random copolymers are characterized by excellent optical properties. The product portfolio also includes specialty grades for pressure pipe applications and copolymers with very low seal initiation temperatures.

Borstar polypropylene heterophasic copolymers or Borstar rTPOs have outstanding low temperature impact on strength/ stiffness ratio with reduced or eliminated tiger skin effect.

The product portfolio includes a broad range of grades for specialty applications such as appliances and automotive bumpers, and reactor-grade high flow heterophasic copolymers for packaging injection molding applications.

3.4.3.2 Spheripol process

One particular development was the commercialization of the Spheripol process by Himont (now licensed by Basell) in 1982. This process combines bulk phase polymerization in loop reactors with gas phase polymerization and has become the most dominant licensed process. More recently, Borealis has taken a similar route with the adaptation of its Borstar bimodal PE process to produce PP.

The first stage of the Spheripol process consists of polymerization in liquid propylene. Usually, two loops are used in series (Simonazzi et al., 1991) to narrow the residence-time distribution of the catalyst particles. For the ethylene-propylene copolymer (EPR) stage, the Spheripol process utilizes a gas phase fluidized bed reactor (FBR). The liquid propylene/polymer suspension from the first reactor is flashed to gas/solid conditions prior to entering the second stage. The second stage operates at pressures of 15−35 atm (Di Drusco and Rinaldi, 1984; Simonazzi et al., 1991) which is often close to the dew point of the gas. Elevated temperatures of approximately ~ 80 °C are used to provide a reasonable amount of copolymer contents in the final product (Figure 3.32).

3.4.3.3 Spherizone process

A recent advancement in reactor technology has been the development of a fluid bed, multi-zone circulating reactor (MZCR) by Basell, called Spherizone. The Spherizone circulating reactor has two interconnected zones. In one, the riser, there is fast fluidization while in the other, the downer, features a slower packed bed mode. The two zones can generate different materials and extend the range of PP properties (Figure 3.33).

3.5 Polyolefin Properties

3.5.1 Polyethylene

3.5.1.1 Physical properties of polyethylene (Table 3.7)

Table 3.7 Physical properties of polyethylene

	LLDPE	**LDPE**	**HDPE**
Optical	**Transparent to opaque**	**Transparent to opaque**	**Transparent to opaque**
T_{melt} (°C)	120−130	105−115	130 − 138
T_g (°C)	−100	−100	−100
H_2O Absorption (%)	<0.01	<0.01	<0.01
Oxidation resistance	Low, oxides readily	Low, oxides readily	Low, oxides readily
UV Resistance	With stabilization high	With stabilization high	With stabilization high
Alkaline resistance	Resistant	Resistant	Resistant
Acid resistance	Oxidizing acids	Oxidizing acids	Oxidizing acids

3.5.1.2 Mechanical properties of polyethylene (Table 3.8)

Table 3.8 Mechanical properties of polyethylene

	LLDPE	LDPE	HDPE
Density (g/cm^3)	0.91 −0.925	0.926 −0.94	0.941 −0.96
Crystallinity (%)	55–65	30–50	70–90
Molecular weight (*10^3)	10–30	30–50	50 −250
Tensile strength (MPa)	8–45	3–56	10–43
Tensile modulus (MPa)	140 −1000	110 −1200	180 −1800
Tensile elongation at yield (%)	8–30	13 −400	6–45
Izod notched low temp. (kJ/m^2)	23–97	24–70	11–80
Hardness, Shore D	44–70	38–60	56–71

3.5.1.3 Processing properties of polyethylene (Table 3.9)

Table 3.9 Processing properties of polyethylene

	LLDPE	LDPE	HDPE
T_{melt} (°C)	120 −130	105 −115	130 −138
Molding pressure (bar)	150 −300	150 −310	233 −388
Mold (linear) shrinkage	0.02	0.02	0.018

3.5.2 Polypropylene

3.5.2.1 Physical properties of polypropylene (Table 3.10)

Table 3.10 Physical properties of polypropylene

	PP Homo	PP Copo	PP Impact
Optical	Transparent to opaque	Opaque	Opaque
T_g (°C)	−5	−20	−35
H_2O Absorption	0.01	0.01	0.01
Oxidation resistance	Low, oxides readily	Low, oxides readily	Low, oxides readily
UV resistance	With stabilization high	With stabilization high	With stabilization high

3.5.2.2 Mechanical properties of polypropylene (Table 3.11)

Table 3.11 Mechanical properties of polypropylene

	PP Homo	PP Copo	PP Impact
Density (g/cm^3)	0.90 −0.91	0.90 −0.91	0.90 −0.91
Tensile strength at yield (MPa)	35–40	20–35	11–28
Tensile modulus (MPa)	1200 −2000	1000 −1500	500 −1200
Shrinkage	0.01 −0.03	0.02 −0.03	0.02 −0.03
Hardness shore D	70–83	70–80	45–55
HDT A (°C)	100 −120	85 −104	75–88
Dielectric constant	2.3	2.3	2.3

3.5.2.3 Processing properties of polypropylene (Table 3.12)

Table 3.12 Processing properties of polypropylene

	PP Homo	PP Copo	PP Impact
Processing temperature (°C)	180 −260	180 −220	180 −220
Drying temperature (°C)	80	80	80
Molding pressure (tons/cm^2)	230 −450	230 −450	230 −450

3.5.3 Polybutene–1

3.5.3.1 Physical properties of polybutene-1 (Table 3.13)

Table 3.13 Physical properties of polybutene-1

Density (g/cm^3)	0.895–0.915
Melt flow (g/10min)	0.400–200
Melting point (°C)	98.0–126
Vicat softening point (°C)	90.0–116
Brittleness temperature (°C)	–34.0–17.0

3.5.3.2 Mechanical properties of polybutene-1 (Table 3.14)

Table 3.14 Mechanical properties of poylbutene-1

Tensile strength (MPa)	22.0–27.6
Tensile strength, Yield (MPa)	3.74–17.2
Elongation at break (%)	300 – 550
Modulus of elasticity (MPa)	0.517–293

3.5.3.3 Processing properties of polybutene-1 (Table 3.15)

Table 3.15 Processing temperatures of polybutene

Processing temperature (°C)	150–200
Mold temperature (°C)	60

3.6 Applications

3.6.1 Appliances

In recent years, there has been a growing use of polypropylene materials in laundry appliances. Advances in mechanical performance and corrosion resistance have increasingly enabled advanced polyolefins to replace stainless steel in appliances, providing significant advantages in terms of material costs, manufacturing processes, and overall product design.

In white goods applications, plastics have grown from less than 1% of material content in the early 1960s, to almost 30% by weight today.

There are many reasons for this growth. The ease with which plastics can be fabricated into complex shapes by injection molding, thermoforming, extrusion, and blow molding, and the thousands of possibilities for specific compounds, each with a tailored set of properties, has made possible:

- Many new product features
- Improved product performance
- Significantly reduced product costs

The white goods industry is highly competitive and is continually striving to increase productivity and reduce costs. Polyolefins meet these requirements as they are lightweight, provide specific property profiles, and are corrosion resistant.

Tables 3.16 and 3.17 represent polypropylene consumption in the appliance industry in Western Europe.

Several characteristics of polypropylene have been the driving force for this remarkable growth in the appliance industry. First and most significant is its stability against detergents.

Besides this detergent stability, further characteristics of polypropylene are also important for applications inside the appliance industry:

- High HDT for dishwasher application
- High stiffness at higher temperatures for washing machine parts
- Uniform shrinkage for all parts

In order to fulfill these wide ranges of application, the resins have to cover an equally wide range of properties. It is not economical or logical to develop new resins for each application—a long and time-consuming process. In order to fulfill all these requirements, it is necessary to blend the polypropylene with fillers.

3.7 Polyolefin Composites

3.7.1 Fillers for Polyolefin Composites

The most used fillers in polyolefins are talc, calcium carbonate, and glass fibers. The figures below represent the influence of different fillers to the mechanical performance.

3.7.1.1 Talc

Talc is the softest of all the mineral fillers (Moh hardness 1) so it does not cause wear during processing. It is a cheap yet effective reinforcing filler, and its sales have rapidly increased in Europe, mainly in appliances and automotive applications. Use of talc gives lower mold shrinkage and better dimensional stability because of its low thermal expansion coefficient.

Table 3.16 Western European injection molding markets—appliances 2001 and 2006

	2001		2006	
Market sectors	**Ktonnes**	**%**	**Ktonnes**	**%**
Washers/dryers	98	34.5	114	32.2
Dishwashers	29	10.2	46	13.0
Refrigerators/freezers	15	5.3	20	5.6
Microwave ovens	5	1.8	6	1.7
Vacuum cleaners	24	8.5	35	9.9
Small appliances	69	24.3	81	22.9
Power tools	5	1.8	6	1.7
Other/undefined	39	13.7	46	13.0
Total	284	100	354	100

Table 3.17 Western European injection molding markets—appliances 2001 and 2006

	2001		2006	
Country	**Ktonnes**	**%**	**Ktonnes**	**%**
Benelux	18	6.3	27	7.6
France	34	11.9	39	11.0
Italy	56	19.7	67	18.9
Germany	58	20.4	66	18.6
United Kingdom	48	16.9	51	14.4
Spain	21	7.4	25	7.1
Austria	4	1.4	4	1.1
All other	45	15.8	75	21.2
Total	284	100	354	100

Source: Phillip Townsend Associates.

3.7.1.2 Calcium carbonate

Calcium carbonate is available in different forms in many parts of the world and has become the most important filler for plastics. This is because calcium carbonate is cheap and non-abrasive. It can be dispersed directly as glass and talc directly into plastic materials while in the extruder or injection molding machine.

3.7.1.3 Glass fibers

Short glass fibers made of E-glass are used to improve the mechanical properties (strength, modulus, impact strength, creep resistance) and heat distortion temperature of plastics (Table 3.18).

Table 3.18 Filler properties

	Talc	**Calcium carbonate**	**Glass**
CLTE (∗10-6 K-1)	8	4.4–10	8.5
Conductivity (W/mK)	–	3	1
Refractive index	1.539	1.65	–
Hardness	1	3	5.5

3.7.2 Influence of Fillers to the Mechanical Performance

3.7.2.1 Melt flow properties (Figure 3.34)

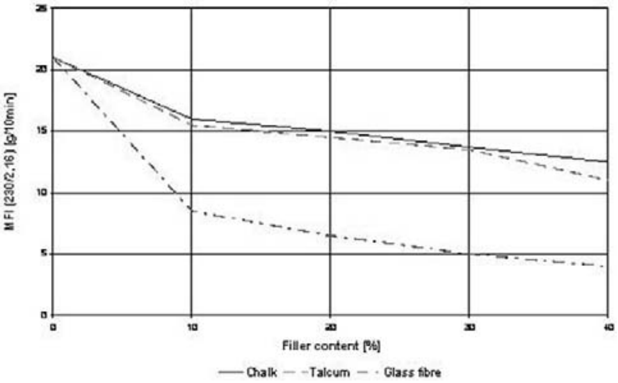


Figure 3.34 Melt flow properties.

3.7.2.2 Flexural modulus (Figure 3.35)

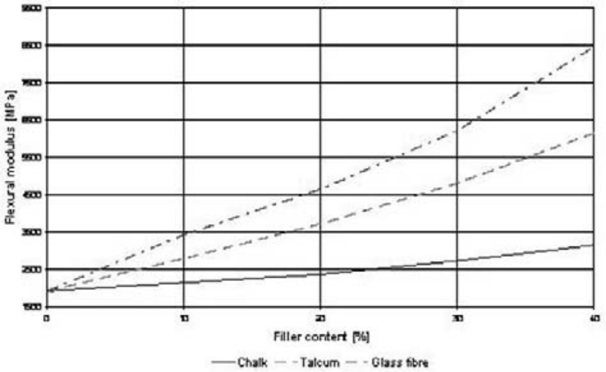


Figure 3.35 Flexural modulus.

3.7.2.3 HDT A (Figure 3.36)

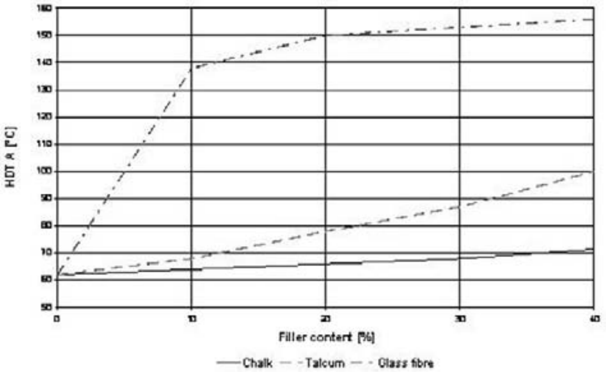


Figure 3.36 HDT-A diagram.

3.7.2.4 Gloss 60 (Figure 3.37)

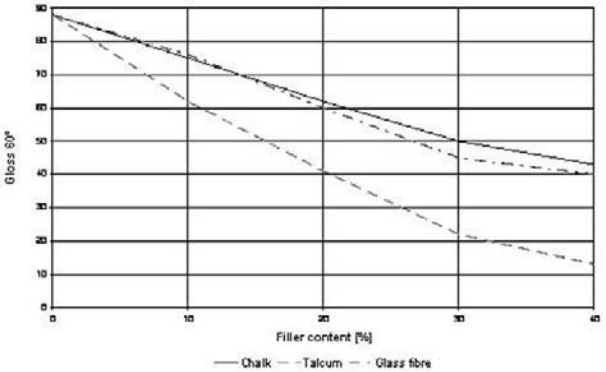


Figure 3.37 Gloss 60°.

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4 Introduction to Fluoropolymers

Sina Ebnesajjad, PhD
FluoroConsultants Group, LLC

4.1 Introduction

Fluoropolymer is usually olefinic polymer which consists of partially or fully fluorinated olefinic monomers such as vinylidene fluoride ($CH_2{=}CF_2$) and tetrafluoroethylene (TFE) ($CF_2{=}CF_2$). These polymers have been covered in great detail in a number of references (see General References). More specialty fluorinated polymers include perfluoroethers, fluoroacrylates, and fluorosilicones which are used in significantly smaller volume than olefinic fluoropolymers. These fluoropolymers and others are covered in detail elsewhere [1,2].

Commercial fluoropolymers include homopolymers and copolymers. Homopolymers contain 99% or more by weight one monomer and 1% or less by weight of another monomer according to the convention by American Society for Testing Materials (ASTM). Copolymers contain more than 1% or more by weight of one or more comonomers. The major commercial fluoropolymers are based on three monomers: TFE, vinylidene fluoride (VF_2), and to a lesser extent chlorotrifluoroethylene (CTFE). Examples of comonomers include perfluoromethyl vinyl ether (PMVE), perfluoroethyl vinyl ether (PEVE), perfluoropropyl vinyl ether (PPVE), hexafluoropropylene (HFP), CTFE, perfluorobutyl ethylene (PFBE), and exotic monomers such as 2,2-bistrifluoromethyl-4,5-difluoro-1,3-dioxole.

The fluoropolymers reviewed in this chapter include polytetrafluoroethylene (PTFE), perfluoroalkoxy polymer (PFA), fluorinated ethylene−propylene polymer (FEP), ethylene−tetrafluoroethylene copolymer (ETFE), ethylene−chlorotrifluoroethylene copolymer (ECTFE), polychlorotrifluoroethylene (PCTFE), polyvinylidene fluoride (PVDF), and polyvinyl fluoride (PVF). Classification, preparation, properties, fabrication, safety considerations, and economics of fluoropolymers are reviewed. Monomer synthesis and properties have also been discussed.

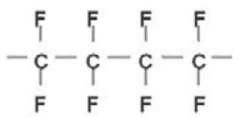
A good rule of thumb to remember is that increasing the fluorine content of a polymer molecule increases its chemical and solvent resistance, flame resistance, and photostability; improves its electrical properties such as lower dielectric constant; lowers coefficient of friction; raises melting point; increases its thermal stability; and weakens its mechanical properties. Solubility of polymers in solvents usually decreases by increasing the fluorine content of the molecule.

4.2 Fluoropolymer Classification

The serendipitous discovery of PTFE in 1938 by Roy Plunkett of DuPont Company [3] began the era of fluoropolymers. PTFE has found thousands of applications because of its unique properties. Various fluoroplastics (Figure 4.1) have been developed since the discovery of PTFE. A number of companies produce these plastics around the world (Tables 4.1 and 4.2). Fluoropolymers are divided into two classes of perfluorinated and partially fluorinated polymers. Perfluorinated fluoropolymers are homopolymers and copolymers of TFE. Some of the comonomers may contain a small amount of elements other than C or F.

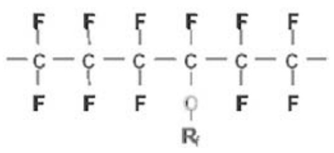
For example, PFA is a copolymer of TFE and perfluoroalkyl vinyl ether that contains oxygen. R_f is a perfluoroalkyl group of $C_1{-}C_4$.

PTFE



$$-\underset{F}{\overset{F}{C}}-\underset{F}{\overset{F}{C}}-\underset{F}{\overset{F}{C}}-\underset{F}{\overset{F}{C}}-$$

PFA



$$-\underset{F}{\overset{F}{C}}-\underset{F}{\overset{F}{C}}-\underset{F}{\overset{F}{C}}-\underset{\underset{R_f}{O}}{\overset{F}{C}}-\underset{F}{\overset{F}{C}}-\underset{F}{\overset{F}{C}}-$$

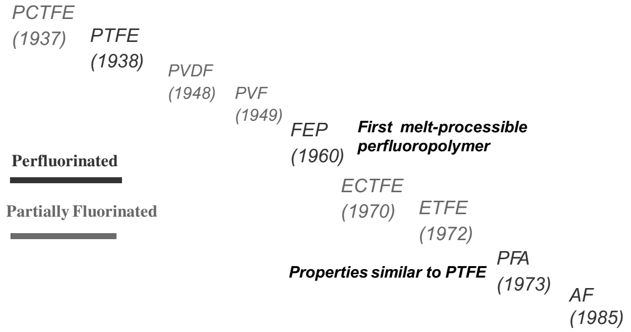


Figure 4.1 Evolution of fluoropolymer development over time. (PCTFE = polychlorotrifluoroethylene, PVDF = polyvinylidene fluoride, PVF = polyvinyl fluoride, FEP = fluorinated ethylene−propylene polymer, ECTFE = ethylene chlorotrifluoroethylene polymer, ETFE = ethylene−tetrafluoroethylene polymer, PFA = perfluoroalkoxy polymer, AF = amorphous fluoropolymers).

Table 4.1 Global producers of fluoropolymers

Company	Product
DuPont	PTFE, FEP, PFA, ETFE, PVF
Daikin	PTFE, FEP, PFA, ETFE, PVDF, PCTFE, E–FEP
Arkema	PVDF, PCTFE
Asahi Glass	PTFE, PFA, ETFE
Solvay Solexis	PTFE, PVDF, ECTFE, PFA/MFA
Dyneon	PTFE, FEP, PFA, THV, PVDF
Constructive Bureau Russia	PTFE, small amounts of other polymers
Tarnowie-Moscicach S.A. Poland	PTFE
Kureha	PVDF
Honeywell	PCTFE

Table 4.2 Global producers of fluoropolymers

Company	Product
Gujarat Fluorochemicals Ltd.	PTFE
Hindustan Fluoropolymer	PTFE
Shanghai 3F	PTFE, PVDF, FEP
Fuxin Hengtong	PTFE
Jiangsu Meilan	PTFE
Jinan 3F	PTFE, FEP
Zhejiang Jusheng	PTFE
Zhonghao Chenguang Res Inst.	PTFE, PVDF
Shandong Dongyue	PTFE

Partially fluorinated fluoropolymers contain hydrogen (H) or other atoms such as chlorine, in addition to fluorine and carbon. The most significant are homopolymers and copolymers of PVDF. There are also copolymers and homopolymers of chlorotrifluoroethylene (PCTFE), although some have elastomeric properties. Other significant fluoroplastics include ETFE, ECTFE, and PVF.

4.3 Polymer Development History

PTFE cannot be fabricated by melt-processing techniques because of its high viscosity (10^{10}–10^{12} poise at 380 °C). Melt-processible fluoropolymers have been developed by copolymerization of TFE. FEP, a copolymer of TFE and HFP, has a lower maximum continuous use temperature than PTFE (200 °C vs. 260 °C) because of the deterioration of mechanical properties. PFA, a copolymer of TFE with PPVE or PEVE, offers thermal stability, melt-processibility and maximum continuous use temperature—260 °C. Both FEP and PFA are considered perfluoropolymers.

Copolymers of ethylene with tetrafluoroethylene (ETFE) and chlorotrifluoroethylene (ECTFE) are mechanically stronger than perfluoropolymers, accompanied with trade-offs of reduction in their chemical resistance and continuous use temperature and an increase in the coefficient of friction.

Amorphous copolymers of TFE are soluble in special halogenated solvents and can be applied to surfaces as a polymer solution to form thin coatings. The dried coating is as resistant to almost as many chemicals as PTFE. [4]

4.4 Monomer Synthesis

4.4.1 Synthesis of Tetrafluoroethylene

The first reliable and complete description of TFE synthesis was published in 1933 by Ruff and Bretschneider [5] in which they prepared TFE ($CF_2{=}CF_2$, CAS number 116-14-3) from decomposition of tetrafluoromethane in an electric arc. TFE was obtained by bromination and separation of the dibromide ($CF_2Br{-}CF_2Br$) from the other reaction products. Dehalogenation with zinc was the next step for obtaining pure TFE. Commercially significant techniques for TFE preparation list fluorspar (CaF_2), hydrofluoric acid, and chloroform as the starting ingredients [6–13], as shown in the reaction sequence in Figure 4.2.

Among other compounds produced are HFP and a small amount of highly toxic perfluoroisobutylene.

Sherratt [14] and others [15] have provided complete descriptions of the preparation of TFE. The overall yield of TFE production depends on the pyrolysis reaction. The products of pyrolysis are cooled, scrubbed with a dilute basic solution to remove HCl, and dried. The resulting gas is

HF preparation:

$$CaF_2 + H_2SO_4 \rightarrow 2HF + CaSO_4$$

Chloroform preparation:

$$CH_4 + 3Cl_2 \rightarrow CHCl_3 + 3HCl$$

Chlorodifluoromethane preparation:

$$CHCl_3 + 2HF \rightarrow CHClF_2 + 2HCl$$

(SbF_3 catalyst)

TFE synthesis:

$$2CHClF_2 \rightarrow CF_2{=}CF_2 + 2HCl$$

(pyrolysis)

Figure 4.2 Synthesis reactions of tetrafluoroethylene.

compressed and distilled to recover the unreacted $CHClF_2$ and high purity TFE. Polymerization of TFE to high molecular weight requires extreme purity, thus ensuring the removal of all traces of telogenic hydrogen or chlorine-bearing impurities. TFE can autopolymerize if it is not inhibited by terpenes, such as α-pinene, terpene B, and d-limonene [16].

4.4.2 Synthesis of Hexafluoropropylene

HFP ($CF_3CF{=}CF_2$, CAS number 116-15-4) was first prepared by Benning et al. [17] by pyrolysis. The full synthesis and identification of HFP was conducted by Henne [18]. A six step reaction scheme starting with the fluorination of 1,2,3-trichloropropane led to 1,2-dichlorohexafluoropropane. The latter was dehalogenated with zinc in boiling ethanol to yield HFP. HFP is a co-product in the synthesis of TFE. HFP yield can be increased, in lieu of TFE production, by altering the reaction conditions such as reduction in the pyrolysis temperature and use of steam as diluent of the reactants [19,20].

4.4.3 Synthesis of Perfluoroalkyl Vinyl Ethers

Perfluoroalkyl vinyl ethers such as perfluoropropyl vinyl ether ($CF_2{=}CF{-}O{-}C_3F_7$, CAS number 1623-05-8) are synthesized according to the steps shown in Figure 4.3 as well as alternative techniques [21]. There are other processes including electrochemical methods for the production of perfluoro-2-alkoxy-propionyl fluoride [22].

4.4.4 Synthesis of Chlorotrifluoroethylene

This monomer is fairly simple to manufacture compared to the perfluorinated monomers [25–28]. The commercial process for the synthesis of CTFE ($CF_2{=}CClF$, CAS number 79-38-9) begins with 1,1,2-trichloro-1,2,2-trifluoroethane (TCTFE). It is dechlorinated by pyrolysis at 500–600 °C in vapor phase. An alternative method for preparation of TCTFE is catalytic dechlorination:

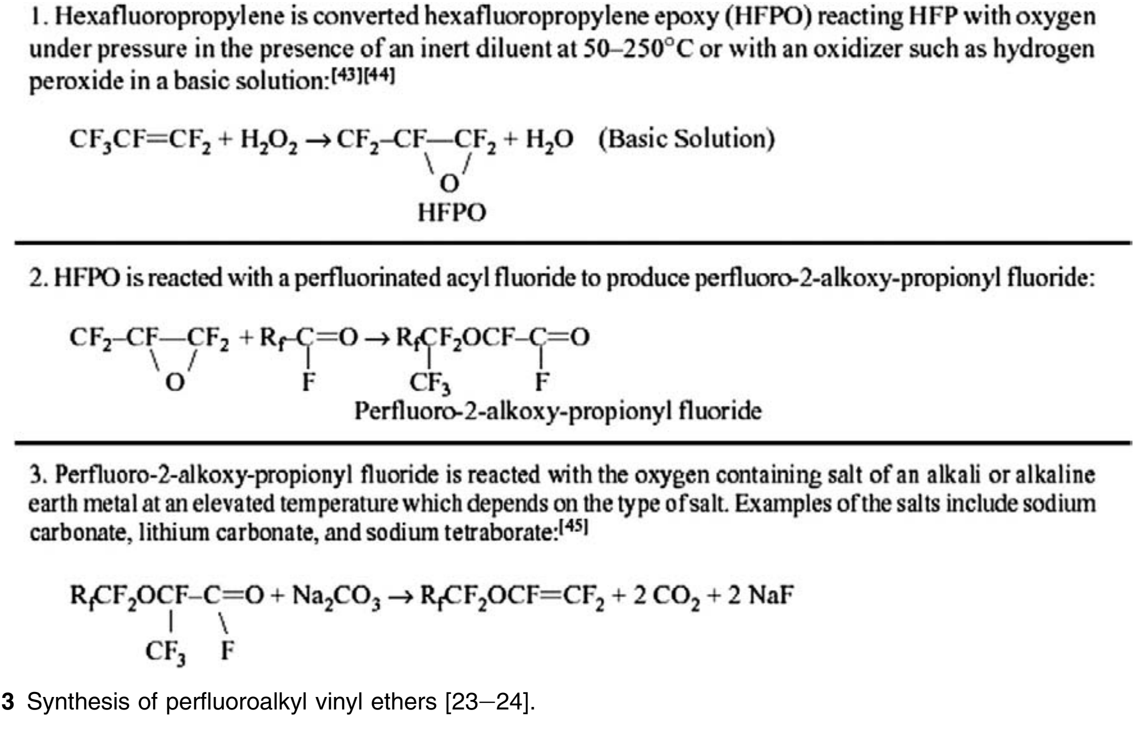
$$CCl_3{-}CCl_3 + HF \rightarrow CCl_2F{-}CClF_2 + 2HCl(\text{catalyst}\,SbCl_xF_y)$$

$$CCl_2F{-}CClF_2 + Zn \rightarrow CFCl = CF_2 + ZnCl_2(\text{at}\,50{-}100\,^{\circ}C\ \text{in methanol})$$

The reaction stream is put through a number of purification and distillation steps to remove the gaseous and liquid contaminants. CTFE is further purified by the removal of methyl chloride, dimethyl ether, and water by passing the gas stream through sulfuric acid. Water and hydrochloric acid are removed by passing the CTFE through an alumina column before condensing it into a liquid.

4.4.5 Synthesis of Vinylidene Fluoride

There are numerous ways to prepare vinylidene fluoride (VDF) ($CF_2{=}CH_2$, CAS number 75-38-7) [29,30]. Two



1. Hexafluoropropylene is converted hexafluoropropylene epoxy (HFPO) reacting HFP with oxygen under pressure in the presence of an inert diluent at 50–250°C or with an oxidizer such as hydrogen peroxide in a basic solution:[43][44]

$$CF_3CF{=}CF_2 + H_2O_2 \rightarrow \underbrace{CF_2{-}CF{-}CF_2}_{\text{O}} + H_2O \quad (\text{Basic Solution})$$

HFPO

2. HFPO is reacted with a perfluorinated acyl fluoride to produce perfluoro-2-alkoxy-propionyl fluoride:

$$\underbrace{CF_2{-}CF{-}CF_2}_{O} + R_f{-}\underset{F}{C}{=}O \rightarrow R_fCF_2O\underset{CF_3}{C}F{-}\underset{F}{C}{=}O$$

Perfluoro-2-alkoxy-propionyl fluoride

3. Perfluoro-2-alkoxy-propionyl fluoride is reacted with the oxygen containing salt of an alkali or alkaline earth metal at an elevated temperature which depends on the type of salt. Examples of the salts include sodium carbonate, lithium carbonate, and sodium tetraborate:[45]

$$R_fCF_2O\underset{CF_3}{C}F{-}\underset{F}{C}{=}O + Na_2CO_3 \rightarrow R_fCF_2OCF{=}CF_2 + 2\,CO_2 + 2\,NaF$$

Figure 4.3 Synthesis of perfluoroalkyl vinyl ethers [23–24].

methods, including the popular commercial technique for VDF production, are described. Conversion of 1,1,1-trifluoroethane [31] begins by passing this gas through a platinum-lined Inconel tube, which is heated to 1200 °C. Contact time is about 0.01 seconds. The exit gases are passed through a sodium fluoride bed to remove the hydrofluoric acid and are then collected in a liquid nitrogen trap. VDF is separated by low temperature distillation. Unreacted trifluoroethane is removed at −47.5 °C and is recycled.

The commercial method begins with hydrofluorination of acetylene followed by chlorination [32], by hydrofluorination of trichloroethane [33], or by hydrofluorination of vinylidene chloride [34]. In each case the final product, 1-chloro-1, 1-difluoroethane, is stripped of a molecule of hydrochloric acid to yield VDF.

4.4.6 Synthesis of Vinyl Fluoride

Vinyl fluoride (VF)($CHF{=}CH_2$, CAS number 75-02-5) [35−39] was first prepared by the reaction of 1,1-difluoro-2-bromoethane (CAS number 359-07-9) with zinc. Most approaches to VF synthesis have employed reactions of acetylene (CAS number 74-86-2) with hydrogen fluoride (HF) either directly or utilizing catalysts. Other routes have involved ethylene (CAS number 74-85-1) and HF, pyrolysis of 1,1-difluoroethane (CAS number 624-72-6) and fluorochloroethanes, reaction of 1,1-difluoroethane with acetylene, and halogen exchange of vinyl chloride (CAS number 75-01-4) with HF [40−42].

4.5 Monomer Properties

4.5.1 Properties of Tetrafluoroethylene

Tetrafluoroethylene **15, 44** is a colorless, odorless, tasteless, nontoxic gas which boils at −76.3 °C and melts at −142.5 °C. The critical temperature and pressure of TFE are 33.3 °C and 3.92 MPa. TFE is stored as a liquid; vapor pressure at −20 °C is 1 MPa. Its heat of formation is reported to be −151.9 kcal/mole. Polymerization of TFE is highly exothermic and generates 41.12 kcal/mole heat—the extent of which can be compared with the heats of polymerization of vinyl chloride and styrene, at 23−26 kcal/mole and 16.7 kcal/mole, respectively.

Safe storage of TFE requires its oxygen content to be less than 20 ppm. Temperature and pressure should be controlled during its storage. Increasing the temperature, particularly at high pressures, can initiate deflagration in the absence of air (TFE degrades into carbon tetrafluoride). In the presence of air or oxygen, TFE forms explosive mixtures in the molar percentage range of 14−43% [44]. Detonation of a mixture of TFE and oxygen can increase the maximum pressure to 100 times the initial pressure.

4.5.2 Properties of Hexafluoropropylene

Hexafluoropropylene is a colorless, odorless, tasteless, and relatively low toxicity gas, which boils at −29.4 °C and freezes at −156.2 °C. In a 4-hour exposure, a concentration of 3000 ppm corresponded to LC50 in rats [45,46]. Critical temperature and pressure of HFP are 85 °C and 3254 MPa. Unlike TFE, HFP is extremely stable with respect to autopolymerization and may be stored in liquid state without the addition of telogen. HFP is thermally stable up to 400−500 °C. At about 600 °C under vacuum, it decomposes and produces octafluoro-2-butene ($CF_3CF{=}CFCF_3$) and octafluoroisobutylene [47].

4.5.3 Properties of Perfluoroalkyl Vinyl Ethers

Perfluoroalkyl vinyl ethers (PAVE) form [22] an important class of monomers in that they are comonomers of choice for the "modification" of the properties of homofluoropolymers in addition to broad use in the structure of copolymers of TFE. The advantage of PAVEs as modifiers over HFP is their remarkable thermal stability. A commercially significant example is perfluoropropyl vinyl ether (PPVE). PPVE is an odorless, colorless liquid at room temperature. It is extremely flammable and burns with a colorless flame. It is less toxic than HFP.

4.5.4 Properties of Chlorotrifluoroethylene

Chlorotrifluoroethylene is a colorless gas at room temperature and pressure. It is fairly toxic with an LC50 (rat) at 4-hour exposure and a concentration of 4000 ppm [49]. It has a critical temperature and pressure of 105.8 °C and 4.03 MPa. Oxygen and liquid CTFE react and form peroxides at fairly low temperatures. A number of oxygenated products, such as chlorodifluoroacetylfluoride, are generated by oxidation of CTFE [48]. The same reaction can occur photochemically in the vapor phase. Chlorotrifluoroethylene oxide is a by-product of this reaction. The peroxides act as initiators for the polymerization of CTFE, which can occur violently.

4.5.5 Properties of Vinylidene Fluoride

Vinylidene fluoride, (CH2=CF2), is [49] flammable and is a gas at room temperature. It is colorless and almost odorless and boils at −84 °C. VDF can form explosive mixtures with air. Polymerization of this gas is highly exothermic and takes place above its critical temperature and pressure.

4.5.6 Properties of Vinyl Fluoride

Vinyl fluoride (75-02-5) (fluoroethene) is a colorless gas at ambient conditions [38]. It is flammable in air between the limits of 2.6 and 22% by volume. Minimum ignition temperature for VF and air mixtures is 400 °C. Adding a trace amount (<0.2%) of terpenes is effective to prevent spontaneous polymerization of VF. Inhibited VF has been classified as a flammable gas by the U.S. Department of Transportation.

4.6 Polymerization and Finishing

4.6.1 Polytetrafluoroethylene, PTFE (CAS number 9002-84-0)

PTFE is produced [43,50] by free-radical polymerization mechanism in an aqueous media via addition polymerization of TFE in a batch process. The initiator for the polymerization is usually a water-soluble peroxide such as ammonium persulfate or disuccinic peroxide. A redox catalyst is used for low temperature polymerization. PTFE is produced by suspension (or slurry) polymerization without a surfactant to obtain granular resins or with a perfluorinated surfactant (emulsion polymerization) such as ammonium perfluorooctanoate to produce fine powder and dispersion products. Polymerization temperature and pressure usually range from 0 to 100 °C and 0.7 to 3.5 MPa. See Section 4.11 for information about ammonium perfluorooctanoate.

Granular PTFE is produced by polymerizing TFE alone or by using trace amounts of comonomers. A peroxide initiator, little or no surfactant, and other additives may be present in the aqueous polymerization medium that is vigorously stirred and sometimes buffered by an alkaline solution. Most of the polymer is formed in the gas phase in the shape of stringy and irregularly shaped particles. The particles are comminuted to different sizes, depending on the powder properties required by the fabrication process. For example, a smoother surface part requires smaller particle size while good flow is improved by larger particle size.

Fine powder PTFE is produced by polymerization of TFE in an aqueous medium in the presence of an initiator and surfactant. The polymerization does not follow a conventional emulsion mechanism but some of the principles, which apply. The stability of the dispersion during the polymerization, to avoid premature coagulation, is balanced against the need to break the emulsion to recover the PTFE. Low shear rate agitation is maintained during the polymerization using surfactant levels below the critical micelle concentration. The rate of polymerization and particle shape and size are affected by the concentration of the surfactant. Majority of the particles is generated in the early part of polymerization and grows as the cycle proceeds. Molecular weight and composition within the particle can be controlled using the polymerization ingredients and conditions.

The same polymerization process makes aqueous dispersions of PTFE as fine powder. The dispersion is concentrated and stabilized using a variety of ionic and nonionic surfactants. Several concentration methods have been reported including electrodecantation, evaporation, and thermal concentration. Chemical additives to match them with the fabrication process or part property requirements can modify the final PTFE dispersion.

Filled compounds are produced from all three forms of PTFE using fillers such as glass fiber, graphite, metal powder, carbon fiber, and others [50].

4.6.2 Perfluoroalkoxy Polymer, PFA (CAS number 26655-00-5)

PFA is a copolymer of TFE and perfluoroalkyl vinyl ether such as PPVE. Copolymerization of perfluoroalkyl vinyl ethers with TFE can be done in a halogenated solvent [51,52] in an aqueous phase [53] sometimes containing some halogenated solvent, usually in the absence of a surfactant [54]. Terpolymers of this class contain other monomers such as HFP.

Commercially, PFA is polymerized by free-radical polymerization mechanism usually in an aqueous media via addition polymerization of TFE and PPVE. The initiator for the polymerization is usually water-soluble peroxide such as ammonium persulfate. Chain transfer agents such as methanol and acetone are used to control the molecular weight of the resin. Generally, the polymerization regime resembles that used to produce PTFE by emulsion polymerization. Polymerization temperature and pressure usually range from 15 to 95 °C and 0.5 to 3.5 MPa.

End groups are stabilized by treating the PFA with methanol, ammonia, amines, and elemental fluorine that produces CF_3 end groups [55−59]. The polymer is recovered, dried, and melt-extruded into cubes for melt fabrication processes. PFA is also available in bead (as polymerized), dispersion, and fine powder forms.

4.6.3 Perfluorinated Ethylene−Propylene Copolymer, FEP (CAS number 25067-11-2)

FEP is a random copolymer of TFE and HFP which can be polymerized, in an aqueous or a nonaqueous media [54,60]. Terpolymers of this class contain other monomers such as perfluoroalkyl vinyl ether (e.g., PPVE) to improve stress crack resistance.

Commercially, it is polymerized by free-radical polymerization mechanism usually in an aqueous (or nonaqueous) media via addition polymerization of TFE and HFP. The initiator for the polymerization is usually water-soluble peroxide such as potassium persulfate. Chain transfer agents could be used to control the molecular weight of the resin. In general, the polymerization regime and conditions resemble those used to produce PTFE by emulsion polymerization. FEP is recovered, dried, and melt-extruded into cubes for melt fabrication processes. FEP is also available in dispersion form.

4.6.4 Ethylene–Co-tetrafluoroethylene Polymers, ETFE (CAS number 68258-85-5)

This plastic is a partially fluorinated straight-chain polymer with very high molecular weight [56]. It is produced by free-radical polymerization mechanism in a solvent or a hybrid (a solvent/aqueous mixture) media, using an organic peroxide initiator. Copolymerization of TFE and ethylene ($CH_2{=}CH_2$, molecular weight 28, CAS number 74-85-1) proceeds by an addition mechanism.

Copolymers of TFE and ethylene are highly crystalline and fragile at elevated temperatures and are modified by a third monomer. Production of ETFE terpolymers having improved high-temperature mechanical (especially tensile) properties has been demonstrated [63]. They comprise of 40–60 mole% ethylene, 40–60% TFE, and a small amount of a polymerizable vinyl termonomer such as perfluoroisobutylene, PPVE, and HFP.

4.6.5 Ethylene–Co-chlorotrifluoroethylene Polymers, ECTFE (CAS number 25101-45-5)

This polymer is formed by the polymerization of ethylene and CTFE [64] in aqueous and solvent mediums using organic peroxides and oxygen-activated triethylboron. Typical polymerization is done at 60–120 °C and a pressure of 5 MPa or higher. The polymerization reaction can also be initiated by radiation like gamma rays. The most effective catalyst is tri-*n*-butyl boron which produces an ECTFE with an alternating 1:1 ethylene to TFE ratio. To control the molecular weight of the resin, chain transfer agents such as chlorinated compounds, alcohols, and ketones are required.

4.6.6 Polychlorotrifluoroethylene, PCTFE (CAS number 9002-83-9)

CTFE is polymerized by bulk, suspension, and emulsion techniques [65]. Bulk polymerization takes place using halogenated acyl peroxide catalysts or UV and gamma rays. Suspension polymerization is carried out in aqueous medium using inorganic or organic peroxide catalysts. Emulsion polymerization yields a polymer with a normal molecular weight distribution and a molecular weight–melt viscosity relationship similar to bulk polymerized polymer. Inorganic peroxy catalysts initiate the reaction in the presence of halogenated alkyl acid salt surfactants. Emulsion polymerization produces the most thermally stable PCTFE.

4.6.7 Polyvinylidene Fluoride, PVDF (CAS number 24937-79-9)

The first successful aqueous polymerization of VDF was reported in 1948 [66] using a peroxide initiator in water at 50–150 °C and 30 MPa. No surfactants or suspending agents were present in the polymerization recipe. PVDF has been polymerized by a number of methods including emulsion, suspension, solution, and bulk. Later, copolymers of VDF with ethylene and halogenated ethylene monomers were also produced [67]. In 1960, a manufacturing process was developed and PVDF was first introduced to the market. Reaction temperature ranges from 10 to 150 °C at pressure of 1 MPa or higher. Similar to TFE, emulsion polymerization of VDF requires a stable fluorinated surfactant and an initiator such as peroxide or persulfate. Suspension polymerization is conducted in an aqueous medium sometimes in the presence of a colloidal dispersant such as a hydroxy cellulose. Solution polymerization of VDF in solvents using free radical initiators is another way of producing PVDF. PVDF is commercially produced by aqueous emulsion or suspension processes.

4.6.8 Polyvinyl Fluoride, PVF (CAS number 24981-14-4)

Vinyl fluoride undergoes free-radical polymerization [39,68]. The first polymerization involved heating a saturated-solution of VF in toluene at 67 °C under 600 MPa for 16 hours. A wide variety of initiators and polymerization conditions have been explored. Examples of bulk and solution polymerizations exist; however, aqueous suspension or emulsion methods are generally preferred. Copolymers of VF and a wide variety of other monomers have been prepared. More recently, interpolymers of VF have been reported with TFE and other highly fluorinated monomers such as HFP, perfluorobutylethylene, and perfluoroethyl vinyl ether.

4.7 Structure–Property Relationship

A way to understand the impact of fluorine is to explore the differences between linear polyethylene (PE) and PTFE [37] which is the ultimate fluoropolymer in terms of properties and characteristics. There are important differences between properties of PE and that of PTFE:

- PTFE is one of the lowest surface energy polymers
- PTFE is the most chemically resistant polymer
- PTFE is one of the most thermally stable polymers
- Melting point and specific gravity of PTFE are more than double those of polyethylene

PTFE and PE differences are attributable to the differences of C–F and C–H bonds. The differences in the electronic properties and sizes of F and H lead to the following observations:

- F is the most electronegative of all elements (4 Paulings)
- F has unshared electron pairs
- F is more easily converted to F^-
- Bond strength of C—F is higher than C—H
- F is larger than H

The electronegativity of carbon at 2.5 Paulings is somewhat higher than that of hydrogen (2.1 Paulings) and lower than the electronegativity of fluorine. Consequently, the polarity of the C—F bond is opposite to that of the C—H bond, and the C—F bond is more highly polarized. In the C—F bond, the fluorine end of the bond is negatively charged compared to the C—H bond in which the carbon is negatively charged.

The difference in bond polarity of C—H and C—F affects the relative stability of the conformations of the two polymer chains. Crystallization of polyethylene takes place in a planar and trans conformation. PTFE can be forced into such a conformation at extremely high pressure [66]. PTFE, below 19 °C, crystallizes as a helix with 0.169 nm per repeat distance: it takes 13 C atoms for a 180° turn to be completed. Above 19 °C, the repeat distance increases to 0.195 nm which means that 15 carbon atoms are required for a 180° turn. At above 19 °C the chains are capable of angular displacement, which increases above 30 °C until reaching melting point (327 °C).

Substitution of F for H in the C—H bond substantially increases the bond strength from 99.5 kcal/mole for the C—H bond to 116 kcal/mole for the C—F bond. Consequently, thermal stability and chemical resistance of PTFE is higher than PE because more energy is required to break the C—F bond. The polarity and strength of the C—F bond render F atom abstraction mechanism for branching difficult. In contrast, highly branched polyethylene (>8 branches per 100 carbon atoms) can be synthesized. Branching mechanism as a tool to adjust crystallinity is not practical for PTFE. Instead comonomers with pendent groups have to be polymerized with TFE.

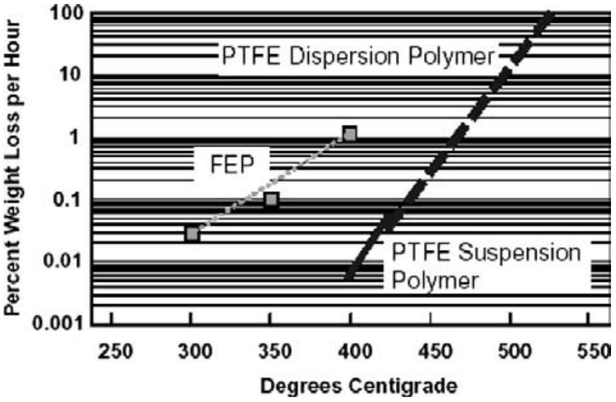


Figure 4.4 A comparison of thermal degradation of FEP and PTFE in air.

Crystallinity of never-melted PTFE is in the range of 92—98% [28], consistent with an unbranched chain structure. FEP, a copolymer of TFE and HFP, has an as-polymerized crystallinity of 40—50%. In FEP, the pendent CF_3 group is bonded to a tertiary carbon that is less thermally stable than primary and secondary carbon atoms. Degradation curves (Figure 4.4) indicate degradation onset temperatures of 300 °C for FEP (0.02% weight loss) and 425 °C for PTFE (0.03% weight loss).

4.8 Polymer Properties of PTFE

4.8.1 PTFE Properties

PTFE has excellent properties such as chemical inertness, heat resistance (both high and low), electrical insulation properties, low coefficient of friction (static 0.08 and dynamic 0.01), and nonstick property over a wide temperature range (−260 to +260 °C). It has a density in the range of 2.1—2.3 g/cm^3 and melt viscosity in the range of 1—10 GPa persecond [44]. Molecular weight of PTFE cannot be measured by standard methods. Instead, an indirect approach is used to judge molecular weight. Standard specific gravity (SSG) is the specific gravity of a chip prepared according to a standardized procedure. The underlying principle is that lower molecular weight PTFE crystallizes more extensively, thus yielding higher SSG values [67].

PTFE that has not been previously melted has a crystallinity of 92—98%, indicating a linear and nonbranched molecular structure. Upon reaching 342 °C, it melts changing from a chalky white color into a transparent amorphous gel. The second melting point of PTFE is 327 °C because it never recrystallizes to the same extent as prior to its first melting.

First-order and second-order transitions have been reported for PTFE. The transitions that are close to room temperature are of practical interest because of impact on processing of the material. Below 19 °C the crystalline system of PTFE is a nearly perfect triclinic. Above 19 °C, the unit cell changes to hexagonal. In the range of 19—30 °C, the chain segments become increasing disorderly and the preferred crystallographic direction disappears, resulting in a large expansion in the specific volume of PTFE (1.8%) [68] which must be considered in measuring the dimensions of articles made from these plastics.

PTFE is by far the most chemically resistant polymer among thermoplastics. The exceptions include molten alkali metals, gaseous fluorine at high temperatures and pressures, and few organic halogenated compounds such as chlorine trifluoride (ClF_3) and oxygen difluoride (OF_2). A few other chemicals have been reported to attack PTFE at or near its upper service temperature. PTFE reacts with 80% sodium or potassium hydroxide and some strong Lewis bases including metal hydrides.

Mechanical properties of PTFE are generally inferior to engineering plastics at the room temperature. Compounding with fillers has been the strategy to overcome this shortage. PTFE has useful mechanical properties in its use temperature range.

PTFE has excellent electrical properties such as high insulation resistance, low dielectric constant (2.1), and low dissipation factor. Dielectric constant and dissipation factor remain virtually unchanged in the range of −40 to −250 °C and 5 Hz to 10 GHz. Dielectric breakdown strength (short term) is 47 kV/mm for a 0.25-mm-thick film (ASTM D149). Dielectric breakdown strength is enhanced with decrease in voids in PTFE, which is affected by the fabrication process.

PTFE is attacked by radiation, and degradation in air begins at a dose of 0.02 Mrad.

4.8.2 PFA Properties

PFA polymers are fully fluorinated and melt-processible [52,69]. They have chemical resistance and thermal stability comparable to PTFE. Specific gravity of perfluoroalkoxy resins is in the range of 2.12−2.17. PFA has an upper continuous use temperature of 260 °C.

Crystallinity and specific gravity of PFA parts decrease when the cooling rate of the molten polymer is increased. The lowest crystallinity obtained by quenching molten PFA in ice was 48% (specific gravity 2.123).

Similar to PTFE, molecular weight of PFA cannot be measured by conventional techniques. An indirect factor called melt flow rate (MFR) also called melt flow index (MFI) is used which is the amount of polymer melt that would flow through a capillary rheometer at a given temperature under a defined load (usually in grams in 10 minutes). MFR is inversely proportional to viscosity; viscosity is directly proportional to molecular weight of the polymer.

PFA exhibits one first-order transition at −5 °C in contrast to two temperatures for PTFE at 19 and 30 °C. It has three second-order transitions at −100, −30 and 90 °C [54].

PFA has excellent electrical properties such as high insulation resistance, low dielectric constant (2.1), and low dissipation factor. Dielectric constant and dissipation factor remain virtually unchanged in the range of −40 to −250 °C and 10^2 Hz to 2.4×10^{10} Hz. Dielectric breakdown strength (short term) is 80 kV/mm for a 0.25-mm-thick film (ASTM D149).

Chemical properties of PFA are similar to those of PTFE.

PFA is attacked by radiation, and degradation in air begins at a somewhat higher dose than that of PTFE which starts to degrade at 0.02 Mrad.

4.8.3 FEP Properties

Fluorinated ethylene-propylene copolymers are fully fluorinated and melt-processible [60,70]. They have excellent chemical resistance and thermal stability. Specific gravity of FEP resins is in the range of 2.13−2.15. FEP has an upper continuous use temperature of 200 °C.

Similar to PTFE, molecular weight of FEP cannot be measured by conventional techniques. Like PFA, MFR is used to characterize molecular weight of FEP. MFR and the molecular weight are inversely related.

Molecular weight distribution is determined by measuring the dynamic module of the polymer melt using rheological analyses. Crystallinity of virgin (unmelted) FEP is 65−75%.

FEP exhibits a single first-order transition that is its melting point. Relaxation temperature of FEP increases with HFP content of the copolymer. FEP has a dielectric transition at −150 °C which is unaffected by the monomer composition or crystallinity (specific gravity).

Chemical properties of FEP are similar to those of PTFE and PFA.

FEP is attacked by radiation, and its degradation in air begins at a dose of 0.2 Mrad (10 times higher than that of PTFE).

4.8.4 PCTFE Properties

PCTFE is a semicrystalline polymer [62] with a helical polymer chain and a pseudohexagonal crystal. Crystal growth is spherulitic and consists of folded chains. Large size of chlorine constrains recrystallization after melting during processing. This resin has good properties at cryogenic temperatures relative to plastics in general, although they are inferior to other fluoropolymers except PVDF.

PCTFE has exceptional barrier properties and superb chemical resistance. It is attacked by a number of organic solvents.

PCTFE has low thermal stability and degrades upon reaching its melting point, requiring special care during processing.

4.8.5 ETFE Properties

PVDF and equimolar ETFE are isomers but the latter has a higher melting point and a lower dielectric loss than the former. ETFE crystallizes into unit cells believed to be orthorhombic or monoclinic [71]. The molecular conformation of ETFE is an extended zigzag. This polymer is dissolved in some boiling esters at above 230 °C, thus allowing determination of molecular weight (weight-average) by light scattering. ETFE has several transitions, alpha relaxation at 110 °C (shifts to 135 °C at higher crystallinity), beta at −25 °C, and gamma relaxation at −120 °C.

ETFE terpolymers have good mechanical properties including tensile and cut-through resistance and lower creep than perfluoropolymers. ETFE is more resistant to radiation than perfluoropolymers (modestly affected up to 20 Mrad) and can be crosslinked by radiation such as electron beam. Crosslinking is used to strengthen cut-through resistance of ETFE wire insulation.

ETFE has a dielectric constant of 2.6–3.4 and dissipation factor of 0.0006–0.010 as frequency increases from 10^2 to 10^{10} Hz.

ETFE terpolymers are resistant to stress cracking and chemical attack by most compounds. Strong oxidizing acids, concentrated boiling sulfonic acids, and organic bases (amines) attack ETFE and any chemical that affects PTFE, PFA, and FEP.

4.8.6 ECTFE Properties

ECTFE is semicrystalline (50–60%) and melts at 240 °C (commercial grade). It has an alpha relaxation at 140 °C, a beta at 90 °C, and gamma relaxation at −65 °C. Conformation of ECTFE is an extended zigzag in which ethylene and CTFE alternate. The unit cell of ECTFE's crystal is hexagonal.

Similar to ETFE, ECTFE terpolymers (same termonomers) have better mechanical and abrasion and radiation resistance than PTFE and other perfluoropolymers.

Dielectric constant of ECTFE is 2.5–2.6, and independent of temperature and frequency. Dissipation factor is 0.02 and much larger than ETFE's.

ECTFE is resistant to most chemicals except hot polar and chlorinated solvents. It does not stress crack dissolve in any solvents. ECTFE has better barrier properties to SO_2, Cl_2, HCl, and water than FEP and PVDF.

4.8.7 PVDF Properties

Polyvinylidene fluoride is a semicrystalline polymer (35–70% crystallinity) with an extended zigzag chain [49]. Head-to-tail addition of VDF dominates but there are head-to-head or tail-to-tail defects that affect crystallinity and properties of PVDF.

PVDF has a number of transitions and its density alters for each polymorph state. There are four known proposed states, named as α, β, γ, and δ. The most common phase is α-PVDF which exhibits transitions at −70 °C (γ), −38 °C(β), 50 °C (α"), and 100 °C (α').

PVDF resists most organic and inorganic chemicals including chlorinated solvents. Strong bases, amines, esters, and ketones attack this resin. The impact ranges from swelling to complete dissolution in these solvents depending on the conditions. PVDF exhibits compatibility with a number of polymers. Commercially useful blends with acrylics and methacrylics have been developed.

PVDF, just as ETFE, readily crosslinks as a result of exposure to radiation. Radiation (gamma rays) has modest effect on the mechanical properties of PVDF.

4.8.8 PVF Properties

Poly(vinyl fluoride) is a semicrystalline polymer with a planar, zigzag conformation [23,24]. The degree of crystallinity can vary significantly from 20 to 60% and is a function of defect structures. Commercial PVF is atactic, contains approximately 12% head-to-head linkages, and displays a peak melting point of about 190 °C [39,40].

PVF displays several transitions below the melting temperature. Lower T_g occurs at −15 to −20 °C and upper T_g is in the 40–50 °C range. Two other transitions at −80 °C and 150 °C have been reported.

PVF has low solubility in all solvents below about 100 °C. Polymers with greater solubility have been prepared using 0.1% 2-propanol polymerization modifier and were characterized in *N*,*N*-dimethylformamide solution containing 0.1 N LiBr. M_n ranged from 76,000 to 234,000 (osmometry), and M_s from 143,000 to 654,000 (sedimentation velocity).

High molecular weight PVF is reported to degrade in an inert atmosphere, with concurrent HF loss and backbone cleavage occurring at about 450 °C. In air, HF loss occurs at about 350 °C, followed by backbone cleavage around 450 °C.

PVF is transparent to radiation in the UV, visible, and near-infrared regions, transmitting 90% of the radiation from 350 to 2500 nm. PVF becomes embrittled upon exposure to electron-beam radiation of 1000 Mrad but resists breakdown at lower doses. It retains its strength at 32 Mrad while PTFE is degraded at 0.2 Mrad.

The self-ignition temperature of PVF film is 390 °C. The limiting oxygen index (LOI) for PVF is 22.6%. HF and a mixture of aromatic and aliphatic hydrocarbons are generated from the thermal degradation of PVF.

4.9 Fabrication Techniques

With the exception of two fluoropolymers, PVF and PTFE, the rest of the resins described in this chapter can be processed by standard melt-processing techniques such as injection, transfer and blow molding, extrusion and rotational molding. Process equipment for fluoropolymers must be made from corrosion-resistant alloys because of the corrosive compound that may be produced when fluoropolymers are heated above their melting points. Higher melt viscosity of these resins may require more powder and higher pressure rating equipment.

PTFE is processed using metal powder-processing techniques in which a preform is molded and "sintered." Compression molding may also be used to fabricate PTFE parts. PTFE dispersions are applied by similar techniques to other coatings. Paste extrusion in which PTFE is blended with a hydrocarbon, prior to molding a preform, is used to continuously fabricate PTFE into tubes, tapes, and wire insulation. The hydrocarbon is vaporized before the part is sintered.

PVF is dispersed in a polar latent solvent such as dimethyl acetamide and is melt-extruded as a plastisol, followed by solvent removal by drying.

4.10 Applications

Properties of fluoropolymers that have led to applications include chemical resistance, thermal stability, cryogenic properties, low coefficient of friction, low surface energy, low dielectric constant, high volume and surface resistivity, and flame resistance. Fluoropolymers are used as liners (process surface) because of their resistance to chemical attack. They provide durable, low maintenance, and economical alternatives to exotic metals for use at high temperatures without introducing impurities. Electrical properties make fluoropolymers highly valuable in electronic and electrical applications as insulators, e.g., FEP in data communications.

In automotive and office equipment, mechanical properties of fluoropolymers are beneficial in low-friction bearings and seals that resist attack by hydrocarbons and other fluids. In food processing, the Food and Drug Administration approved fluoropolymer grades are fabrication material for equipment due to their resistance to oil and cleaning materials, and their anti-stick and low friction properties. In houseware, fluoropolymers are applied as nonstick coatings for cookware and appliance surfaces. Medical articles such as surgical patches and cardiovascular grafts rely on the long-term stability of fluoropolymers as well as their low surface energy and chemical resistance.

For airports, stadiums, and other structures, glass fiber fabric coated with PTFE is fabricated into roofing and enclosures. PTFE provides excellent resistance to weathering, including exposure to UV rays in sunlight, flame resistance for safety, and low surface energy for soil resistance, and easy cleaning.

4.11 Safety

Fluoropolymers are chemically stable and inert or relatively unreactive. Reactivity, generally, decreases as fluorine content of the polymer increases. Fluorine induces more stability than chlorine. Fluoropolymers can produce toxic products if overheated. Precautions should be taken to exhaust any degradation fragments produced during the processing and fabrication of parts from fluoropolymers [72]. This family of plastics has low toxicity and almost no toxicological activity. No fluoropolymers have been known to cause skin sensitivity and irritation in humans.

4.11.1 Ammonium Perfluoro Octanoate (APFO, also C8)

APFO is an essential processing aid in the manufacture of fluoropolymers. It is a polymerization aid that plays a critical role in the polymerization of TFE and fluorinated comonomers used to produce PTFE, PFA (MFA), and FEP. It acts as an intermediate for the majority of fluoropolymers and is eliminated during the finishing steps. Solid phase fluoropolymers contain extremely small amounts of C8 of the order of a few parts per million. In the case of aqueous dispersion products a fraction of percent of APFO would normally be present in the dispersion products.

APFO has been found to be persistent in the environment. Consequently, since mid-2000's fluoropolymer manufacturers have taken steps to abate environmental emissions and reduce and eliminate the C8 from dispersion products. The industry has reduced the presence of C8 in its products by 95% as of 2010. Fluoropolymer manufacturers have committed to US Environmental Protection Agency (www.EPA.gov) to eliminate the use of C8 completely by finding alternative polymerization aids by 2015. For more information readers are encouraged to contact *Fluoropolymers Division* of the Society of Plastics Industry, Inc. (www.Fluoropolymers.org) or fluoropolymer manufacturers directly.

4.12 Economy

Fluoropolymers are more costly to produce than polyolefins and many other plastics due to capital costs and the cost of fluorine. Polymerization and finishing of these resins require processing of highly flammable hazardous materials, thus mandating the use of expensive construction material and elaborate equipment. In 2008, the cost ranged from less than US $9 per kg for mechanical grade PTFE [73] to $70 per kg for specialty grade PFA. Soluble perfluoropolymers cost $10−20 per gram and are only used in high value applications.

4.13 Summary

Commercial fluoropolymers are based on TFE, VDF, and to a lesser extent CTFE. Examples of comonomers include PMVE, PEVE, PPVE, HFP, CTFE, and PFBE. The general consequences of substitution of fluorine for hydrogen in a polymer include increased chemical and solvent resistance, enhanced electrical properties such as lower dielectric constant, lower coefficient of friction, higher melting point, increased photostability and thermal stability, improved flame resistance, and weakened mechanical properties. The ultimate properties are achieved when a polymer is entirely fluorinated.

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5 Poly(Vinyl Chloride)

William F. Carroll, Jr., Richard W. Johnson, Sylvia S. Moore and Robert A. Paradis
The Vinyl Institute, 1737 King Street, Suite 390, Alexandria, VA 22314, USA

5.1 Introduction [1,2,3]

Polyvinylchloride, otherwise known as PVC or “vinyl,” is a thermoplastic and the third largest production polymer in the world. In the US, there is approximately 16 billion pounds of PVC annual capacity. Used for nearly three quarters of a century, vinyl is one of the most analyzed, tested, and versatile materials.

PVC can be rigid or flexible, clear or opaque. It can be processed as a solution, paste, or powder; extruded; injection-, dip-, or roto-molded; knife- or reverse-roll coated. It is easily printed and bonded by heat, radio frequency welding, or solvent. This chapter reviews monomer synthesis, types of resin and their manufacturing methods, additives, compounding, and processing into the myriad finished products of the vinyl industry.

PVC was developed as a flexible material in the late 1920s by Waldo Semon at BFGoodrich [4]. He heated PVC with plasticizer in the hope of developing improved rubber-to-metal adhesives. While that search was largely not successful, Semon found that plasticizer and vinyl formed a tight admixture with outstanding flexibility and elasticity and might be useful in its own right.

Fundamental technologies for processing PVC were initially based on analogous technologies used to process rubber, to some degree because rubber companies were the first to pursue commercialization of PVC products. In the 1940s vinyl was used in large quantities in wiring on ships to replace rubber cable jacketing based on vinyl’s superior fire resistance. In the 1950s and 1960s flexible commercial compounds and products were developed. Rigid applications, particularly bottles and pipe followed.

When PVC is flexible, it is because it has been compounded with a plasticizer. The amount and type of plasticizer governs—among other things—the flexibility, toughness, medical applicability, and hot-and-cold properties of the finished product. Examples of flexible products are upholstery and clothing; wall covering, blood and IV bags, and tubing; meat wrap film, shower curtains, wire insulation, and coatings on metal sheet.

Rigid PVC, by comparison, contains no plasticizer but may contain other rigid-specific additives such as impact modifiers. Rigid applications include pipe, siding, windows, fence and many custom profiles for furniture, automotive, and industrial applications. Some of these profile products are now also being made of rigid foamed PVC, which offers the same material benefits at lower weight.

Whether rigid or flexible, the vast majority of PVC is used in durable, long-life applications (Figure 5.1). PVC has a long history of use in critical applications such as medical devices, food packaging, and potable water delivery among others. As a result, PVC resin, compounds, and products meet stringent national and international standards supervised by agencies from the U.S. Food and Drug Administration (FDA) and NSF International to ASTM and ISO. Thus, PVC is easily one of the most-studied and critically assessed materials on the market (see Figure 5.1).

5.1.1 Making PVC Work

PVC resin applicability is defined mainly by particle size and molecular weight. Small-particle PVC made by emulsion or dispersion polymerization is typically compounded into a liquid or paste formulation and spread coated, sprayed, or molded by a number of techniques. Large particle PVC made by suspension or mass polymerization is typically extruded, calendered, or injection molded.

The melt viscosity and tensile properties of PVC are generally a function of its molecular weight. PVC forms a fairly viscous melt; thus, to avoid degradation from shear heating, lower molecular weight resin (injection molding) or plasticized higher molecular weight resin (wire and cable jacketing) is typically required. Pipe, siding, and other extruded applications are in the middle of the spectrum of PVC molecular weights. Figure 5.2 shows the material flow from raw resin to finished products.

PVC compounds are formulated for specific applications with specific requirements; thus, certain additives are used in some applications and not in others. For example, plasticizers used in roofing membrane may not be acceptable for food wrap film. In some cases, additives are reviewed and approved for applications. U.S. FDA and NSF International review and/or approve resins and additives for food grade bottle and potable water pipe, respectively.

PVC compounds can contain as few as 2 or as many as 10−15 additives. Standard practice in the industry is to base

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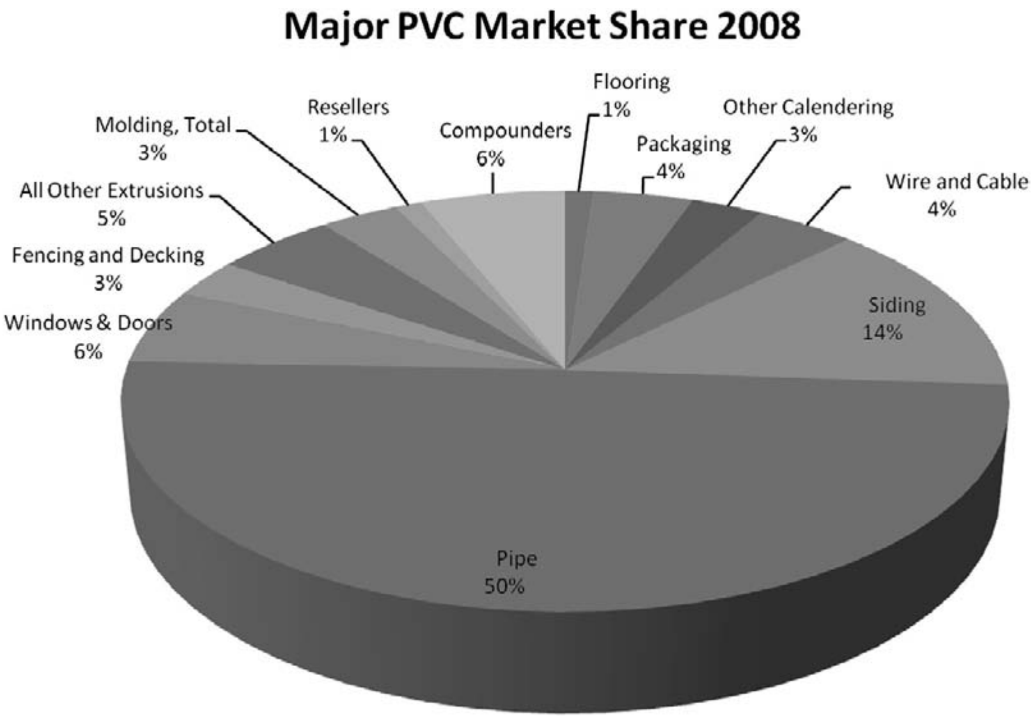

Figure 5.1 Markets for PVC, 2008.

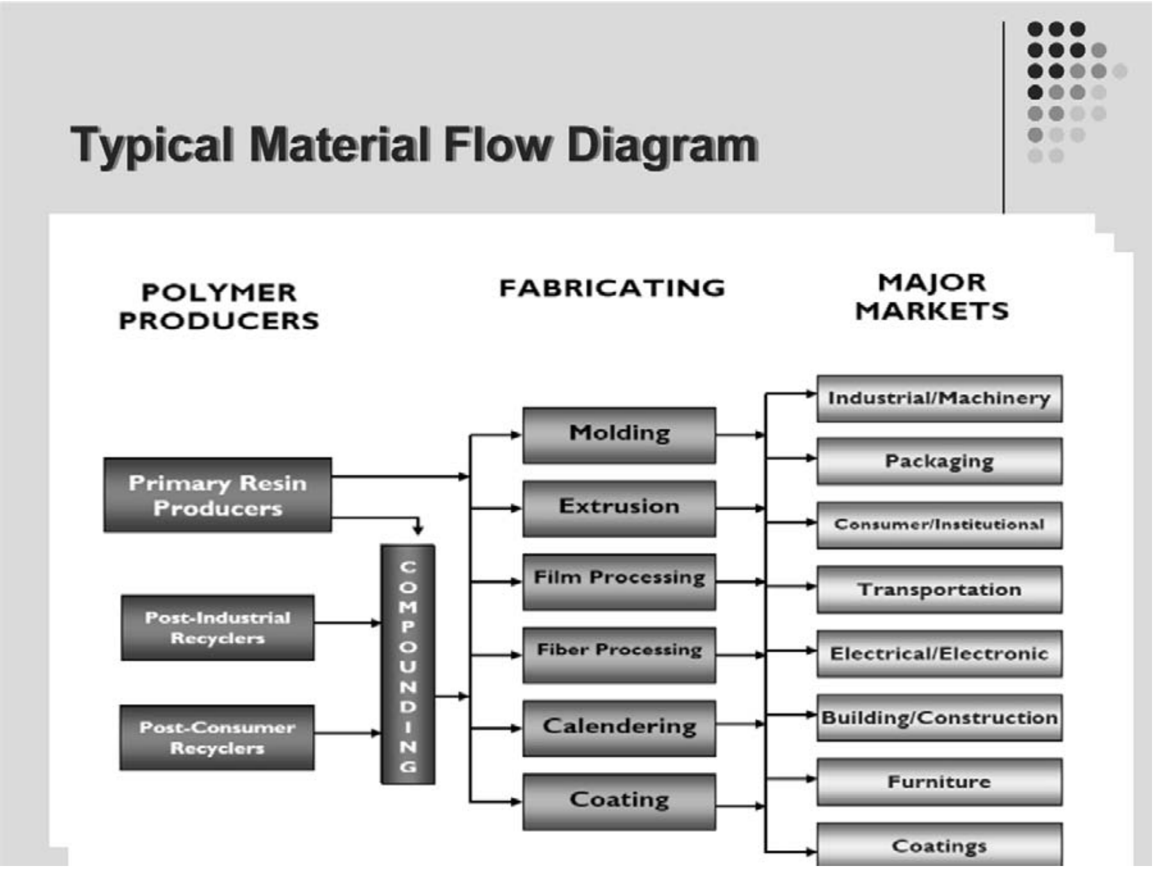

Figure 5.2 Typical material flow diagram.

additive use on additions to 100 parts by weight of resin (phr) rather than percent. Additive manufacturers maintain technical support organizations that develop application-specific additives and formulations and should be consulted for specifics.

Because PVC is less thermally stable than many other polymers, lubricants and thermal stabilizers are always included in PVC formulations. Lubricants are typically oxidized polyethylene waxes, simple 165-degree melting paraffin waxes that have a range of melt temperatures. Lubricants are used to vary the fusion properties of PVC and to facilitate flow at the metal—polymer interface in the processing equipment. Thermal stabilizers are used to prevent dehydrohalogenation or "unzipping" of the polymer by loss of HCl which, even at well less than 1% decomposition, results in discoloration. Calcium stearate at low levels acts as an internal lubricant and enhances fusion. At higher levels it acts as an external lubricant. In addition it has some stabilizer properties, analogous to other metal soaps.

Impact modifiers are used in rigids and impart toughness or ductility to PVC as needed for the finished application. Processing aids are acrylic copolymers used in compounds to assist in PVC fusion and surface finish and are important to the cell structure of rigid foamed parts.

Pigments include titanium dioxide (TiO_2), the main white pigment used in applications from toothpaste to paper. In addition, TiO_2 is an extremely effective UV stabilizer, absorbing light and converting it to small amounts of heat harmlessly in the polymer matrix. Organic UV stabilizers also exist for clear applications. Fillers—calcium carbonate, clay, natural cellulose, or other inert materials—are added either for physical properties, product attributes or to reduce the cost of the material. Antimicrobial additives retard fungal or bacterial growth.

Because of its chlorine content, rigid PVC and some flexible PVC naturally resists burning and will self-extinguish when a source of flame is removed. Many products are specially formulated for low smoke generation and low flame spread. Vinyl is one of the few materials that meet the stringent National Fire Protection Association (NFPA) requirement for insulating electrical and data transmission cables including plenum applications. Flame and smoke retardation is enhanced by addition of calcium carbonate, gypsum, aluminum trihydrate, talc, magnesium hydroxide, or antimony trioxide. Fire properties can be affected by the presence of flammable plasticizers in the formulation.

5.2 Synthesis of Vinyl Chloride [3,5]

Vinyl chloride monomer (VCM) is prepared commercially in two processes based on different two-carbon hydrocarbons. The "balanced process" is based on ethylene and the "carbide" process is based on acetylene.

5.2.1 Balanced Process

The balanced process is the dominant method of preparation of VCM in the world, and virtually the only method used outside China. It is based on ethylene produced by cracking either naphtha or natural gas liquids.

Ethylene is reacted with elemental chlorine over an iron-based catalyst to produce 1,2-dichloroethane, commonly called ethylene dichloride (EDC). This process is called "direct chlorination." EDC is thermally cracked to generate VCM and hydrogen chloride (HCl). Vinyl chloride is then purified by distillation. It boils at −13 °C.

Side-product HCl from EDC cracking is combined with oxygen and more ethylene over a copper-based catalyst at elevated temperature to generate more EDC. This EDC is also cracked, and VCM distilled. The process is called oxychlorination; in it, chloride is effectively oxidized to elemental chlorine.

Other higher chlorinated small-molecule products may be generated in the EDC-to-VCM process. These materials, which boil at higher temperature than VCM, are known as "light ends," which are separated from VCM in the distillation column and become raw material for solvents.

As in any reaction, some (about 1—2%) higher boiling point materials are generated; these still-bottoms known in the industry as "heavy ends" are highly chlorinated and contain some chlorinated dibenzodioxins and furans (see Section 5.8). Heavy ends are rigorously destroyed by either combustion or other thermal oxidation; either operation generates mainly CO_2 and HCl. HCl can be isolated and recycled by oxychlorination or harvested for sale as the aqueous solution, commercial grade muriatic acid (see Figure 5.3).

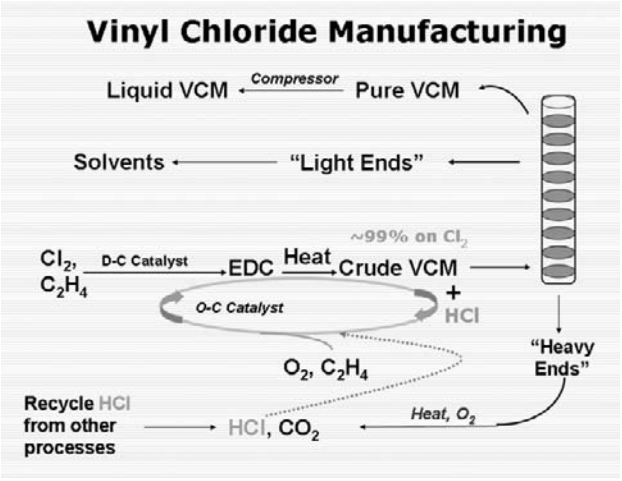

Figure 5.3 Schematic representation of vinyl chloride manufacturing.

5.2.2 Carbide Process

One of the oldest processes for generating small-molecule organics—predating the modern petrochemical industry—is the process of making acetylene. Acetylene results when calcium carbide, synthesized from limestone and coke at a temperature exceeding 2000 °C, is reacted with water. Direct addition of HCl to acetylene over a mercury chloride/activated carbon catalyst yields VCM. VCM is washed with water and base, and then distilled. Wash water and spent catalyst must be treated to remove and recycle mercury.

The carbide process was the dominant process for production of VCM in China when small, geographically dispersed chloralkali facilities were built in the late 1950s. After the opening of China in the late 1970s, balanced process facilities were built in the eastern part of the country, close to ethylene crackers. However, because there were no ethylene crackers in the west, but limestone and coal were plentiful, the need for locally produced VCM was satisfied by expansion of the old technology.

5.3 PVC Resin Synthesis and Characterization [1,2,3]

PVC is manufactured by the free-radical polymerization of VCM. In general, about 1000 monomer units comprise a PVC chain. Usual addition of monomer units is head-to-tail; however, when head-to-head addition occurs, the unstable end of the growing chain rearranges to yield a terminal double bond and a chlorine atom. Since the chlorine atom is a free radical, it starts polymerization of another chain (see Figure 5.4).

Chain transfer and control of molecular weight are mediated by the activation energy of head-to-head addition, and thus by polymerization temperature alone. PVC is the only major commercial polymer wherein polymerization temperature controls molecular weight and molecular weight distribution.

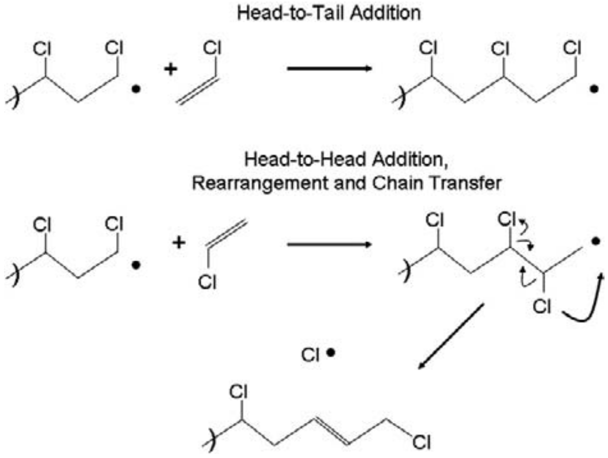

Figure 5.4 Addition of VCM to growing PVC chain.

Polymerization takes place at temperatures generally between 40 and 70 °C. As VCM boils at −13 °C, all polymerization of PVC is at elevated pressure; however, that pressure is only of the order of 100 psig.

Because vinyl chloride is a monosubstituted ethylene and not a symmetric molecule, in principle it could have explicit tacticity as does, for example, polypropylene. In practice, however, vinyl chloride polymerized commercially does not have regular tacticity because the growing end of the chain is a free radical at an sp^2 hybridized carbon center which can freely rotate. This rotation rate varies with temperature; by polymerizing vinyl chloride at very low temperature the rotation can be slowed significantly, preferentially trapping certain conformations and allowing for polymerization of a more syndiotactic polymer.

Since it is an atactic polymer, PVC also has very low crystallinity. Unlike PE or other crystalline polymers, the strength of PVC is largely due to chain entanglement.

There are three major types of PVC polymerization. Each is designed to produce vinyl resin of different resin particle size and morphology (see Figure 5.5).

5.3.1 Emulsion/Microsuspension Polymerization

Small-particle PVC (<1 micron diameter) can be produced either by true emulsion or by microsuspension polymerization. VCM, surfactant (usually a soap such as sodium lauryl sulfate), and a peroxide or azo initiator are charged to a reactor along with water. Polymerization yields latex at about 40% solids, which is steam-stripped and then spray-dried.

Small-particle PVC is a powder with particles in the range of 0.1−10 microns and agglomerates ranging to about 50 microns. Generally, the fundamental particles are about 1 micron in diameter. Although dried material is commonly pulverized, not all agglomerates are destroyed in the post processing. All the particles have surfactant or other residues on the surface as residual from the manufacturing process.

Small-particle PVC is typically made into a paste with various plasticizers, stabilizers, diluents, and other additives. Because it is processed as a liquid, rheological properties of that paste are important. To a great extent, those rheological properties are determined by the identity of the surfactant and the particle size distribution of the fundamental particles and spray drier aggregates.

Mono- or multimodal distributions of latex particles can be generated by controlling the amount, identity, and dispersion of soap and organic adjuvants (if microsuspension type) as well as by copolymerization or postaddition of seed latex. Small-particle PVC accounts for <5% of U.S. production.

5.3.2 Suspension Polymerization

Most PVC is produced by suspension polymerization. Roughly 50−100 micron scale droplets of VCM are created in water by the shearing action of an agitator. These droplets

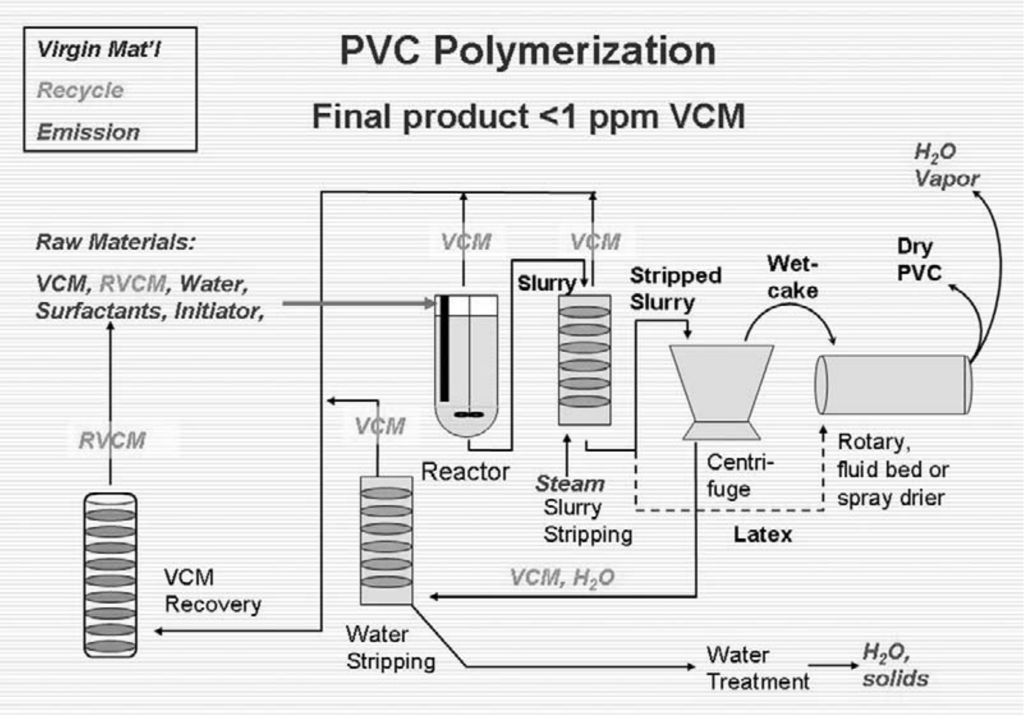

Figure 5.5 Schematic representation of PVC polymerization. A small amount of VCM (<0.005% of raw material) is emitted from the drier. Fine solids are trapped by coagulation and settling in water treatment and are harvested as lower grade resin.

are stabilized by a protective colloid, usually a functionalized cellulose or partially hydrolyzed poly(vinyl acetate).

In suspension polymerization, free-radical initiation, due to decomposition of a peroxide or azo initiator, generally occurs in droplets. As PVC is insoluble in monomer, submicron-sized particles precipitate in the droplets virtually immediately. These particles migrate to the surface of the droplet and very quickly form a film at the interface called the pericellular membrane. Polymerization and precipitation continue to occur in the droplet until the droplets are converted from solids-in-liquid to liquid-sorbed-in-solid (~20% conversion).

At about this point in the polymerization, the particles become unstable and agglomerate into larger aggregates. As this occurs, the pericellular membrane of individual particles is broken, the agglomerated particles are porous, and the interior structure is that of agglomerated 1 micron particles.

Since PVC is denser than VCM, the particles shrink as polymerization proceeds, and the porous particles imbibe water. PVC, as a polymer, has a density of about 1.4 g/cm^3; the porosity of PVC particles reduces the bulk density of dry PVC resin to about 0.55 g/cm^3. Polymerization is typically stopped between 70 and 90 % conversion. Final particle size is in the order of 140 microns.

Porosity enhances the ability of PVC particles to easily release VCM dissolved in polymer, to absorb additives such as plasticizer, and to be easily deformable under heat and shear in an extruder. Secondary suspending agents that stabilize internal structure and early termination of polymerization enhance porosity.

After removal and recovery of gaseous unpolymerized VCM, resin slurry at about 45% solids is sent to a steam stripper, usually a counter-current column. VCM is recovered, slurry is centrifuged, and wetcake is sent to be dried in a rotary or fluid-bed drier.

5.3.3 Mass Polymerization

VCM can be polymerized without the presence of water or any other dispersant. Mass or bulk polymerization is usually carried out in a two-step process. First, a low-solid prepolymerization is carried out to create PVC seed particles as a suspension in VCM. This prepolymer is added to a larger postpolymerization reactor with more monomer, where, under initiation and agitation, PVC powder is generated.

Seemingly simple, there are unique issues associated with mass polymerization; among them are reactor fouling, heat transfer, VCM removal, and particle porosity. Methods have been developed to address most of those issues; however, mass polymerization comprises a small minority of global PVC production.

5.3.4 PVC Molecular Weight

While, in general, PVC molecules are about 800−1500 monomer units long, more precise determinations of molecular weight are needed because of the effects of molecular weight on resin processing. For example, higher molecular weight resin is usually specified for flexible applications. Lower molecular weight resin is typically used in injection molding.

In practice, molecular weight is measured by solution viscometry. Dissolving a precise amount of resin in a solvent and measuring the change in viscosity of the solution versus pure solvent is correlated with resin molecular weight. While solution viscometry does not give a direct measure of molecular weight distribution, the Mw/Mn of PVC is very nearly two in all cases as a result of the polymerization and chain transfer mechanism.

The most common method in the U.S. is called intrinsic viscosity or IV, ASTM D1243, although relative viscosity is occasionally used. European manufacturers use K-value, a two digit number between 35 and 80 derived from solution viscosity measurements. By intrinsic viscosity determination, PVC resin spans 0.65 and 1.10. Pipe resin has an IV of 0.88–0.92. Resins of this IV and higher are used for flexible products. A sample of resin types and applications can be found in Table 5.1.

5.3.5 PVC Particle Internal Morphology [3,6]

A typical suspension resin grain is built up of three distinct types of particles, derived from the polymerization, precipitation, and agglomeration previously mentioned. The discreet resin grain, having diameter approximately 150 microns in size is called a Stage III particle. Within the Stage III particle are agglomerated structures consisting of smaller particles about 1 micron in size called Stage II particles. Between the Stage II particles are voids derived from shrinkage of the droplet as it polymerizes. This shrinkage occurs because PVC polymer is denser and thus requires less volume per unit mass than liquid monomer. Individual PVC molecules, folded and arranged but not generally crystalline, are called Stage I particles.

As the pericellular membrane ruptures, internal void volume—empty space amidst Stage II particles—forms due to shrinkage. This void volume is most prevalent in high molecular weight resins. During polymerization, void volume fills with water which is later removed in the dewatering step. Plasticizer is absorbed into this void volume during mixing of flexible PVC compound, where it sorbs onto the internal particle surface. As a result the blend is "dry" and not sticky. Void volume also plays a role in processing rigid PVC formulations. Compression of resin grains in an extruder, which eliminates the voids, helps to generate shear heating on a microscale between the Stage II particles, aiding in fusion.

Good internal morphology—relatively small Stage II particles and sufficient void volume—also enhances removal of vinyl chloride during the stripping process. Removal of bulk VCM under vacuum and steam heat is relatively easy; however, the rate-determining step for stripping PVC to low residual monomer is diffusion of VCM from solid PVC. VCM has a shorter mean distance to diffuse out of the solid polymer phase if Stage II particles are smaller; thus, monomer removal is enhanced by good internal structure (see Figure 5.6).

Table 5.1 Starting formulations for PVC applications

Application	Pipe	Windows/Siding/Profiles	Clear Bottles/ Sheet	Injection Molding/ Pipe Fittings
Resin	100	100	100	100
Resin IV	0.88–0.92	0.88–0.92	0.65–0.84	0.65–0.75
K-Value	65–67	65–67	55–64	55–60
Stabilizer	Low tin	High tin	High tin	High tin
Filler	0–5	0–5		0–5
TiO_2	0.5–1.0	9–13		0–2
Impact modifier		3–6	6–10	
Processing aid	0–1	0.5–1.5	0.5–2	0–3
Lubricants				
Calcium Stearate	0.5–0.9	0.7–1.5		0.8–2
Paraffin wax	0.8–1.5	0.4–1		1–2
Oxidized PE	0.1–0.3	0–0.3	0–0.3	0–0.4
Other (esters)		0–1	1–2	0–1
Pigments	As needed	As needed	Tint	As needed

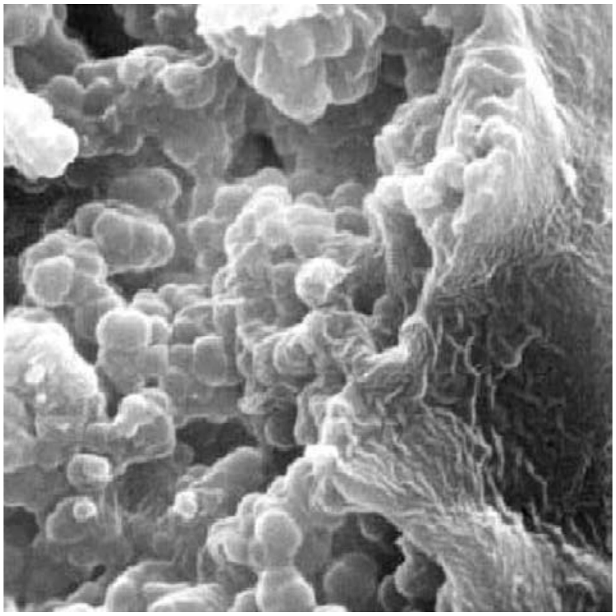

Figure 5.6 Stage II particles and void space.

5.4 PVC Compounds: Processing and Applications [7,8]

PVC is a versatile polymer, whose utility in a wide range of applications is made possible by the use of additives that impart impact strength, flexibility, or thermal stability. At the same time, it is quite dependent upon these additives to provide the processability and stability required to transform the resin into usable items. The most common additives used include stabilizers, plasticizers (for flexible compounds), impact modifiers/processing aids (for rigid compounds, in some cases), fillers, pigments, and lubricants.

PVC resin starts as a powder. Because PVC resins are sorptive, when other ingredients are added, the result is a free-flowing a dry blend—also a powder. By volume, most PVC applications are made directly from dry blend. However, some products are best produced from pellets—for example, wire and cable and other flexible compounds as well as some small-to medium-volume extrusion and injection molding applications.

While the additives are critical to performance, they must be blended with PVC resin of the correct molecular weight in order for the final processed material to possess the desired properties. Choice of resin molecular weight is driven by processing and tensile property requirements of the specific application.

5.4.1 Additives

5.4.1.1 Plasticizers

Plasticizers are bulky organic molecules, generally 300−600 g/mole in molecular weight, and also somewhat polar so as to be compatible with the PVC matrix. Good plasticization involves interspersing plasticizer molecules between PVC chains, breaking the small amount of native PVC crystallinity, and internally lubricating the polymer blend. While there is no formal chemical bond between plasticizer and polymer, the polar attraction between them makes plasticized PVC more than a simple physical mixture. The two are not readily separable in normal use.

To make PVC flexible at least 15 phr plasticizer is required. Less than this amount induces antiplasticization, and actually increases stiffness. Plasticizers can be used alone or in combination to get the desired properties such as tensile and tear strength or low temperature flexibility. The molar mass and physical size of the plasticizer and the solubility parameters of PVC plasticizers have the major effect on the dipole attraction and thus the final properties of a flexible compound.

Phthalates and adipates are the most commonly used plasticizers. Trimellitates are used in wire and cable and certain other applications where a relatively higher service temperature is required.

Phthalates (esters of phthalic acid, also called 1,2-benzenedicarboxylic acid). DOP (DEHP), dioctyl phthalate (di-2-ethylhexyl phthalate); DUP, diundecyl phthalate; DINP, diisononyl phthalate; DIDP, diisodecyl phthalate; 6−10P, mixture of C5, C7, and C9 straight-chain phthalates; 711P, mixture of C6, C8, and C10 linear and branched-chain phthalates; 9−11P, mixture of C8, C9, and C10 linear and branched-chain phthalates; DOTP, di-2-ethylhexyl terephthalate.

Adipates (esters of 1,4-butanedicarboxylic acid—a six-carbon aliphatic acid). DIDA, diisodecyl adipate; DOA (DEHA), dioctyl adipate (di-2-ethylhexyl adipate); DBEA, dibutoxyethyl adipate; DBEEA, dibutoxyethoxyethyl adipate.

Azelates. DOZ (DEHZ), (esters of 1,7-heptanedicarboxylic acid—a nine-carbon aliphatic acid): dioctyl azelate (di-2-ethylhexyl azelate).

Sebacates (esters of 1,8-octanedicarboxylic acid—a ten-carbon aliphatic acid). DOS (DEHS), dioctyl sebacate (di-2-ethylhexyl sebacate); DBES, dibutoxyethyl sebacate.

Trimellitates (esters of 1,2,4-benzenetricarboxylic acid). 8-10-TM-E, mixture of C7 and C9 trimellitates (plus trace bisphenol-A).

Others. Glutarates: 7050, dialkyl diether glutarate and citrates: for example, acetyl tributyl citrate and acetyl triethyl citrate.

Plasticizer usage varies over a broad range by the properties desired for the product from a low of 15 phr to a high of 500 phr. Generally, 60−100 phr is used.

5.4.1.2 Stabilizers [9]

PVC is well known to be thermally unstable as the neat polymer, and the development of useful vinyl products depended as much on the development of thermal stabilizers as it did on the discovery of plasticization.

Early on it was known that decomposition of PVC was accompanied by evolution of HCl, and that HCl also helped to catalyze further decomposition. Similarly early on it was found that simply compounding PVC with alkaline materials that absorb HCl did not yield satisfactory stabilization.

It may have been that additives packages used for rubber processing were adapted to PVC in the same way that processing equipment was. To that end, some early stabilizers consisted of litharge (lead oxide, used as a curing agent for rubber) and sodium silicate (to absorb HCl).

Over time it was found that defect structures in PVC arising from head-to-head polymerization were at the root of PVC instability. As a result, the stabilizers found to be most useful for PVC were those capable of preferentially binding to a defect site and doing chemistry to prevent the initial loss of HCl and thereby prevent further unzipping, and as a result more chemically engineered organometallics and some organics appeared in the marketplace.

Stabilizers are generally based on a metal that can chelate to a double bond-type defect on the chain and transfer a nucleophilic ligand to the chain to replace a labile chlorine. Materials that can scavenge HCl without inducing base-catalyzed dehydrohalogenation are also helpful.

Lead-based compounds were some of the earliest stabilizers used, but particularly for rigids they were generally supplanted in the US by tin-based stabilizers starting in the late 1950s to early 1960s. Today, use of lead is declining globally. Lead was used for this application originally because of the very low solubility of lead chloride and thus the outstanding dielectric qualities of the jacket.

Mixed metal stabilizers combine soaps of chelating metals, such as zinc, that catalyze the ligand-exchange reaction, with soaps of metals such as calcium that then react with the chelating metal, accepting chloride and replenishing the chelating metal ligands. Barium/cadmium/zinc mixes, formerly very common mixed metal stabilizers, have been replaced by barium/zinc so as to eliminate the use of cadmium.

Mixed metal stabilizers, such as those used in flexible compounds, have generally not been used for rigids, with the exception of calcium/zinc stabilizers for some food grade bottles and sheet. Recently, more robust calcium/zinc formulations have been developed for rigid extrusion, including for pipe.

The counterion for these metals is generally a fatty acid anion such as glycolate, octoate, or stearate. Stabilizers themselves may be compounded with other liquid ingredients to enhance material-handling properties.

These additives may have other beneficial properties for the PVC compound in that they may also provide lubrication or costabilization. Traditional external lubricants are used only in small amounts in flexibles and internal lubrication is not needed. Long-chain fatty acids, if part of a stabilizer package at <1 phr, also act as external lubricants. Oxidized PE wax at low levels can also be used effectively. The exact blends are usually trade secrets.

Tin stabilizers are predominantly used for rigid PVC. These consist of mixtures of mono- and di-alkyltin(IV) chemicals with other labile ligands. They have two major types of labile ligands: carboxylate and alkylthioglycolate. Stabilization action comes because the labile ligands can be substituted onto the PVC chain with transfer of a labile chloride to the tin complex. The first major tin stabilizer was dibutyltin isooctyl thioglycolate, but today octyl, butyl, and methyl tins are used.

Lead and tin stabilizers provide very broad processing windows for rigid material, allowing for longer or multiple processing steps, and a wider temperature range for processing. As a result, the polymer does not so readily discolor or degrade despite the high melt viscosity and shear heating that comes along with processing rigid PVC.

Stabilizer use patterns are different in different parts of the world. Europe used lead stabilizers for rigids such as pipe and window profile until the early part of this century. Many European processors are converting to modified calcium/zinc-based systems as well as tin. Stabilizer usage varies by product but is in the range of 0.5−5.0 phr.

Epoxidized oils such as soybean or linseed are used to help long-term stability and to act as a softening agent (secondary plasticizer). Other plasticizing extenders like chlorinated paraffin wax are used to improve fire resistance.

5.4.1.3 Lubricants [10]

Lubricants are included in PVC compounds—especially rigids—to control fusion and metal release. There are two extremes of lubrication: internal and external. External lubrication mainly facilitates metal release. Internal lubrication aids fusion and also has similar effect on polymer chains as plasticization; however, much less internal lubricant is added than plasticizer. Real-life lubricants have a spectrum of properties between these two poles.

The early choice for PVC extrusion lubricant mixtures included calcium stearate and paraffin wax, typically a wax with a melt temperature of about 165 °F. These two materials are differentiated in a broad sense on the basis of polarity. The nonpolar wax tends to act as a metal release and is not well adsorbed into the relatively more polar PVC resin. More polar calcium stearate adheres to and interacts with the polar resin.

Calcium stearate shortens the time for fusion because it has a very broad melting range and as it liquefies it causes particles of PVC to become “sticky” and thus induces interparticle friction and heat. Paraffin, on the other hand, melts at 165 °F and lubricates the particles reducing friction and delaying the onset of fusion. By controlling the ratio of these two lubricants, early compounders learned to adjust fusion characteristics of the material to meet processing and final product requirements.

Many production processes need a more sophisticated lubrication system due to complex dies and the need for longer runs. So to the basic wax/calcium stearate system many different types of long-chain esters can be added. Oxidized PEs of different molecular weight and different oxidation levels are also useful lubricants.

For clear products such as bottles and sheet, ester waxes must be used as lubricants, as the use of calcium stearate and paraffin would result in nontransparent product. Common ester lubricants are stearyl stearate, distearyl phthalate, glyceryl dioleate, glyceryl hydroxystearate plus other similar materials. Small amounts of oxidized PE wax can improve metal release without hurting clarity in some recipes.

5.4.1.4 Impact modifier

Some rigid PVC products such as bottles or siding require excellent impact efficiency, either due to design or due to specification. Usually these products require addition of impact modifier.

Impact modifiers are discreet submicron crosslinked elastomer particles engineered to anchor to the polymer matrix without being totally miscible. There are methacrylate/butadiene/styrene (MBS) modifiers, all-acrylic modifiers, and chlorinated polyethylene (CPE). MBS is efficient in providing ductility and can be synthesized to match the refractive index of PVC, thus producing a clear compound for bottles or sheet; because it contains styrene, MBS is not useful for applications exposed to weathering. All-acrylic modifiers are very weatherable but due to differences in refractive index are useful only for opaque applications. CPE is very cost-effective and over time has improved in its ability to provide ductility and ease of processing. Usage of impact modifier varies from 2.0 parts to 14 parts, depending on application.

5.4.1.5 Processing aids

Processing aid is another key additive used in rigid compounds, although minor amounts are used in some flexibles. Processing aid acts as a fusion promoter that also increases melt elasticity.

Controlling melt elasticity is important for many types of PVC processing such as profile extrusion and calendering. High melt elasticity is a major requirement in rigid foam products which are used as substitutes for thick wood board such as brick molding and trim molding. While generally acrylic, the chemical identity and molecular weight of the processing aid govern its exact properties and the mix of fusion assistance and internal or external lubrication. Processing aids also usually improve the appearance of the finished product.

Pigments and fillers are needed for opaque products. Normally, calcium carbonate, titanium dioxide, clay (wire and cable), and inorganic pigments are preferred so as to not affect the stability of the PVC. Siding and window profiles generally have about 10 phr of titanium dioxide to provide the necessary weathering characteristics. Calcium carbonate is a common filler because it is plentiful and is available in many different sizes with and without coatings. Coatings on filler and pigment particles are important because they improve dispersion and reduce metal wear in the extruders.

Some pigments are formulated with special chemistry for certain applications; for example, there are weather-resistant (inorganic) and non-weather-resistant (organic) grades. Infrared-reflecting pigments were developed by the military and adapted to the building products industry to allow for dark exterior colors with reduced heat buildup. Pigments must be chosen so as to be chemically compatible with the polymer matrix under processing and use. This is particularly sensitive for PVC as metals such as free iron cause the polymer to degrade and accelerate weathering.

Sample formulations for a number of applications are found in Table 5.1.

5.4.2 Compounding Large Particle Size (Suspension or Mass) PVC [3,10]

As mentioned above, the versatility of PVC is rooted in its ability to be compounded with a wide spectrum of additives to produce plastic materials having a very diverse performance range. In order to achieve this goal the additives must be properly blended with the PVC in a process that is tailored to the type of formulation and components that are to be used.

Flexible PVC is used to produce wire and cable jacketing, wall coverings, blood/IV bags, shower curtains, car door panels, bags and purses, landfill liners, energy-efficient roof membrane, outer rain wear, tarps and awnings, furniture laminates, and many more items. All these articles have two components in common: plasticizer and stabilizer. Other additives may be included as indicated above. Resin tends to be toward the high end of the molecular weight range.

Rigid PVC compounds are more difficult to develop than flexible compounds. Rigid recipes contain no plasticizer; when processed they have higher melt viscosity and thus shear heating and back pressure in the process can be very high. This places high demand on stabilizer performance. The resin used for rigid applications tends to the lower range of PVC molecular weight. High molecular weight PVC is very difficult to mix, heat, and melt without overheating, causing discolored and potentially degraded resin.

5.4.2.1 Mixing

Mixing can be accomplished in several ways but by far the most common (most pounds mixed) method utilizes a high intensity mixer. These mixers consist of a large bowl with blades rotating up to 2000 rpm, which are capable of mixing 200−2500 pounds of material. Blade shapes differ. In some cases they are straight and locked in an "X" configuration in the bowl. In other cases they are curved blades as in a turbine, to force the power in specific directions.

The blades have two effects. First is physical mixing of the dry blend. Second, energy expended in the process heats the material by friction. Dry blending is a dynamic process where ingredients are generally added sequentially and at different temperatures. Resin is added, then stabilizer, to protect the polymer from thermal degradation. In flexible compounds, plasticizer is added when the compound reaches about 150 °F, at which point the polymer particles start to swell and allow liquids access to the inner space of the particle. In rigid compounds, lubricants, modifiers, and process aids are added next with fillers and pigments added last. When the batch reaches its final temperature—between 200 and 215 °F—the material is dropped to a cooling mixer.

Instead of mixing individual additives, in some cases a compounder will use a masterbatch, which is a very concentrated mixture of additives predispersed on resin. Use of masterbatch—whether made internally by the compounder or purchased as a "one-pack"—limits the exposure of workers to potentially hazardous components, such as lead stabilizers, and can predisperse components that might be used at very low levels.

Ribbon blenders are still sometimes used to process flexible compounds. In these low-intensity mixers, heat applied through a jacket raises the resin temperature to about 150 °F for optimum plasticizer absorption. Stabilizers and other additives are also added at the beginning or during the cycle. Mixing times are about 1 hour depending on the mixer size and amount of plasticizer and other additives. After mixing, the blender is used to cool the compound prior to transport.

In all cases these compounds are produced as dry blends of free flowing powder, even though liquid additives may have been added to the formulation. The powders are packaged into drums, cartons, and even rail cars. Most importantly, cleaning between batches is minimal, and water is not used since the presence of moisture in subsequent processing gives rise to many problems.

5.4.2.2 Pelletizating

The original thermoplastic compounds were produced in the same way rubber compounds were produced. Base polymer was added to a Banbury mixer, and then the additives metered in according to some predetermined sequence. In this case, compound is heated, mixed, and melted, then dropped as a melt onto a large mill, and subsequently sheeted off.

To make the original pellet PVC compounds the same process was used except that the melted compound was removed continuously from the mill as a strip about 6 inches wide, cooled in water, then fed into a stair-step dicer to produce cube compound. These cubes were then processed into wire jacket and pipe/profile by end-products manufacturers.

Today, while most processes use dry blend to save the cost and heat history of a pelletization step, some applications still require melt preprocessing. Generally, those markets include flexible compound that will be shipped (flexible dryblend can clump), compound for rigid bottles or sheet, or any material that requires thorough fluxing, such as injection molding.

For market segments requiring pellets, there are now newer processing technologies based on extruders: twin screw (counter rotating, corotating, as well as short barrel continuous compounders), single screw, and planetary (6−8 small screws around a large central screw with open discharge).

Pellets are still produced with stair-step dicers (producing cubes). In addition they can be made by extrusion through a die that produces multiple strands of about 1/8 inch which are then cooled in water and chopped into small cylinders. There are also die-face-cut pellets where the melt is again extruded through a multiple-orifice die but a rotating blade against the die face slices pill-shaped pellets as the melt emerges from the die. These then can be air or water-cooled; however, in the latter, thorough drying of the pellets becomes critical to the success of the operation.

5.4.2.3 Processing

Extrusion. On the basis of volume, by far the majority of PVC is extruded. Rigid applications include pressure and drain/waste/vent pipe, siding, window profile, fence deck, and rail. Packaging applications include bottles (by extrusion blow molding) and rigid sheet. Flexible applications include medical tubing, hose, wire insulation (by extrusion coating), and cove base.

There are two main considerations particular to PVC extrusion. First, in most cases, the feedstock will be dryblend, and there is a need to remove air and volatile components as the material fuses. To accomplish this, a vented barrel was developed in the early 1960s. The screw had two compression areas, one before the vent to start the fusion and the other after the vent to finish the melting and push the melt through the die. Both single- and twin-screw extruders today for PVC dry blend have a vent connected to a vacuum for gas removal.

Second, as discussed elsewhere, resin molecular weight, lubrication, stabilization, and processing conditions need to be carefully balanced to manage shear heating, to allow the blend to fuse completely and at the right time and position in the extruder. Pipe, siding, and window profile extrusion use medium molecular weight resin. Extrusion blow molding of PVC bottles requires low molecular weight resin.

Thin PVC for packaging is produced by extrusion, casting, or blown film processes. *Calendering* operations produce thicker PVC film and sheet, most commonly flexible PVC although some rigid calendered sheet is also used for thermoformed packaging applications. Calenders are supplied with well-melted and uniform starting material. Banbury mixers, mill(s), short single-screw extruders (with a screen pack to remove foreign metal particles) or other combinations can be used to supply this well-fluxed feed.

A calender normally consists of four large rolls of 3−4 feet in diameter. They are heated and stacked together. An inverted “L” type is most common (Figure 5.7).

The rolls are typically 4−10 feet wide. The gap between rolls becomes progressively smaller as melt moves from 1−2, 2−3, and 3−4 rolls, and the final thickness is controlled by the last gap. The forces generated are immense; rolls are crowned in the middle to compensate for the pressure and some systems employ roll bending to control the forces. Rolls turn at a differential rate to produce shear; film exits the calender at 80−180 feet/minute, and pounds per hour varies with the thickness and width. Calendered film thickness ranges from about 0.003 to 0.080 in.

Rigid compound can be calendered as well; however, as with other processing techniques the higher melt viscosity risks discoloration or burning at high shear. Where flexible calendering recipes are barium−zinc stabilized, most rigids need the extra performance of a tin stabilizer.

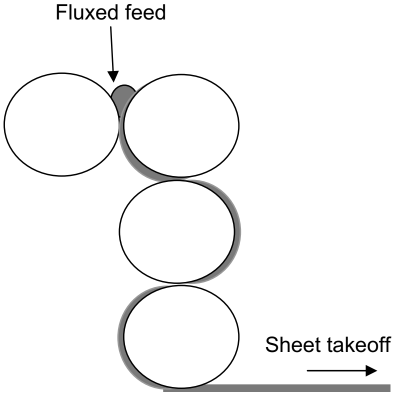

Figure 5.7 Inverted “L” four roll calender.

Injection molding (pipe fittings) can be used to process PVC, but there are some limitations—mostly similar to those already described. Some powder blend is processed this way but most processors use pellets for these applications. The process involves high shear rates and a viscous melt; thus gates and runners must be sized to minimize shear burning. Low molecular weight resins are used in these processes, and stabilization is critical.

5.4.3 Compounding and Processing Small-Particle PVC (Dispersion Resin)

Dispersion resin is mixed with plasticizer and other additives to form a paste, and that is the form in which it is molded or processed. Paste can be relatively thick (like caulk) or thin (like pancake batter) depending upon how the material is to be processed.

5.4.3.1 Formulation and Handling

All the plasticizers covered in Section 5.5.4 can be used with dispersion resins but the phthalates are the most common. A sample plastisol formulation might include 100 parts of resin, 60 phr plasticizer plus 2−3 phr barium/zinc stabilizer.

While this simple formulation makes a liquid system, that system has viscosity properties, which affect the way it is processed, and thus are key to its use. The important performance measure is paste rheology.

Paste rheology is the viscosity response of the paste to the application of shear to the liquid. Consider house paint. It stays on the brush without dripping when removed from the can (low shear) yet flows like water when brushed on a wall (high shear). Material that “thins” with shear is pseudoplastic.

A paste that exhibits opposite behavior—shear thickening—is called dilatant. Consider Silly Putty®. Under low shear the material rolls and flows easily but if pulled quickly, breaks. Liquids that show no change in viscosity with shear rate, such as water, are called Newtonian (see Figure 5.8).

A plastisol can exhibit both pseudoplastic and dilatant behavior—a U-shaped curve on Figure 5.8—at different shear rates. Paste rheology is affected by the PVC particle size, the surfactant used in polymerization, the agglomeration in drying, the grinding, the plasticizer(s) used, the stabilizers, and any other additives used in the mixture. It can be very complex.

Plastisols are produced using high-intensity liquid mixers similar to that used for making dry blends or Hobart or dough mixers for smaller batches. A high-speed (high-shear) mixer has a blade (turbine, paddle, or other), which is used to

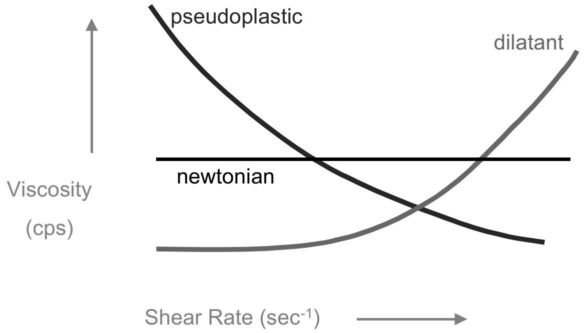

Figure 5.8

disperse all the ingredients into smooth paste. Hobart or dough mixers generate shear at the blade—bowl interface to facilitate dispersion. The speed of the mixer is lower so a longer mix time is required.

5.4.3.2 Additives

Other than plasticizer and stabilizers the other additives are similar to those used in other flexible applications. Fillers and pigments such as titanium dioxide and calcium carbonate are commonly used but because of the large surface area of these solids, will dramatically increase the paste viscosity. Low molecular weight plasticizers, oils, and solvents are used in special circumstances as diluents to reduce and control viscosity.

PVC blending resin (called that because it is blended with dispersion resins) can also be used to reduce viscosity. Blending resin particles are about 30 microns in diameter and are nonporous suspension resin particles. Because of its larger size (and thus lower surface-to-volume ratio) use of blending resin reduces paste viscosity. The large particle size of blending resin prevents its use in thin applications.

Lubricants such as those used in flexible and rigid recipes can be used to provide metal release. Levels are generally considerably lower, however.

5.4.3.3 Test methods [2,11]

Brookfield viscometer. Measures low shear viscosity related to the flow out or leveling.

Severs viscometer. Measures high shear viscosity related to application at high line speeds.

Gelation and fusion. Temperatures are measured with a temperature gradient panel. The gelation temperature is the point at which the film has integrity so that other layers could be put on top or it could be handled.

Air release. This is important because as the material is mixed, air is inadvertently whipped in to the system which, if retained during fusion, could cause voids in the final product. Two tests are common: A syringe is used to inject a defined volume of air into the plastisol contained in a paper cup. The time for the air to rise to the surface and break is the measure of air release; alternatively a cup of plastisol is put into a vacuum chamber and as vacuum is applied the rising foam or “head” is measured.

Gloss and Clarity is measured with a fused sample measuring light transmission and 60° gloss. This is very important to flooring products (rolled goods) where the surface needs to simulate a high polish.

5.4.3.4 Processing

Processing for dispersion systems (plastisols) involves putting the liquid in the right place, having it stay there, heating so as to swell the polymer particles and create a gel, and then heating to full fusion. When fully fused, despite the lack of mechanical shear there is intimate polymer chain and plasticizer interaction and full mechanical strength has been reached.

Fusion characteristics are especially important for fabrication of chemically blown foams. Blowing agent decomposition temperature and kinetics must be carefully matched to paste fusion so as to produce ideally dispersed foam pores.

Spread Coating (fabric, wall covering, and flooring). In this process plastisol is coated on a flexible substrate and passed through an oven to obtain fusion. The coating can be done with a knife (called a doctor bar) or various roll applications. Fabric coating, probably the earliest use of plastisol, is used to produce artificial leather for furniture, car seats, and travel luggage. In fabric coating the plastisol viscosity must not be so low that it wets too much of the fabric, yet low enough to be applied by the knife. Spread coating works best with a medium viscosity system showing some pseudoplasticity at low shear.

Wall coverings are made by applying a thin coating of plastisol on thin cloth or paper at high speeds. The coatings contain fillers and pigments to give the covering color and opacity. These plastisols must be of low viscosity and some pseudoplasticity at low shear is desirable. Blending resin cannot be used in these very thin applications.

Dipping. A metal form of the desired object is dipped into a plastisol so that a liquid coating remains on the outside of the form. It is then fused in an oven. Surgical gloves, fabric gloves, and tool handles are good examples of this process. For cloth, a high viscosity system minimizes fabric penetration. For thin coatings on metal, a medium viscosity is preferred.

Slush molding. Plastisol is poured into a preheated mold (one part of the mold has to be open). The mold is either filled to the top and excess is removed or a lesser amount can be added and the mold moved to cover all the desired surfaces and excess is removed. Thicker films or multilayer films may be produced by repeating the process—mold, fuse, and mold again—with the same plastisol or a different one (such as a foaming system). Once the film(s) have been fused and cooled the part is removed from the mold. Only low-shear rates are involved in this process but low temperature gelation is desirable. Blending resins can be used to reduce the viscosity in slush molding relatively thick parts.

Rotational molding. The precise amount of plastisol needed for the part is put into the mold and the mold is closed. There are no openings in the mold, which is attached to a device capable of rotating in all dimensions to create a uniform internal coating. The arm and mold are put in an oven for fusion. Once the material is fused and cooled the mold is opened and the part removed. Balls and doll heads—and other nearly round parts—are most often rotomolded. Part properties are the same as that for slush molding.

5.5 Recycling PVC [12]

Because PVC is a thermoplastic, it can be recycled using technology that is comparable to that of the other regularly recycled commodity materials. By far, more postindustrial PVC is recycled than postconsumer due to the durability of PVC applications. Depending on the application, recycled PVC can be used as a raw material in the same application, as a layer in a coextruded part, or as a raw material for an entirely different application. Thermoform scrap can be reused in new sheet; wire scrap becomes garden hose; window lineal cut-offs become pipe; siding scrap becomes the base layer laminated with an appearance film. Pipe goes back into more pipe.

5.5.1 Bottles

In the U.S., because of curbside collection programs, postconsumer plastic bottles are recycled at a rate of approximately 25%; however, 95% of those bottles are either polyethylene terephthalate (PET) (resin code 1) or high-density polyethylene (HDPE) (resin code 2). While there is no technological barrier to recycling the remaining materials (and commercial recycling programs for those bottles, by material, have operated at times) the low relative volume of bottles with resin code 3 through 7 has made explicit collection and recycling problematic. In recent years these bottles, along with many of the HDPE and PET bottles, have been exported where they are sorted and reprocessed.

Separation of PVC is relatively easy using automated sorting equipment, especially that based on either infrared or X-ray spectroscopy. Reprocessing of PVC bottle material is similar to reprocessing of other material to the extent it must be chopped, washed, and dried to recover pure flake. Recycled bottle material is generally not used at a loading of 100%; rather, it is blended with virgin PVC material, which in many cases carries an augmented stabilizer and lubricant package.

5.5.2 Other Packaging

Like most other plastics, PVC extruded or calendered sheet used in making blisters and clamshells is generally not collected in postconsumer streams. On the other hand there is a robust market for in-process sheet scrap derived from package off-cuts. This material is chopped and sold into various applications including packaging sheet and sea wall and wall and rigid profile substrates.

Postindustrial flexible PVC packaging, such as material used in medical solution bags, is recovered and used for blending with other recovered flexible PVC. The products made with this material are generally not packaging products.

5.5.3 Rigid Profiles

The overwhelming majority of PVC resin—over 99 %—sold for the fabrication of pipe, siding, conduit, and windows eventually becomes salable product. There is very little in-process waste in the pipe and conduit industry; if in-process materials are unsuitable for pressure pipe, it can be used in a product ranging from first-grade Drain Waste and Vent to slotted underground drainage pipe.

In-process recovered material from siding operations can either be used in-house as a dimensional stability layer in multilayer siding formulations or sold into pipe or mobile home skirting applications. Off-cuts of window lineals during the window fabrication process are easily collected, chopped, and used in other extrusion operations. There is virtually no waste in any of these processes except for material too burned or contaminated for good extrusion.

Programs for recycling of virgin materials (such as pipe and siding installation off-cuts) at the construction site exist but are challenged by the need to recover materials explicitly, keep them free of contamination, and transport them to a site for chopping and refabrication into one of the aforementioned applications. Since only a few hundred pounds of material of this kind might be recovered from a house under construction, the most successful programs are those involving a high density of stick-built new construction or alternatively, manufactured housing.

Because most rigid profile extrusion products have a long in-service lifetime, most of those products ever produced are still in service. When pipe, siding, and windows are removed from service, however, they are recyclable but in addition to low volume face many of the same barriers that other postconsumer plastics face.

Buried pipe is occasionally removed from service, although more commonly, it is left in place and new pipe is installed. If recovered, belling gaskets, dirt, and contamination must be removed from this material by some means up to and including washing. Chopped material can be reformulated, blended with virgin, or used in multilayer applications, including siding or fence, deck, and rail.

Siding removed from houses that have been demolished or are under renovation has similar problems; most important is the need to first remove metal such as nails and flashing, then segregating other plastics or demolition material. If lengths of siding can be obtained in this way they can be chopped, cleaned, and reused in a similar fashion to what has been described for pipe. In some cases, siding that has been carefully removed can be reused directly.

Relatively new windows in which the gaskets and operating mechanisms are in good shape can be carefully removed and reused; however, because windows are a multimaterial-fabricated product recycling of those materials requires more separation steps.

If windows are carefully disassembled, glass, metal joiners, coextruded flexible gaskets, and other non-PVC materials can be separated from recoverable PVC. Some window recycling operations crush the entire window, separating non-PVC materials by mechanical means before recovering PVC. Either material must be appropriately cleaned and chopped before refabrication into a less critical end product.

5.5.4 Flexible Materials

In-process wire and cable insulation is recovered and can be used in other multilayer-extruded applications; garden hose is a common example. This is feasible because in-process wire is generally stripped of insulation rather than chopped. On the other hand, postconsumer wire is generally sent to rendering operations where it is chopped and the metal is harvested for remanufacture. After most of the metal is removed, the remaining chopped insulation is a mix of rubber, PVC, nylon, paper, fiber, and small amounts of metal. This material is problematic for reuse.

Recovered in-process flexible sheeting materials such as off-cuts may be recycled within the same process or chopped and sold. Flexible sheet that has been laminated to other materials—for example, roofing and billboards—requires different processing. These kinds of materials have been recycled into carpet back and flooring.

In Europe, which converted from lead stabilizers in rigid extrusions much later than the U.S., calcium/zinc (Ca/Zn) stabilizers are becoming very popular. This is because Ca/Zn stabilizers are compatible with lead stabilizers and regrind or recycle containing each can be combined. On the other hand, if tin-stabilized and lead-stabilized PVC are mixed together, the product becomes discolored due to the reaction of sulfur-based tin ligands with lead ions causing a black, lead-sulfide-like staining.

5.6 Vinyl: Sustainability and Energy Efficiency [13]

Today environmental and economic pressures are causing society to consider the sustainability of products, and the materials that are used to make them. Sustainability attributes of vinyl, both as a material and in its varied applications, is best addressed through life cycle analysis (LCA) of the overall impact of vinyl on the environment.

LCA consistently shows that pound-for-pound, PVC has one of the lowest manufacturing impacts—especially embodied energy—of any commonly used polymer. More important, however, for many products—especially those with long lives—is the use phase of its product life cycle. PVC pipe has a life-expectancy of at least 100 years with a very low field breakage rate. Because it does not corrode and resists biofilm formation, it provides safe drinking water reliably over time to millions of people around the world. High-performance vinyl roofing systems are Energy Star rated, not only reducing energy usage for each building but lowering the heat island effect of neighborhoods to entire cities. Energy Star-rated vinyl windows reduce energy usage in buildings over their estimated 50-year life span.

The combination of strength, low maintenance, long service life, and low extrusion cost gives vinyl a strong sustainability case.

5.7 Vinyl Chloride and Health

The first ACGIH standard for worker exposure to vinyl chloride, set in the 1950s, was 500 parts per million (ppm) in air. Vinyl chloride was first found to cause reversible changes in rodent livers in the early 1960s. Authors of the study recommended reduction of exposure levels to 50 ppm, where they saw no lesions.

In the mid-1960s, some workers, whose primary job responsibility involved cleaning scale from the inside of PVC and PVC copolymer reactors, developed a condition of bone-mass loss from fingertips, known as acroosteolysis. Bone-mass loss reversed when the workers were removed from conditions involving hand labor and exposure to monomer(s).

In the late 1960s and early 1970s, two developments dramatically altered our understanding of the health effects of VCM. While exploring an animal model for acroosteolysis at VCM exposure near the explosive limit, researchers unexpectedly discovered cancerous tissues in their experimental animals. This result was further investigated with a series of animal studies designed to test exposure at multiple concentrations of VCM. In the spring of 1973 the researchers reported at a conference in Italy that exposure of animals to VCM resulted in the occurrence of a rare form of liver cancer called angiosarcoma.

Also during 1973, three doctors treating separate workers at one PVC plant found each with angiosarcoma of the liver

(ASL). The incidence rate of ASL in the general population is quite low, about 1 death per 100,000 annually and is associated with only a small number of assignable causes. Therefore, the probability was extremely small that three workers at the same plant contracted this rare cancer only by happenstance. The connection of ASL to exposure to VCM in the workplace was confirmed after examination of death certificates of other plant workers. In January of 1974, the apparent human carcinogenicity of VCM was reported in the medical literature.

In response, the Occupational Safety and Health Administration (OSHA) and Environmental Protection Agency (EPA) quickly enacted regulations. The worker exposure standard for VCM was immediately lowered to 10 ppm, and eventually to 1 ppm, where it remains today. Emissions of vinyl chloride in air and water plant streams were reduced and regulated as well.

By 1977, new technology was developed and implemented across the industry to reduce residual VCM in PVC resin and to recover and recycle VCM from reactions, air, and water. Typically, this involves the use of steam to remove monomer either batchwise or in continuous counter-current columns. VCM thus stripped goes to a recovery area where moisture is knocked out of the vapor steam, and crude VCM is distilled. VCM recovered in this way is charged to new polymerization at a rate so as to balance its generation and use in the process.

Another invention of the late 1960s and early 1970s found acceptance as the need to reengineer PVC polymerization technology became critical. Clean-reactor technology, a combination of reactor design and wall treatment which inhibited scale formation on reactor walls, domes, and reflux condensers, was developed and implemented by a number of companies. It eliminated the need for human entry for reactor cleaning.

Eventually, about 150 workers out of over 20,000 in the U.S. and Europe died of ASL. While a tragedy, the absence of new cases in any worker hired after 1971 in countries that adopted low-exposure rules suggests that compliance with the worker exposure limits adopted in the mid-1970s has protected human health.

While small amounts of VCM are emitted from the process (mostly from driers), it is important to note that it is not persistent (decomposes in air and sunlight with half-life of hours) nor bioaccumulative.

5.8 Dioxin

Polychlorinated dibenzodioxins and furans (PCDD/Fs) are persistent, bioaccumulative toxic by-products of incomplete combustion—whether manmade or natural—and certain chemical processes. 2,3,7,8-tetrachlorodibenzodioxin (TCDD) is the most toxic of the family of 210 compounds.

Seventeen of these PCDD/F compounds having chlorines in the 2,3,7, and 8 positions are designated for special concern because their shape makes them particularly bioactive. These seventeen so-called "toxic congeners" vary in potency by a factor of 10,000; typically, the most chlorinated are the least toxic.

PCDD/F can be formed whenever carbon, hydrogen, oxygen, and chlorine are present at elevated temperatures. Certain metals, most prominently copper, promote the formation reaction. In combustion devices, PCDD/Fs usually form when postcombustion gases containing the needed elements are kept between 250 and 400 °C, particularly in the presence of fly ash particles containing traces of metal on an active surface.

PCDD/Fs have been associated with PVC due to their presence in oxychlorination heavy ends, and because PVC could provide a source of chloride for their production in combustion processes. It is certainly true that forcing PVC to burn (which it does not do readily) will generate some PCDD/F. Removal of PVC does not impact PCDD/F generation in burning of normal waste, especially in modern incinerators.

While this has been shown experimentally, recognizing that incinerators take in about 0.5−1 % chloride by weight (about half of which is derived from PVC) they emit only nanograms of dioxins per cubic meter of exhaust air. Other sources of chloride besides PVC, including inorganic chlorides such as salt are stoichiometrically sufficient by orders of magnitude to account for the amounts of PCDD/F generated.

Most importantly, dioxin emissions to the environment and dioxin found in environmental samples ranging from lake sediments to human tissues have declined by well over 90% in the past 30 years, even as PVC production has tripled. Dioxin emission to the environment is a problem well on its way to solution.

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6 Thermoplastic Elastomers

Geoffrey Holden
Holden Polymer Consulting, Incorporated, PMB 473, 1042 Willow Creek Road, A101 Prescott, AZ
86305-1670, USA

6.1 Introduction

Thermoplastic elastomers have become a significant part of the elastomers industry since they were first produced about 55 years ago. Several books [1−3] and articles [4−6] have covered this subject in detail. Two of the books [1,3] concentrate mostly on the scientific aspects of these polymers, while the other [2] concentrates on their end uses.

The properties of thermoplastic elastomers in relation to other polymers are summarized in Table 6.1. This table classifies all polymers by two characteristics—how they are processed (as thermosets or as thermoplastics) and the physical properties (rigid, flexible, or rubbery) of the final product. All commercial polymers used for molding, extrusion, etc., fit into one of the six resulting classifications—the thermoplastic elastomers are the newest. Their outstanding advantage can be summarized in a single phrase—they allow rubber-like articles to be produced using the rapid processing techniques developed by the thermoplastics industry. They have many physical properties of rubbers, e.g., softness, flexibility, and resilience. However, they achieve their properties by a physical process (solidification) compared to the chemical process (crosslinking) in vulcanized rubbers.

Table 6.1 Comparison of thermoplastic elastomers with conventional plastics and rubbers

	Thermosetting	**Thermoplastic**
Rigid	Epoxies Phenol-formaldehyde Urea-formaldehyde	Polystyrene Polypropylene Poly(vinyl chloride) High-density polyethylene
Flexible	Highly filled and/or highly vulcanized rubbers	Low-density polyethylene EVA Plasticized PVC
Rubbery	Vulcanized rubbers (NR, SBR, IR, etc.)	Thermoplastic Elastomers

In the terminology of the plastics industry, vulcanization is a thermosetting process. Like other thermosetting processes, it is slow, irreversible, and takes place upon heating (see Chapter 7). With thermoplastic elastomers, on the other hand, the transition from a processable melt to a solid, rubber-like object is rapid, reversible, and takes place upon cooling (Figure 6.1).

Thus thermoplastic elastomers can be processed using conventional plastics techniques, such as injection molding and extrusion; scrap can be recycled. Additionally, some thermoplastic elastomers are soluble in common solvents and so can be processed as solutions.

At higher temperatures, the properties of thermoplastic elastomers are usually not as good as those of the conventional vulcanized rubbers. Applications of thermoplastic elastomers are, therefore, in areas where these properties are less important, e.g., footwear, wire insulation, adhesives, polymer blending, but not in areas such as automobile tires.

6.2 Classification and Structure

Thermoplastic elastomers can be divided into six basic types:

- Styrenic thermoplastic elastomers
- Multiblock copolymers
- Hard polymer−elastomer combinations
- Graft copolymers

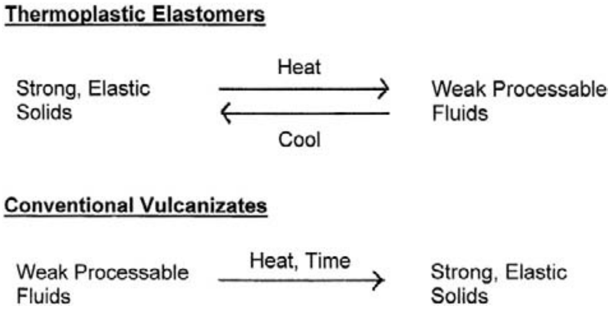


Figure 6.1 Polymer transitions.

- Ionomers
- Core-shell morphologies

Only the first three are commercially important.

Almost all thermoplastic elastomers contain two or more distinct polymeric phases and their properties depend on these phases being finely and intimately mixed. In some cases, the phases are not chemically bonded, but in others they are linked together by block [2] or graft copolymerization.

At least one elastomeric phase and one hard phase must be present, and the hard phase (or phases) must become soft and fluid at higher temperatures so that the material as a whole can flow as a thermoplastic.

6.2.1 Styrenic Thermoplastic Elastomers

These are based on simple molecules such as an A-B-A block copolymer, where A is a polystyrene and B an elastomer segment [1a,3,7,8]. If the elastomer is the main constituent, the polymers should have a morphology similar to that shown in Figure 6.2. Here, the polystyrene end segments form separate spherical regions, i.e., domains, dispersed in a continuous elastomer phase. Most of the polymer molecules have their polystyrene end segments in different domains. At room temperature, these polystyrene domains are hard and act as physical crosslinks, tying the elastomeric mid-segments together in a three-dimensional network. In some ways, this is similar to the network formed by vulcanizing conventional rubbers using sulfur crosslinks. The difference is that in thermoplastic elastomers, the domains lose their strength when the material is heated or dissolved in solvents. This allows the polymer or its solution to flow.

When the material is cooled down or the solvent is evaporated, the domains harden and the network regains its original integrity.

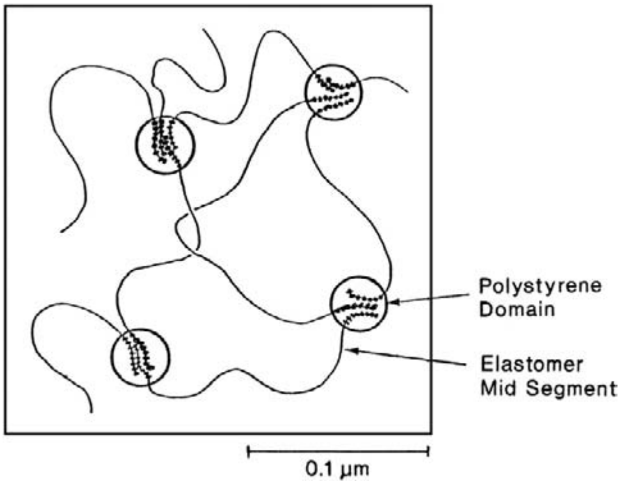


Figure 6.2 Morphology of styrenic block copolymers.

Analogous block copolymers with only one hard segment (e.g., A-B or B-A-B) have quite different properties. The elastomer phase cannot form a continuous interlinked network, since only one end of each elastomer segment is attached to the hard domains. These polymers are not thermoplastic elastomers, but are weaker materials similar to *unvulcanized* synthetic rubbers [8].

In commercial applications, three elastomeric mid-segments have been used for many years—polybutadiene, polyisoprene, and poly(ethylene-butylene). The corresponding block copolymers are referred to as S-B-S, S-I-S and S-EB-S. Later, polymers with poly(ethylene-propylene) mid-segments (S-EP-S) were introduced. A more recent development, now commercialized, is styrenic block copolymers with an isobutylene mid-segment (S-iB-S) [9,10]. These can also be produced with substituted polystyrene end segments.

6.2.2 Multiblock Copolymers

The multiblock copolymers have structures that can be written as A-B-A-B-A-B-A-B-... or (A-B)*n*. For most of those of commercial importance, the hard (A) segments are crystalline thermoplastics while the softer, elastomeric (B) segments are amorphous. In best known types, the hard segments are thermoplastic polyurethanes [10], thermoplastic polyesters [11], or thermoplastic polyamides [12] and the soft segments are either polyesters or polyethers. Similar materials have been recently introduced in which the hard segments are polyethylene [13,14] or polypropylene [13−16] and the soft segments are copolymers of ethylene and α-olefins such as propylene, 1-butene, 1-hexene, and 1-octene. The morphology of these (A-B)*n* multiblock copolymers is shown diagrammatically in Figure 6.3. Another type of (A-B)*n* multiblock copolymer has hard segments of polyetherimides (these are amorphous) and polysiloxane soft segments [17].

The structure shown in Figure 6.3 has some similarities to that of a poly(styrene-b-elastomer-b-styrene) equivalents (Figure 6.2) and also some important differences. First, the

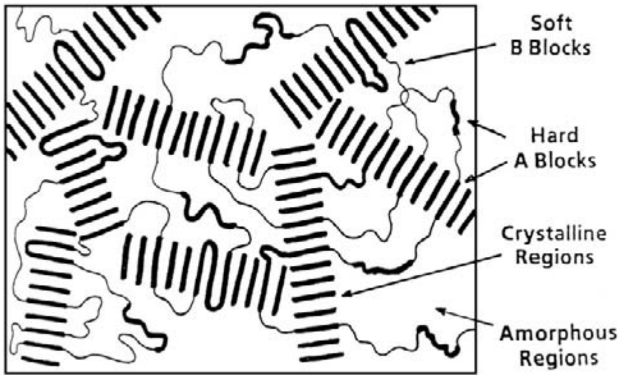


Figure 6.3 Morphology of multiblock polymers with crystalline hard segments.

hard domains are much more interconnected. Second, in most cases, they are crystalline. Third, each long (A-B)n molecule may run through several hard and soft regions. A list of thermoplastic elastomers based on block copolymers of all types is given in Table 6.2.

6.2.3 Hard Polymer–Elastomer Combinations

Other thermoplastic elastomers are not block copolymers, but instead are fine dispersions of a hard thermoplastic polymer and an elastomer. Some of these are simple blends, while others are produced by dynamic vulcanization (see later). A list of the various polymers used to produce thermoplastic elastomers based on hard polymer—elastomer combinations of all types is given in Table 6.3.

The two materials usually form interdispersed co-continuous phases with a final morphology similar to that shown in Figure 6.4.

Polypropylene is often chosen as the hard thermoplastic because it is readily available, low priced, and solvent resistant, and has a high crystal melting point (165 °C). Combinations with ethylene—propylene—diene monomer (EPDM) or ethylene—propylene copolymer (EPR) are the most important commercial products based on polypropylene [13—15,28]; other elastomers that can be used include nitrile [28], butyl [29], and natural [30] rubbers. Softer, more impact resistant materials can be produced by using propylene copolymers as the hard phase [13,14]. Halogen-containing polyolefins [33] are another option. Two examples are blends of PVC with nitrile rubber [31—33] and blends of halogenated polyolefins with ethylene interpolymers [33]. Mixtures of the last two polymers are claimed to give a single phase system.

In these blends, dispersion of the two phases is most often achieved by intensive mechanical mixing, but in the polypropylene—EPR combinations, polymerizing the finely dispensed elastomer phase simultaneously with the hard polypropylene is possible [13—15].

Table 6.2 Thermoplastic elastomers based on block copolymers

Hard Segment A	Soft or elastomeric segment B	Structure[a]	References
Polystyrene	Polybutadiene and polyisoprene	T, B	1—8
Polystyrene	Poly(ethylene-*co*-butylene) and Poly(ethylene-*co*-propylene)	T	1—7
Polystyrene and substituted polystyrenes	Polyisobutylene	T, B	9
Poly(α-methylstyrene)	Polybutadiene, polyisoprene	T	7
Polyurethane	Polyester and polyether	M	10
Polyester	Polyether	M	11
Polyamide	Polyester and polyether	M	12
Polyethylene	Poly(α-olefins)	M	13—15
Polyethylene	Poly(ethylene-*co*-butylene) and Poly(ethylene-*co*-propylene)	T	13, 14
Polypropylene(isotactic)	Poly(α-olefins)	M*	13,
Polypropylene(isotactic)	Polypropylene(atactic)	M*	13, 14
Polypropylene(isotactic)	Poly(ethylene-*co*-propylene)	B	13, 16
Polyetherimide	Polydimethylsiloxane	M	17
Polystyrene	Polydimethylsiloxane	T, M	18
Poly(α-methylstyrene)	Polydimethylsiloxane	T	7, 18
Polysulfone	Polydimethylsiloxane	M	19
Poly(silphenylene siloxane)	Polydimethylsiloxane	M	20
Polycarbonate	Polydimethylsiloxane	M	22—24
Polycarbonate	Polyether	M	25,26
Polymethyl methacrylate	Poly(alkyl acrylates)	T, B	27

[a] *T, Triblock, A-B-A; B, branched, (A-B)$_n$x; M, multiblock, A-B-A-B-A-…; M*, mixed structures, including multiblock.*

Table 6.3 Thermoplastic elastomers based on hard polymer–elastomer combinations

Hard polymer	Soft or elastomeric polymer	Structure[a]	References
Polypropylene	EPR or EPDM	B	13–15
Polypropylene	EPDM	DV	14, 28
Polypropylene	Poly(propylene/1-hexene)	B	14
Polypropylene	Poly(ethylene/vinyl acetate)	B	14
Polypropylene	Butyl rubber	DV	28, 29
Polypropylene	Natural rubber	DV	28, 30
Nylon nitrile	Rubber	DV	28
Polypropylene	Nitrile rubber	DV	28
PVC	Nitrile Rubber + DOP[b]	B, DV	31–33
Halogenated polyolefin	Ethylene interpolymer	B	14
Polyester	EPDM	B, DV	14
Polystyrene	S-B-S + Oil	B	34
Polypropylene	S-EB-S +Oil	B	34

[a] *B, Simple blend; DV, dynamic vulcanizate.*
[b] *DOP, Dioctyl phthalate. Other plasticizers can also be used.*

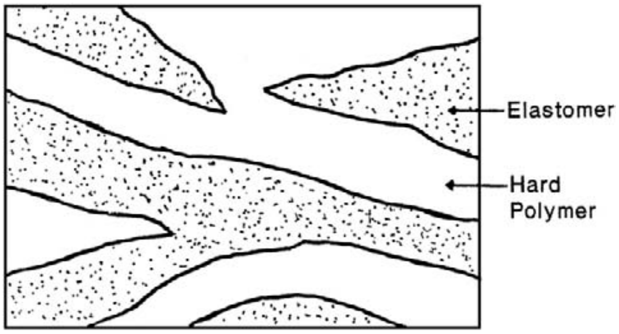


Figure 6.4 Morphology of hard polymer–elastomer blends.

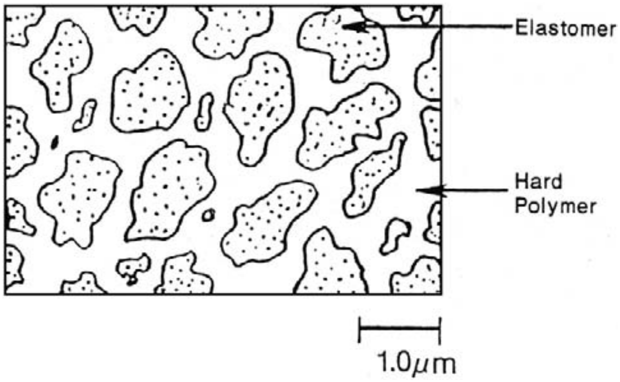


Figure 6.5 Morphology of dynamic vulcanizates.

Sometimes, the elastomer phase is deliberately crosslinked during the intensive mechanical mixing. This is described as "dynamic vulcanization" [28,35]. It produces a finely dispersed, *discontinuous*, crosslinked elastomer phase (see Figure 6.5). The products are called dynamic vulcanizates or thermoplastic vulcanizates. This process is more complex than simple mixing, but the products have two important advantages. First, the crosslinked elastomer phase is insoluble and so oil and solvent resistance is improved. Second, crosslinking reduces or eliminates the flow of this phase at high temperatures and/or under stress. This improves resistance to compression set.

At least three other types of thermoplastic elastomers have been investigated [36] but have not become commercially important. These are as follows.

6.2.4 Graft Copolymers

Thermoplastic elastomers have also been produced from graft copolymers. These may be represented as

$$\begin{array}{l}\text{B-B-B-B-B-B} \ \ldots \ \text{B} \\ \qquad\quad | \\ \qquad\ (\text{A})_n\end{array}$$

This represents a polymer where each elastomeric B chain has (on average) *n* random grafts of hard A blocks. B chains that do not have at least two A blocks grafted onto them will not be elastically effective, because they cannot form a continuous interlinked network that is similar to the one shown in Figure 6.2. To ensure that almost all the B chains have at least two A blocks grafted onto them, *n* should be greater than 2, perhaps as high as 10.

6.2.5 Ionomers

Commercial ionomers are based on polyethylene with acidic groups as part of the backbone chain. These are neutralized by metallic counterions, typically Na^+ or Zn^{2+}.

This gives a flexible thermoplastic. When the polyethylene is replaced by an elastomer (e.g., EPDM), the product is a thermoplastic elastomer.

6.2.6 Core–Shell Morphologies

These usually have a rigid core and an elastomeric shell, with a transition zone in-between. In the opposite morphology (elastomeric core and a rigid shell), the core could be crosslinked to give a product similar to a dynamic vulanizate.

6.3 Production

As noted above, many copolymers and polymer combinations can give thermoplastic elastomers. This section covers the production of only the most commercially significant.

6.3.1 Styrenic Thermoplastic Elastomers

The block copolymers on which these materials are based are made by anionic polymerization [7,37]. In principle, this is a very simple system in which the polymer segments are produced sequentially from the monomers. The first step in the polymerization is the reaction of an alkyl-lithium initiator (R^-Li^+) with styrene monomer:

$$R^-Li^+ + nS \rightarrow R\text{-}(S)_n{}^-Li^+$$

For simplicity, we denote the product as S^-Li^+. It is called a "living polymer" because it can initiate further polymerization. If a second monomer, such as butadiene, is added:

$$S^-Li^+ + mB \rightarrow S\text{-}(B)_m{}^-Li^+$$

We denote this product as $S\text{-}B^-Li^+$. It is also a "living polymer" and by repeating these steps, block copolymers with multiple alternating blocks (S-B-S-B-S…) can be produced. In practice, there are no apparent advantages in going beyond triblocks (i.e., S-B-S). Another variation is to use a coupling reaction to make linear or branched structures such as $(S\text{-}B)nx$ (where x represents an n-functional junction point). A typical example is

$$2S\text{-}B^-Li^+ + X\text{-}R\text{-}X \rightarrow S\text{-}B\text{-}R\text{-}B\text{-}S + 2LiX$$

Many coupling agents have been described, including esters, organo-halogens, and silicon halides [37,38]. The example above shows the reaction of a difunctional coupling agent, but those of higher functionality (e.g., $SiCl_4$) can also be used. These give branched or star-shaped molecules such as $(S\text{-}B)nx$.

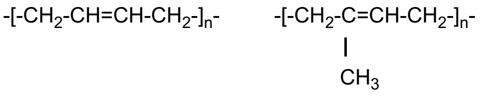
The third method of producing these block copolymers uses multifunctional initiation [38,39,41]. In this method, a multifunctional initiator ($^+Li^-R^-Li^+$) is first reacted with the diene (in this case, butadiene).

$$2nB + {}^+Li^-R^-Li^+ \rightarrow {}^+Li^-(B)_n{}^-R^-(B)_nLi^+$$

We denote this product as $^+Li^-B^-$ i^+. The final two steps are similar to the corresponding steps in the sequential polymerization described above. When the reaction to produce the $^+Li^-B^-Li^+$ is completed, styrene monomer is added and it in turn initiates its polymerization onto the "living" chain ends to give $^+Li^-S\text{-}B\text{-}S^-Li^+$. A protonating species is then added to stop the reaction and give final product, S-B-S. This example shows the use of a difunctional initiator. There is no reason in principle why initiators of higher functionality could not be used but none appears to have been reported in the literature.

All these reactions take place only in the absence of terminating agents such as water, oxygen, or CO_2; thus, they are usually carried out under nitrogen and in an inert hydrocarbon solvent. These conditions produce polymers with narrow molecular weight distributions and precise molecular weights.

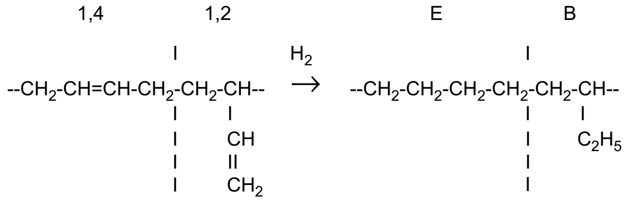
Only three common monomers—styrene, butadiene, and isoprene—are easily polymerized anionically and so only S-B-S and S-I-S block copolymers are directly produced on a commercial scale. In both cases, polymerization of the elastomer segments in a nonpolar solvent predominantly gives the 1,4 polymeric structures:



$$\text{-[-}CH_2\text{-}CH{=}CH\text{-}CH_2\text{-]}_n\text{-} \qquad \text{-[-}CH_2\text{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH\text{-}CH_2\text{-]}_n\text{-}$$

Polybutadiene   Polyisoprene

Both these polymers contain one double bond per molecule of the original monomer. These bonds are quite reactive and limit the stability of the product. More stable analogues can be produced from S-B-S polymers in which the polybutadiene mid-segments are polymerized in relatively polar solvents. These conditions produce a random copolymer of the 1,4 and 1,2 isomers. After hydrogenation, this gives a saturated elastomer that can be considered a copolymer of ethylene and butylene (EB).



Polybutadiene   Poly(ethylene-butylene)

Similarly, S-EP-S block copolymers are produced by hydrogenating S-I-S precursors.

Block copolymers with polyisobutylene mid-segments (e.g., S-*i*B-S) are made by carbocationic polymerization [8,42]. This is a more complex system than the anionic system described above. The initiators have functionalities of two or more. They have the general formula $(X\text{-}R)nx$ (where X-R represents a hydrocarbon moiety with a functional group X and x represents an n-functional junction point). X can be a chlorine, hydroxyl, or methoxy group. Polymerization is carried out at low temperatures (about −80 °C) in a moderately polar solvent and in the presence of a co-initiator ($TiCl_4$ or BCl_3). As in anionic polymerization, the polymer segments are produced sequentially from the monomers. Thus, an S-*i*B-S block copolymer would be produced in two stages:

$$\text{X-R-X} + 2n(i\text{B}) \rightarrow {}^{+}(i\text{B})_n\text{-R-}(i\text{B})_n{}^{+}$$

The product, which we can denote as ${}^{+}i\text{B}^{+}$ is a difunctional living polymer. It can initiate further polymerization, so if a second monomer, such as styrene, is added.

$${}^{+}i\text{B}^{+} + 2m(\text{S}) \rightarrow {}^{+}(\text{S})_m\text{-}i\text{B-}(\text{S})_m{}^{+}$$

After termination, this gives the block copolymer S-*i*B-S. Polyisobutylene is the only elastomeric mid-segment that can be produced by carbocationic polymerization. There are many aromatic polymers (mostly substituted polystyrenes) that can form the end segments [8].

6.3.2 Multiblock Copolymers

The thermoplastic elastomers based on polyurethanes, polyesters, and polyamides are produced from prepolymers by condensation reactions. For those based on polyurethanes, three starting materials are used:

- A long-chain diol, also called a polyglycol ($\text{HO-R}_\text{L}\text{-OH}$)
- A short-chain diol, also called a chain extender ($\text{HO-R}_\text{S}\text{-OH}$)
- A diisocyanate (OCN-R*-NCO) that can react with the hydroxyl groups in the diols to give a polyurethane

The basic reaction can be written:

$$-\text{NCO} + \text{HO}- \rightarrow -\text{NHCOO}-$$

In the first stage of polymerization, an excess of the diisocyanate is reacted with the long-chain diol. This gives a prepolymer terminated with the reactive isocyanate groups:

$$\text{OCN-R*-NCO} + \text{HO-R}_\text{L}\text{-OH} \rightarrow \text{OCN}$$
$$\text{-(R*-U-R}_\text{L}\text{-U)}_\text{n}\text{-R*-NCO (Prepolymer)}$$

where U represents the urethane linking group, ${}^{-}\text{NHCOO}^{-}$. We can denote the prepolymer as OCN-prepoly-NCO. It will further react with the short-chain diol and more diisocyanate:

$$\text{OCN-prepoly-NCO} + \text{HO-R}_\text{S}\text{-OH} + \text{OCN-R*}$$
$$\text{-NCO} \rightarrow \text{OCN-[prepoly-U-(R*-U-R}_\text{S}\text{-U)}_\text{n}\text{-]}_\text{m}\text{-R*-NCO}$$

The final product is an alternating block copolymer with two types of segments:

- These are formed in the first stage and are based on the prepolymer. They are alternating copolymers of the long-chain diols and the diisocyanate.
- These are formed in the second stage. They are alternating copolymers of the short-chain diols and the diisocyanate.

The long-chain diols have a broad molecular-weight distribution. Thus the prepolymers formed from them and the diisocyanate monomers do not have a regular repeating structure and are amorphous. Typical glass transition temperatures of the long-chain diols are in the range of −45 to −100 °C [10], so at room temperatures these prepolymers are elastomeric. They form the soft elastomeric phase in the final polymer. By contrast, the short-chain diols are single molecular species (e.g., 1,4-butanediol or ethylene glycol). Thus the copolymers formed from them and the diisocyanate or diacid monomers do have a regular repeating structure and so are crystalline. Typical crystallization temperatures of these segments are above 150 °C [10], so at room temperatures they are hard. They form the hard phase in the final polymer.

Diphenylmethane 4,4′-diisocyanate (MDI) and 2,4 toluene-diisocyanate (TDI) are the most common diisocyanates used to produce polyurethane thermoplastic elastomers. The long-chain diols are usually polyesters (e.g., poly(-ethylene adipate) glycol) or polyethers (e.g., poly(oxytetramethylene) glycol). Polycaprolactone glycol is used in premium products.

The various possible combinations of all three starting materials (diisocyanates, long-chain diols and short-chain diols) give a very wide variety of commercial thermoplastic polyurethanes [10]. By contrast, although thermoplastic polyesters are produced in a similar way (with diacids or diesters replacing diisocyanates), only three starting materials are used commercially [11]. These are as follows:

- poly(oxytetramethylene) glycol (the long-chain diol)
- 1,4-butanediol (the short-chain diol)
- terephthalic acid (the diacid) or its methyl diester

There are two ways to produce polyamide thermoplastic elastomers [12]. The first is based on the reaction of a carboxylic acid with an isocyanate to give an amide:

$$-\text{NCO} + \text{HOOC}- \rightarrow -\text{NHOOC}- + \text{CO}_2$$

The reaction scheme is similar to that shown above for the production of thermoplastic polyurethane and polyester elastomers. Again, the product is a copolymer with alternating segments.

The second method is more important commercially. In this method, a polyamide terminated by carboxylic acid groups, HOOC-PA-COOH (or the corresponding ester, ROOC-PA-COOR) reacts with a long-chain diol:

$$\text{HOOC-PA-COOH} + \text{HO-R}_L\text{-OH} \rightarrow \text{HO-(R}_L\text{-E-PA-E)}_n\text{-R}_L\text{-OH} + 2n\text{H}_2 0$$

$$\text{ROOC-PA-COOR} + \text{HO-R}_L\text{-OH} \rightarrow \text{HO-(R}_L\text{-E-PA-E)}_n\text{-R}_L\text{-OH} + 2n\text{ROH}$$

where $\underline{E}$ represents an ester link.

This amounts to preparing an alternating block copolymer from two prepolymers: one (the polyamide) crystalline and the other (the long-chain diol) amorphous.

The block copolymers of ethylene or propylene with α-olefins are produced using metallocene catalysts [13–16]. For those based on polyethylene, the α-olefins are typically 1-butene, 1-hexene, or 1-octene. These copolymerize with ethylene to give segments with pendant groups, usually arranged atactically. Because of their random and atactic structures, these segments cannot crystallize. Instead, they are amorphous materials with low glass transition temperatures and so are soft and rubber-like at room temperature. They form the soft phase. The remainder of the polymer is polyethylene. This has a linear, symmetrical structure and therefore does not exhibit tacticity. Thus, the long polyethylene segments in the polymer chain are regular and so can crystallize. They form the hard phase. Similarly, block copolymers based on polypropylene have long isotatic polypropylene segments that give a crystalline polypropylene hard phase together with a soft phase that is a random copolymer of ethylene and propylene.

In all these multiblock (A-B)*n* polymers, both the number of segments and their individual molecular weights have a very broad distribution, in contrast to the simple A-B-A triblocks in the styrenic thermoplastic elastomers.

6.3.3 Hard Polymer–Elastomer Combinations

There are two types of these materials—simple blends of the hard polymer and the elastomer and the dynamically vulcanized products in which the elastomer is crosslinked during the mixing process. Both the hard polymers and the elastomers used to make these products can be obtained "off the shelf." Thus an almost unlimited range of combinations can be investigated quickly and easily. Similarly, commercial products can be made without the very high capital investment required to produce novel polymers.

To produce simple unvulcanized blends, the two polymers are mixed on high shear compounding equipment. For the dynamically vulcanized versions, vulcanizing agents must be added and the temperature controlled so as to crosslink the rubber particles during mixing. In both cases, only fine dispersions will produce optimum properties. A good match of the viscosities of the two polymers will aid the production of a fine dispersion [43], as will a match in solubility parameters. If the two polymers have very different solubility parameters (e.g., one is polar, while the other is not), a coarse dispersion with poor adhesion between the phases can result. This can often be avoided by using block or graft copolymers as compatibilizing agents [28,43].

6.4 Structure–Property Relationships

With such a variety of materials, it is to be expected that the properties of thermoplastic elastomers cover an exceptionally wide range. Some are very soft and rubbery, whereas others are hard and tough and in fact approach the ill-defined interface between elastomers and flexible thermoplastics.

Since most thermoplastic elastomers are phase-separated systems, they show many of the characteristics of the individual polymers that constitute the phases. For example, each phase has its own glass transition temperature (T_g), (or crystal melting point (T_m), if it is crystalline). These, in turn, determine the temperatures at which a particular thermoplastic elastomer goes through transitions in its physical properties. Thus, when the modulus of a thermoplastic elastomer is measured over a range of temperatures, there are three distinct regions (see Figure 6.6).

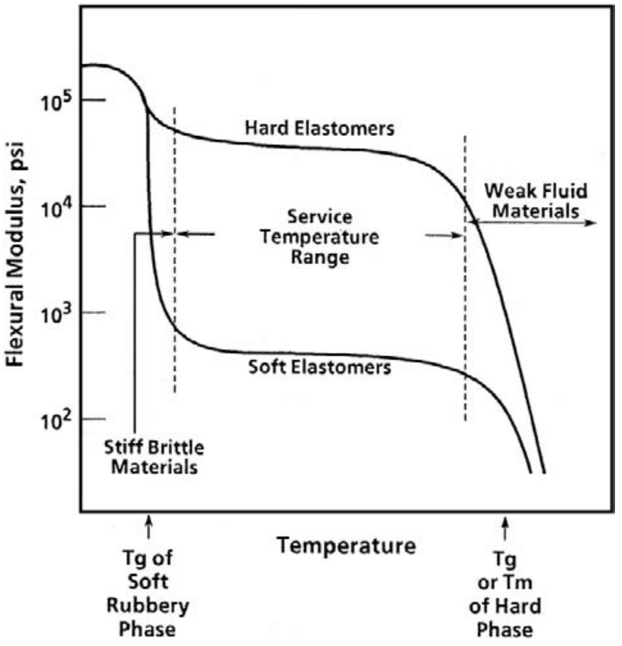


Figure 6.6 Stiffness of thermoplastic elastomers at various temperatures.

At very low temperatures, both phases are hard and so the material is stiff and brittle. At a somewhat higher temperature, the elastomer phase becomes soft and the thermoplastic elastomer now resembles a conventional vulcanizate. As the temperature is further increased, the modulus stays relatively constant (a region often described as the "rubbery plateau") until finally the hard phase softens. At this point, the thermoplastic elastomer becomes fluid. Thus, thermoplastic elastomers have two service temperatures. The lower service temperature depends on the T_g of the elastomer phase, while the upper service temperature depends on the T_g or T_m of the hard phase. Values of T_g and T_m for the various phases in some commercially important thermoplastic elastomers are given in Table 6.4. As noted above, many different polymers are used to make the hard and soft phases in all these types of thermoplastic elastomers. Their influence on some properties of the products can be summarized as follows:

6.4.1 Hard Phase

The choice of polymer in the hard phase strongly influences the oil and solvent resistance of the thermoplastic elastomers. Even if the elastomer phase is resistant to a particular oil or solvent, if this oil or solvent swells the hard phase, all the useful physical properties of the thermoplastic elastomer will be lost. In many commercial thermoplastic elastomers, this hard phase is crystalline and so resistant to oils and solvents. Styrenic thermoplastic elastomers are an exception. As pure polymers they have poor oil and solvent resistance (although this can be improved by compounding—see p. 87). However, this gives them the advantage that they can be applied from solution.

6.4.2 Soft Elastomer Phase

In the styrenic thermoplastic elastomers, analogous S-B-S, S-I-S S-EB-S, S-EP-S polymers and S-*i*B-S have somewhat different properties. S-B-S polymers are lowest in cost and have medium hardness. S-I-S equivalents are the softest, while the S-EB-S and S-EP-S polymers are the most stable [9] but also higher in price. The S-iB-S polymers are also very stable [9] and are relatively soft [1a]. In the thermoplastic elastomers with crystalline hard segments, those with poly*ester*-based elastomer segments are tougher and have better resistance to oils and solvents. The poly*ether*-based materials are more flexible at low temperatures and show better hydrolytic stability. In the hard polymer—elastomer combinations, resistance to oil and solvents and to compression set are dramatically improved, if the elastomer phase is dynamically vulcanized. Oil and solvent resistance can be still further improved if the elastomer is a polar material such as nitrile rubber.

Table 6.4 Glass transition and crystal melting temperatures

Thermoplastic Elastomer Type	**Soft, Rubbery Phase T_g (°C)**	**Hard Phase T_g or T_m (°C)**
Polystyrene/elastomer block copolymers		
S-B-S	−90	95 (T_g)
S-I-S	−60	95 (T_g)
S-EB-S and S-EP-S	−60	95 (T_g) and 165 (T_m)[a]
S-iB-S	−60	95 (T_g) and 165 (T_m)[a]
Multiblock copolymers		
Polyurethane/elastomer	−40 to −60[b]	190 (T_m)
Polyester/elastomer	−40	185−220 (T_m)
Polyamide/elastomer	−40 to −60[b]	220−275 (T_m)
Polyethylene/poly(α-olefin)	−50	70 (T_m)[c]
Polypropylene/poly(ethylene-propylene)	−50	50−70 (T_m)[c]
Polyetherimide/polysiloxane block copolymers	−60	225 (T_g)
Hard polymer−elastomer combinations		
Polypropylene/EPDM or EPR	−50	165 (T_m)
Polypropylene/butyl rubber	−60	165 (T_m)
Polypropylene/natural rubber	−60	165 (T_m)
Polypropylene/nitrile rubber	−40	165 (T_m)
Polypropylene/poly (butylacrylate)	−50	165 (T_m)
Polyamide or polyester/silicone rubber	−85	225−250 (T_m)
PVC/nitrile rubber/DOP	−30	80 (T_g) and 210 (T_m)

[a] *In compounds containing polypropylene.*

[b] *The values are for polyethers and polyesters respectively.*

[c] *These low values for* $\mathrm{T_m}$ *are presumably the result of the short length of the polyethylene or polypropylene segments.*

Table 6.5 Approximate price and property ranges for thermoplastic elastomers

	Price Range ($/kg)	Specific Gravity	Hardness Shore A or D
Polystyrene/elastomer[a] block copolymers			
S-B-S (pure)	2.2–3.3	0.94	62A–75A
S-I-S (pure)	2.4–3.3	0.92	32A–37A
S-EB-S and S-EP-S (pure)	4.7–7.1	0.91	65A–75A
S-*i*B-S (pure)	7.0–7.5	0.96	41A
S-B-S (compounds)	2.3–3.8	0.9–1.1	40A–45D
S-EB-S (compounds)	1.4–2.5	0.9–1.2	5A–60D
Multiblock copolymers			
Polyurethane/elastomer block copolymers	5.8–9.5	1.05–1.25	70A–75D[b]
Polyester/elastomer block copolymers	7.0–9.5	1.15–1.40	35D–80D
Polyamide/elastomer block copolymers	11–14	1.0–1.15	60A–65D
Polyethylene/poly(α-olefin) block copolymers	2.1–2.8	0.85–0.91	65A–85A
Polypropylene/poly(ethylene/propylene) block copolymers	2.0–2.6	0.86–0.88	60A–80A
Polyetherimide/polysiloxane block copolymers	50	1.2	70D
Hard polymer – elastomer combinations			
Polypropylene/EPDM or EPR blends	2.1–3.0	0.9–1.0	60A–65D
Polypropylene/EPDM dynamic vulcanizates	4.1–7.6	0.95–1.0	35A–50D
Polypropylene/butyl rubber dynamic vulcanizates	5.3–9.1	0.95–1.0	50A–80D
Polypropylene/natural rubber dynamic vulcanizates	3.6–4.0	1.0–1.05	60A–45D
Polypropylene/nitrile rubber dynamic vulcanizates	5.1–6.3	1.0–1.1	70A–50D
Polypropylene/poly(butyl acrylate) dynamic vulcanizates	4.5–6. 0	1.0	55A–75D
Polyamide or polyester[c]/silicone rubber dynamic vulcanizates	12–18	1.1–1.2	50A–60D
PVC/nitrile rubber/DOP[d] blends	3.3–3.8	1.20–1.33	50A–90A
Chlorinated polyolefin/ethylene interpolymer blends	5.8–7.0	1.10–1.25	50A–80A

These price and property ranges do not include fire retardant grades or highly filled materials for sound deadening.

[a] *B, Polybutadiene; I, polyisoprene; EB, poly(ethylene-*co*-butylene); EP, poly(ethylene-*co*-propylene);* i*B, polyisobutylene.*

[b] *As low as 60A when plasticized.*

[c] *And other proprietary resins.*

[d] *DOP, Dioctylphthalate.*

6.4.3 Hard/Soft Phase Ratio

The hardness of these materials depends on the ratio of the volume of the hard phase to that of the softer elastomer phase. In the styrenic thermoplastic elastomers, this ratio can be varied within quite wide limits. Thus, in an S-B-S block copolymer, as the ratio of the S to B segments is increased, the phase morphology changes from a dispersion of spheres of S in a continuous phase of B to a dispersion of rods of S in a continuous phase of B and then to a lamellar or "sandwich" structure in which both S and B are continuous [1a,44]. If the proportion of S is increased still further, the effect is reversed in that S now becomes disperse and B continuous. As the polystyrene phase predominates, the block copolymer gets harder and stiffer until eventually it becomes a clear flexible thermoplastic such as K-Resin® (Chevron Phillips).

In hard polymer—elastomer combinations, there are limits on the proportions of the elastomer phase in both the simple blends and the thermoplastic vulcanizates. In the simple blends, if too much elastomer is used, the morphology changes from an interdispersed structure (in which both phases are continuous) to a dispersion of the hard polymer in the elastomer. Since the elastomer is not vulcanized, it has little strength. Thus when it becomes the only continuous phase, the properties of the blend are unsatisfactory. In the thermoplastic vulcanizates, the dispersed elastomer phase is crosslinked and so cannot flow. It can thus be considered as an elastomeric filler, and when too much is present, processability suffers. Because of these limits on the amount of the elastomer phase, producing very soft products from hard polymer—elastomer combinations is difficult. The multiblock polymers with crystalline hard segments also have limits on softness. The hard-phase segments must have high enough molecular weights so that they can crystallize. Softer versions of these polymers

Table 6.6 Some trade names of thermoplastic elastomers based on styrenic block copolymers

		Elastomer	
Trade Name (Manufacturer)	**Type**	**Segment[a]**	**Notes**
KRATON® D (Kraton Performance Polymers)[b]	Linear and branched	B or I	General purpose, soluble, some compounded products
VECTOR® (Dexco)[c]	Linear and Branched	B or I	General purpose, soluble Not available as compounded products
TAIPOL® TPE (Taiwan Synthetic Rubber Company)	Linear and Branched	B or I	
QUINTAC® (Zeon Chemical)	Linear	I	
FINAPRENE® (Total)	Linear	B	
COPERFLEX TR® (Petroflex)	Linear and branched	B or I	
TUFPRENE® and ASAPRENE®T (AKelastomer)	Linear	B	
CALPRENE® and SOLPRENE® (Dynasol)	Linear and branched	B	
KIBITON® (Chi Mei)	Linear and branched	B	
EUROPRENE®SOL T (Polimeri Europa)	Linear and branched	B or I	
KOSYN®KTR (Kumho)	Linear and Branched	B or I	
GLOBALPRENE (LCY Elastomers)	Linear	B or I	
STYROAFLEX® (BASF)	Linear	SB	Styrene/butadiene copolymer midblock
HYBRAR® (Kuraray)	Linear	I or EP	High 3,4 content
STEREON® (Firestone)	Linear	B	High polystyrene content
K-RESIN® (Chevron-Phillips)	Branched	B	Very high polystyrene content, hard and rigid
STYROLUX® and STYROFLEX® (BASF)	Branched	B	
FINACLEAR® (Total)	Branched	B	
KRATON® G (Kraton Performance Polymers)[b]	Linear	EB or EP	Improved stability, soluble when uncompounded
TUFTEC® (AKelastomer)	Linear	EB	
SEPTON® (Kuraray)	Linear	EB, EP, and EEP	
TAIPOL® TPE (Taiwan Synthetic Rubber Company)	Linear	EB	
CALPRENE® H (Dynasol)	Linear	EB	
EUROPRENE® SOL TH (Polimeri Europa)	Linear	EB	
GLOBALPRENE (LCY Elastomers)	Linear	EB	

Table 6.6 Some trade names of thermoplastic elastomers based on styrenic block copolymers (*Continued*)

Trade Name (Manufacturer)	Type	Elastomer Segment[a]	Notes
SIBSTAR® (Kaneka)	Linear	iB	Soluble, improved stability, soft, low gas permeability, and high damping
THERMOPLAST® (Kraiburg)	Linear	EB	Only compounded products
DYNAFLEX® (GLS)	Linear	B or EB	
MULTI-FLEX® TPE and TEA (Multibase)[d]	Linear	EB	
J-FLEX®, J-SOFT®and J-LAST® (J-Von)	Linear	B or EB	
TEKRON®, TEKBOND® and MONOPRENE® (Teknor Apex)[e]	Linear	EB or EP	
ONFLEX®, VERSAFLEX®, and VERSALLON® (GLS)[e]	Linear	B or EB	
ELEXAR® (Teknor Apex)[b]	Linear	EB	Wire and cable
C-FLEX® (Saint-Gobain)	Linear	EB	Medical tubing, contains silicone oil

[a] *B, Polybutadiene; I, polyisoprene; SB, poly(styrene-*co*-butadiene); EB, poly(ethylene-*co*-butylene); EP, poly(ethylene-*co*-propylene); EEP, poly(ethylene-*co*-ethylene-propylene); iB, polyisobutylene.*

[b] *Formerly shell.*

[c] *Joint venture of Dow and Exxon.*

[d] *Now a part of Dow Corning.*

[e] *Some grades can be overmolded onto engineering thermoplastics such as ABS, nylon, polycarbonates, and polyacrylates.*

require the molecular weights of the elastomer segments to be higher still so as to increase the soft/hard phase ratio. Thus for very soft products, the total molecular weight of the block polymer is increased to the point where processing can be difficult.

6.5 Applications

Applications of thermoplastic elastomers of all types have been extensively described [2,45—47]. Some highlights are as follows.

6.5.1 Styrenic Thermoplastic Elastomers

The anionically polymerized versions of these block copolymers (i.e., S-B-S, S-I-S, S-EB-S, and S-EP-S) have been produced commercially for many years and much commercial experience has been obtained on these materials. Thus the information in this section is based on these materials. The S-iB-S equivalents are much newer. In many ways, especially thermal stability, they are similar to S-EB-S and S-EP-S and so they should have similar applications.

Styrenic block copolymers differ from most other thermoplastic elastomers in at least two significant ways. First, both the hard and soft phases are amorphous, and thus the pure polymers are soluble in common solvents such as toluene. Second, in their various end uses, these polymers are always compounded with large amounts of ingredients such as other polymers, oils, resins, and fillers. In the majority of their applications, the styrenic block copolymer comprises less than 50% of the final product.

Compounding significantly changes many properties (e.g., solubility). Thus although the pure styrenic thermoplastic elastomers are completely soluble in solvents such as toluene, compounded products containing insoluble polymers (e.g., polypropylene) are not. The properties of compounded products produced from styrenic thermoplastic elastomers cover an exceptionally wide range and so their applications are more varied than those of the other thermoplastic elastomers.

For injection molding, extrusion, etc. (i.e., processing on conventional thermoplastics equipment), most end users prefer to buy precompounded products, and grades have been developed for the various specialized end uses. Products based on S-B-S are typically compounded with polystyrene (or styrenic resins), hydrocarbon oils, and fillers. Probably, the largest application of these S-B-S-based compounds is in footwear. By varying the proportions of the polystyrene, oil, and filler, compounds have been developed for applications ranging from work boots to slippers. In compounds based on S-EB-S, polypropylene often replaces polystyrene. This polymer gives better solvent resistance and increases the upper service temperature. Typical applications include wire and cable insulation, and automotive and pharmaceutical items. Processing of these compounded products is simple. Usually, compounds based on S-B-S block copolymers are processed under conditions suitable for polystyrene, while those based on S-EB-S block copolymers are processed under conditions suitable for polypropylene. Overmolding onto metal or conventional thermoplastics is a significant end

Table 6.7 Some trade names of thermoplastic elastomers based on multiblock copolymers

Trade Name (Manufacturer)	Type	Elastomer Segment[a]	Notes
ESTANE® (Lubrizol)	Polyurethane		
IROGRAN®[a] (Huntsman)		Polyether or amorphous Polyester[b]	Hard and tough. Abrasion and oil resistant. Good tear strength
PELLETHANE®[a] Dow)			
ELASTOLLAN® (BASF)			
DESMOPAN® and TEXIN® (Bayer)			
HYTREL® (DuPont)			
LOMOD®[c] and ARNITEL® (DSM) Polyester	Polyester	Polyether	Similar to polyurethanes Better low temperature flexibility.
RITEFLEX® (Ticona)			
PIBIFLEX® (P-Group)			
ECDEL® (Eastman)			
PEBAX® (Arkema)[d]	Polyamide	Polyether or amorphous polyester	Similar to polyurethanes but can be softer. Good low temperature flexibility. Expensive
VESTAMID® E (Evonik)[e]			
GRILAMID® and GRILON® (EMS America)			
AFFINITY®, FLEXOMER®, ENGAGE® and INFUSE® (Dow)	Polyethylene	Poly(α-olefins)	Flexible and low cost. Good low temperature flexibility. Limited at higher temperatures
EXACT® (ExxonMobil)			
VISTAMAXX® (ExxonMobil)	Polypropylene	Poly(ethylene-co-propylene)	
SILTEM® (GE)	Poly(etherimide)	Polysilicone	Fire resistant. Very high cost

[a] *Formerly Elf-Atochem.*
[b] *Formerly Degussa.*
[c] *Formerly MORTHANE® (Rohm and Haas).*
[d] *Including some with polycaprolactone segments.*
[e] *Formerly GE.*

use for these and other thermoplastic elastomers. Final products include rubber handles for knives, pens, toothbrushes, etc. Generally, thermoplastic elastomers adhere well when overmolded onto thermoplastics of similar types. Further details on processing these and other thermoplastic elastomers are given in the following book [47].

Another major application of styrenic thermoplastic rubbers is in adhesives, sealants, and coatings. Tackifying and reinforcing resins are used to achieve a desirable balance of properties. Oils and fillers can also be added. These adhesives and sealants can be applied either from solvents or as hot melts. One very important application is in pressure-sensitive hot melt adhesives. S-I-S block copolymers are softer and stickier and so they are often used to formulate adhesives of this type—in fact it is probably their largest single end use. S-iB-S block copolymers are also very soft [1a,44] and may also be suitable [9] for this end use, especially when improved stability is desired.

A final application is in blends with thermoplastics or other polymeric materials. Styrenic block copolymers are technologically compatible with a surprisingly wide range of other polymers. Blends with many other thermoplastics have improved impact resistance. These block copolymers can also be used as compatibilizers—i.e., they can produce useful products from blends of thermoplastics that otherwise have poor properties [6].

6.5.2 Multiblock Polymers with Crystalline Hard Segments

The very tough and relatively hard materials based on polyurethane, polyester, or polyamide hard segments are generally regarded as premium products [10—12]. Articles made from them are produced by the typical techniques used to process thermoplastics (e.g., injection molding, blow molding, extrusion). Because of their crystalline hard

Table 6.8 Some trade names of thermoplastic elastomers based on hard polymer/elastomer combinations

Trade Name (Manufacturer)	Type	Hard Polymer	Elastomer	Notes
DEXFLEX® and INDURE® (Solvay Engineered Polymers)[a] FLEXATHENE® (LyondellBasel)[b] POLYTROPE® (Schulmam) TELCAR® (Teknor Apex) FERROFLEX® (Ferro)	Blend	Polypropylene	EPDM or EPR	Relatively hard, low density, not highly filled
SANTOPRENE® (ExxonMobil)[c] MULTI-FLEX TPO (Multibase)[d] SARLINK® 3000 & 4000 (DSM) UNIPRENE® (Teknor Apex) VERSALLOY (GLS) NEXPRENE® (Solvay)	DV[e]	Polypropylene	EPDM	Better oil resistance, low compression set, softer
TREFSIN® (ExxonMobil)[c] and SARLINK® 2000 (DSM)	DV	Polypropylene	Butyl Rubber	Low permeability, high damping
VYRAM® (ExxonMobil)[c]	DV	Polypropylene	Natural Rubber	Low Cost
GEOLAST® (ExxonMobil)[c]	DV	Polypropylene	Nitrile Rubber	Oil resistant
TPSiV (Multibase)[d]	DV	Polyamide or Polyester[f]	Silicone Rubber	High Temperature Applications
VERSALON® (GLS)	Blend	Polyurethane TPE	Not specified	Overmolding ABS, Polycarbonate
ALCRYN® (Advanced Polymer Alloys)[g]	Blend	Chlorinated Polyolefin	Ethylene Interpolymer	Single phase, oil resistant
SARLINK® 1000 (DSM) CHEMIGUM® (Eliokem)[h]	DV Blend	PVC	Nitrile Rubber	Oil Resistant
RIMPLAST® (Evonik)[i]	Blends	Various TPEs	Silicone Rubbers	Medical applications

[a] *Formerly D&S Plastics.*
[b] *Product is a blend of PP and EPR produced in the polymerization reactor.*
[c] *Formerly Advanced Elastomer Systems (AES).*
[d] *Now a part of Dow Corning.*
[e] *Dynamic vulcanizate—a composition in which the soft phase has been dynamically vulcanized, i.e., crosslinked during mixing.*
[f] *And other proprietary resins.*
[g] *Division of Ferro. Formerly a part of DuPont.*
[h] *Formerly Goodyear.*
[i] *Formerly Degussa.*

segments and polar elastomer segments, they have excellent oil resistance. Thus they are used in demanding applications as blow-molded boots for automobile steering gear assemblies, grease seals, drive belts, and hydraulic hose. They can also be blended with polar polymers such as PVC or used as the hard phase in hard polymer—elastomer combinations [33].

The polymers with polyethylene or polypropylene hard segments are lower in cost. Their suggested applications include blends with polyethylene or polypropylene and partial replacement of polypropylene in S-EB-S/polypropylene/oil blends. Other applications include hot melt adhesives for use in diapers, etc.

6.5.3 Hard Polymer—Elastomer Combinations

Polypropylene—EPDM or EPR combinations are the most important [13,14] and are used to make products such as injection-molded bumpers for automobiles, where a combination of toughness, low temperature flexibility, and low cost makes them very attractive. However, their use is limited because they can only be used to produce fairly hard products (typically above 60 Shore A hardness). Almost all applications for the polypropylene/EPDM thermoplastic vulcanizates [28] are as replacements for vulcanized rubber. They are used in automotive and appliance parts and also in the construction industry for window seals, etc. They have good compression set and can give softer products (as low as 35 Shore A hardness). Similar thermoplastic vulcanizates based on polypropylene and nitrile rubber blends have improved solvent resistance.

Blends based on halogen-containing polymers are also significant [31—33]. Those based on halogenated polyolefin/ethylene interpolymer blends are claimed to be single-phase systems [33]. They are often used where solvent and fire resistance is important. PVC/nitrile rubber/dioctyl phthalate blends are used in similar applications and also in footwear [31—33].

Finally, the S-B-S/polystyrene/oil and S-EB-S/polypropylene/oil compounds described above can also be considered as blends of a hard polymer (polystyrene or polypropylene) with a soft elastomer phase (S-B-S/oil or S-EB-S/oil) respectively [34].

6.6 Economic Aspects and Trade Names

The worldwide annual production of thermoplastic elastomers of all types is estimated at about 2,500,000 metric tons in 2005 [48] with a value of almost $12 billion. Production is expected to rise to about 4,200,000 metric tons in 2014 [49]. This is equivalent to an annual growth rate of about 5.3%. In 2009, North America consumed about 25% of this amount, Western Europe about 20%, and China about 33%. Japan and other Asia/Pacific countries accounted for most of the rest. The styrenic block copolymers represented about 45% of the total market and polypropylene/EPDM or EPR combinations (including thermoplastic vulcanizates) about another 30%. The thermoplastic polyurethanes and the thermoplastic polyesters together made up another 20% [49]. Major end uses are transportation, footwear, industrial goods, wire insulation, medical (growing very rapidly), adhesives, coatings, etc.

Table 6.5 gives values of three important properties (price, specific gravity, and hardness) for some commercially available thermoplastic elastomers. Trade names and suppliers of commercial thermoplastic elastomers of all types are given in Tables 6.6—6.8.

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7 Thermoset Elastomers

J.E. Mark
Department of Chemistry and the Polymer Research Center, University of Cincinnati, Cincinnati, Ohio 45221−0172, USA

7.1 Introduction

7.1.1 Basic Concepts

Elastomers are defined by their very large deformability with essentially complete recoverability. In order for a material to exhibit this type of elasticity, three molecular requirements must be met: (i) the material must consist of polymeric chains, (ii) the chains must have a high degree of flexibility and mobility, and (iii) the chains must be joined into a network structure [1−6].

The first requirement arises from the fact that the molecules in a rubber or elastomeric material must be able to alter their arrangements and extensions in space dramatically in response to an imposed stress, and only a long-chain molecule has the required very large number of spatial arrangements of very different extensions. The second characteristic required for rubber-like elasticity specifies that the different spatial arrangements be *accessible*, i.e., changes in these arrangements should not be hindered by constraints as might result from inherent rigidity of the chains, extensive chain crystallization, or the very high viscosity characteristic of the glassy state [1,2,7−9]. The last characteristic cited is required in order to obtain the elastomeric recoverability. It is obtained by joining together or "crosslinking" pairs of segments, approximately one out of a hundred, thereby preventing stretched polymer chains from irreversibly sliding by one another. The network structure thus obtained is illustrated in Figure 7.1, in which the crosslinks are generally chemical bonds (as would occur in sulfur-vulcanized natural rubber). An interchain entanglement is included since some workers have concluded that they can also contribute to the modulus of a network [7]. These elastomers are frequently included in the category of "thermosets," which are polymers having a network structure which is generated or "set" by thermally induced chemical crosslinking reactions. The term has now frequently taken on the more specific meaning of networks that are very heavily crosslinked and below their glass transition temperatures [10,11]. Such materials, exemplified by the phenol-formaldehyde and the epoxy resins, are very hard materials with none of the high extensibility associated with typical elastomers.

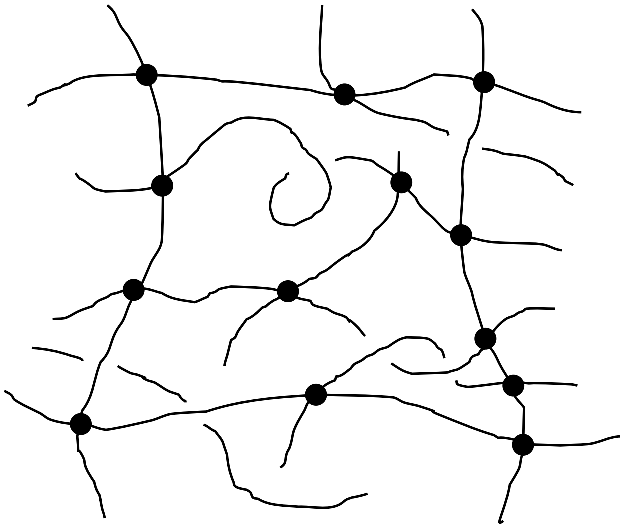

Figure 7.1 Sketch of a typical elastomeric network, with an interchain entanglement depicted in the lower right-hand corner. The filled dots represent crosslinks.

The crosslinks in an elastomeric network can also be temporary or physical aggregates, e.g. the small crystallites in a partially crystalline polymer or the glassy domains in a multi-phase triblock copolymer [3,7]. Additional information on the crosslinking of chains is given below.

7.1.2 Some Historical High Points

The earliest elasticity experiments involved stress−strain−temperature relationships, or network "thermoelasticity." They were first carried out many years ago, by J. Gough, back in 1805 [1,2,9,12,13]. The discovery of vulcanization or curing of rubber into network structures by C. Goodyear and N. Hayward in 1839 was important in this regard since it permitted the preparation of samples which could be investigated in this regard with much greater reliability. Such more quantitative experiments were carried out by J.P. Joule, in 1859. This was, in fact, only a few years after the entropy was introduced as a concept in thermodynamics in general! Another important experimental fact relevant to the development of these molecular ideas was the fact that mechanical deformations of rubber-like materials generally occurred essentially at constant volume, so long as crystallization was not induced [1]. (In this sense, the deformation of an elastomer and a gas are very different.)

A molecular interpretation of the fact that rubber-like elasticity is primarily entropic in origin had to await H. Staudinger's much more recent demonstration, in the 1920s, that polymers were covalently bonded molecules, and not some type of association complex best studied by the colloid chemists [1]. In 1932, W. Kuhn used this observed constancy in volume to point out that the changes in entropy must therefore involve changes in orientation or configuration of the network chains [7,9].

Later in the 1930s, W. Kuhn, E. Guth, and H. Mark first began to develop quantitative theories based on this idea that the network chains undergo configurational changes, by skeletal bond rotations, in response to an imposed stress [1,2]. More rigorous theories began with the development of the "Phantom Network" theory by H.M. James and E. Guth in 1941, and the "Affine Model" theory by F.T. Wall, and by P.J. Flory and J. Rehner, Jr. in 1942 and 1943 [1,14]. Modern theories generally begin with the phantom model and extend it, e.g. by taking into account interchain interactions [7].

7.1.3 Some Rubber-like Materials

Since high flexibility and mobility are required for rubber-like elasticity, elastomers generally do not contain stiffening groups such as ring structures and bulky side chains [2,9]. These characteristics are evidenced by the low glass transition temperatures T_g exhibited by these materials. Such polymers also tend to have low melting points, if any, but some do undergo crystallization upon sufficiently large deformations. Examples of typical elastomers include natural rubber and butyl rubber (which do undergo strain-induced crystallization), and poly(dimethylsiloxane) (PDMS), poly (ethyl acrylate), styrene-butadiene copolymer, and ethylene-propylene copolymer (which generally don't). In the case of PDMS, it is possible to use enzyme-based polymerizations, in parallel to the preparative reactions used by Nature [15,16].

The most widely used elastomers are natural rubber [17], synthetic polyisoprene and butadiene rubbers, styrene-butadiene copolymers, ethylene-propylene rubber (specifically EPDM), butyl and halobutyl elastomers, polyurethanes, polysiloxanes, polychloroprenes, nitrile rubber, polyacrylic rubbers, fluorocarbon elastomers, and thermoplastic elastomers [18−20]. The examples which have unsaturation present in the repeat units (such as the diene elastomers) have the advantage of easy crosslinkability, but the disadvantage of increased vulnerability to attack by reactants such as oxygen and ozone.

Some polymers are not elastomeric under normal conditions but can be made so by raising the temperature or adding a diluent ("plasticizer"). Polyethylene is in this category because of its high degree of crystallinity. Polystyrene, poly(vinyl chloride), and the biopolymer elastin are also of this type, but because of their relatively high glass transition temperatures require elevated temperatures or addition of diluent to make them elastomeric [9].

A final class of polymers is inherently non-elastomeric. Examples are polymeric sulfur, because its chains are too unstable, poly(*p*-phenylene) because its chains are too rigid, and thermosetting resins because their chains are too short [9].

7.1.4 Preparation of Networks

One of the simplest ways to introduce the crosslinks required for rubber-like elasticity is to carry out a copolymerization in which one of the comonomers has a functionality φ of three or higher [9,21]. This method, however, has been used primarily to prepare materials so heavily crosslinked that they are in the category of hard thermosets rather than elastomeric networks, as it has already been mentioned [11]. The more common techniques include vulcanization (addition of sulfur atoms to unsaturated sites), peroxide thermolysis (covalent bonding through free-radical generation), end linking of functionally terminated chains (isocyantes to hydroxyl-terminated polyethers, organosilicates to hydroxyl-terminated polysiloxanes, and silanes to vinyl-terminated polysiloxanes) [18].

For commercial materials, the compounding recipe generally contains numerous ingredients in addition to the polymer and crosslinking agent (e.g., sulfur, a peroxide, or an isocyanate) [22]. Examples are activators (to increase crosslinking efficiency), retarders (to prevent premature crosslinking or "scorch"), accelerators, peptizing agents, antioxidants and antiozonants, softeners, plasticizing aids, extenders, reinforcing fillers (typically carbon black or silica), and processing aids. Specific applications can require even more additives, e.g. blowing agents in the case of elastomeric foams, thermally conducting particles in the case of heated rollers, fiber meshes in the case of high pressure tubing, etc.

A sufficiently stable network structure can also be obtained by physical aggregation of some of the chain segments onto filler particles, by formation of microcrystallites, by condensation of ionic side chains onto metal ions, by chelation of ligand side chains to metal ions, and by microphase separation of glassy or crystalline end blocks in a triblock copolymer [9]. The main advantage of these materials is the fact that the crosslinks are generally only temporary, which means that such materials frequently exhibit reprocessability. This temporary nature of the crosslinking can, of course, also be a disadvantage since the materials are rubber-like only so long as the aggregates are not broken up by high temperatures, presence of diluents or plasticizers, etc.

7.1.5 Some Typical Applications

Typical non-biological applications are tires, gaskets, conveyor belts, drive belts, rubber bands, stretch clothing, hoses, balloons and other inflatable devices, membranes, insulators, and encapsulants [23,24]. Biological applications include parts of living organisms (skin, arteries, veins, heart, and lung tissue, etc.), and various biomedical devices (contact lens, prostheses, catheters, drug-deliver systems, etc.) [25,26]. It is interesting to note that most of these applications require only small deformations; relatively few take advantage of the very high extensibility that is characteristic of most elastomeric materials.

Frequently, specific applications require a particular type of elastomer [27]. For example, a hose should have as large a mismatch of solubility parameters with the fluid it will be transporting. Thus, polar elastomers such as polychloroprene would be best for hoses used with hydrocarbon fluids such as gasoline, jet fuel, greases, oils, lubricants, etc.

7.2 Some Experimental Details

7.2.1 Mechanical Properties

The great majority of studies of mechanical properties of elastomers have been carried out in elongation, because of the simplicity of this type of deformation [3,9,28,29]. Results are typically expressed in terms of the nominal stress $f^* =$ chains f/A^* that, in the simplest molecular theories, is given by:

$$f^* = (\upsilon kT/V)(\alpha - \alpha^{-2}) \tag{1}$$

where υ/V is the density of network chains, i.e., their number per unit volume V, k is the Boltzmann constant, T is the absolute temperature, and α is the elongation or relative length of the stretched elastomer. Also frequently employed is the modulus, defined by

$$[f^*] \equiv f^* v_2^{1/3}/(\alpha - \alpha^{-2}) = \upsilon kT/V \tag{2}$$

where v_2 is the volume fraction of polymer in the (possibly swollen) elastomer. There are a smaller number of studies using types of deformation other than elongation, e.g., biaxial extension or compression, shear, and torsion. Some typical studies of this type are mentioned below.

7.2.2 Swelling

This non-mechanical property is also much used to characterize elastomeric materials [1,2,9,21]. It is an unusual deformation in that volume changes are of central importance, rather than being negligible. It is a three-dimensional dilation in which the network absorbs solvent, reaching an equilibrium degree of swelling at which the free energy decrease due to the mixing of the solvent with the network chains is balanced by the free energy increase accompanying the stretching of the chains. In this type of experiment, the network is typically placed into an excess of solvent, which it imbibes until the dilational stretching of the chains prevents further absorption. This equilibrium extent of swelling can be interpreted to yield the degree of crosslinking of the network, provided the polymer—solvent interaction parameter χ is known. Conversely, if the degree of crosslinking is known from an independent experiment, then the interaction parameter can be determined. The equilibrium degree of swelling and its dependence on various parameters and conditions provide, of course, important tests of theory.

The swollen material is of itself of considerable interest, particularly in the case of water-based systems or “hydrogels.” [30] Also of interest are gels formed as a result of having reactants of functionality larger than two as participants in a polymerization process. In these cases, characterizing the gelation process is also of considerable importance, and some relevant simulations have been of interest [31].

7.2.3 Optical and Spectroscopic Properties

An example of a relevant optical property is the birefringence of deformed polymer network [21]. This strain-induced birefringence can be used to characterize segmental orientation, both Gaussian and non-Gaussian elasticity, crystallization and other types of chain ordering, and short-range correlations [2,9]. Other optical and spectroscopic techniques are also important, particularly with regard to segmental orientation. Some examples are fluorescence polarization, deuterium NMR, and polarized infrared spectroscopy [9,32,33].

7.2.4 Scattering

The technique of this type of greatest utility in the study of elastomers is small-angle neutron scattering, e.g., from deuterated chains in a non-deuterated host [9,21,34—38]. One application has been the determination of the degree of randomness of the chain configurations in the undeformed state—an issue of great importance with regard to the basic postulates of elasticity theory. Of even greater importance is determination of the manner in which the dimensions of the chains follow the macroscopic dimensions of the sample, i.e., the degree of “affineness” of the deformation. This relationship between the microscopic and macroscopic levels in an elastomer is one of the central problems in rubber-like elasticity.

Some small-angle X-ray scattering techniques have also been applied to elastomers. Examples are the characterization of fillers precipitated into elastomers, and the corresponding incorporation of elastomers into ceramic matrices—in both cases to improve mechanical properties [9,39—42].

Newer techniques for characterizing elastomers include Brillouin scattering [43], and pulse propagation measurements [44].

7.3 Typical Stress—Strain Behavior

A typical stress—strain isotherm obtained on a strip of crosslinked elastomer such as natural rubber is shown schematically in Figure 7.2 [1—3].

The units for the force are generally Newton, and the curves obtained are usually checked for reversibility. In this type of representation, the area under the curve is frequently of considerable interest since it is proportional to the work of deformation $w = \int f \mathrm{d}L$. Its value up to the rupture point is thus a measure of the toughness of the material [45—47].

The upturn in modulus at high elongation is of particular interest since it corresponds to an increase in toughness. The crystallites act as physical crosslinks, and also as filler particles. They also increase the strain sensed by the chains since the crystallites don't deform at all, in what is known as "strain amplification." [5,48] The upturn is generally due to strain-induced crystallization, resulting from increase in melting point of the network chains. This is, in turn, due to the decreased entropy of the stretched chains and the fact that the melting point is inversely proportional to the entropy of melting. In some cases, however, the upturns can be due to the limited extensibility of the chains. These instances are easy to identify since these upturns will not be diminished by decreasing the amount of crystallilzation by increase in temperature or by addition of a diluent. It is in this sense that the stretching "induces" the crystallization of some of the network chains.

The initial part of the stress—strain isotherm shown in Figure 10.2 is of the expected form in that f^* approaches linearity with α as α becomes sufficiently large to make the subtractive α^{-2} term in Equation (1) negligibly small. The large increase in f^* at high deformation in the particular case of natural rubber is due largely if not entirely to strain-induced crystallization.

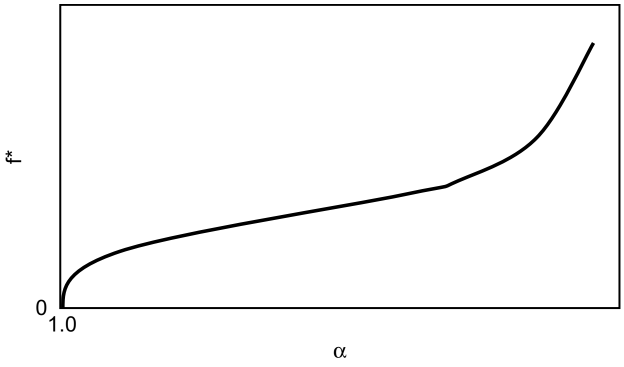

Figure 7.2 Stress-elongation curve for an elastomer showing an upturn in modulus at high elongations.

Additional deviations from theory are found in the region of moderate deformation upon examination of the usual plots of modulus against reciprocal elongation [2,49]. Although Equation (2) predicts the modulus to be independent of elongation, it generally decreases significantly upon increase in α [49]. The intercepts and slopes of such linear plots are generally called the Mooney—Rivlin constants $2C_1$ and $2C_2$, respectively, in the semi-empirical relationship $[f^*] = 2C_1 + 2C_2\alpha^{-1}$. As described above, the more refined molecular theories of rubber-like elasticity [7,50—55] explain this decrease by the gradual increase in the non-affineness of the deformation as the elongation increases toward the phantom limit.

Generally, the isotherm in retraction lies well below the isotherm in elongation, and the area between the two curves is a measure of the energy lost in an elongation—retraction cycle [56]. This phenomenon of "hysteresis" is illustrated in Figure 7.3. It is of considerable importance since the associated "heat build-up" can increase the rate of degradation of an elastomer. The flexing of automobile tires is perhaps the best-known example of this effect.

Although quantities such as toughness are important in essentially all applications of elastomers, some applications require additional properties, as already mentioned. An important example involves soft contact lenses, which also have to be transparent and to be hydrophilic at least on their surfaces in order to ride smoothly on the surface of the eye [57].

7.4 Control of Network Structure

Until recently, there was relatively little reliable quantitative information on the relationship of stress to structure; primarily because of the uncontrolled manner in which elastomeric networks were generally prepared [1—3,9]. Segments close together in space were linked irrespective of

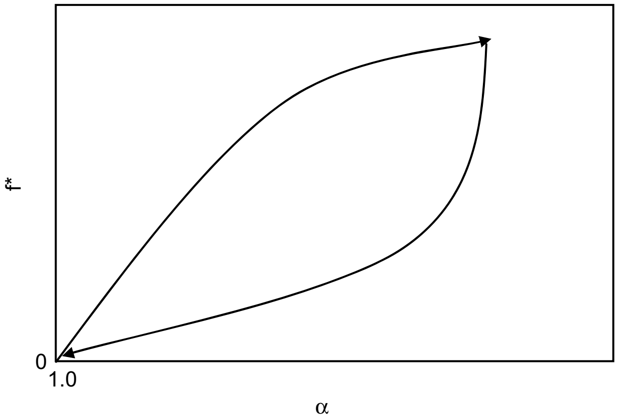

Figure 7.3 Hysteresis in the stress—strain isotherms for the elongation—retraction cycle of an elastomer. The enclosed area between the two curves is a measure of the elastic energy lost as heat.

their locations along the chain trajectories, thus resulting in a highly random network structure in which the number and locations of the crosslinks were essentially unknown. Such a structure is shown in Figure 7.1. New synthetic techniques are now available, however, for the preparation of "model" polymer networks of known structure [3,7,9,58−74]. An example is the reaction in which hydroxyl-terminated chains of PDMS are end-linked using tetraethyl orthosilicate. Characterizing the uncrosslinked chains with respect to molecular weight M_n and molecular weight distribution, and then running the specified reaction to completion gives elastomers in which the network chains have these characteristics, in particular a molecular weight M_c between crosslinks equal to M_n, and crosslinks having the functionality of the end-linking agent.

The end-linking reactions described above can also be used to make networks having unusual chain-length distributions [75−78]. Those having a bimodal distribution are of particular interest with regard to their ultimate properties, as will be described below.

7.5 Networks at Very High Deformations

7.5.1 Non-Gaussian Effects

As already described in Figure 7.2 [1−3], some (unfilled) networks show a large and rather abrupt increase in modulus at high elongations. This increase [79,80] is very important since it corresponds to a significant toughening of the elastomer. Its molecular origin, however, has been the source of considerable controversy [2,9,79,81−87]. It could be due to either the "limited extensibility" of the network chains (i.e., to an inadequacy in the Gaussian distribution function), or the strain-induced crystallization.

The issue has now been resolved [7,85,88−90], however, by the use of end-linked, non-crystallizable model PDMS networks. These networks have high extensibilities, presumably because of their very low incidence of dangling-chain network irregularities. They have particularly high extensibilities when they are prepared from a mixture of very short chains (molecular weights around a few hundred g mol^{-1}), as further discussed below. In these bimodal elastomers, the very short chains are apparently important because of their limited extensibilities, and the relatively long chains because of their ability to retard the rupture process.

Comparisons of stress−strain measurements on such bimodal PDMS networks with those in crystallizable polymer networks such as natural rubber and *cis*-1,4-polybutadiene were carried out, particularly as a function of temperature and presence of a plasticizing diluent [85,91]. The results showed that the anomalous upturn in modulus observed for crystallizable polymers such as natural rubber is largely if not entirely due to strain-induced crystallization.

7.5.2 Ultimate Properties

The ultimate properties of interest are the tensile strength, maximum extensibility, and toughness (energy to rupture), and all are affected by strain-induced crystallization [88]. The higher the temperature, the lower the extent of crystallization and, correspondingly, the lower the ultimate properties. The effects of increase in swelling parallel those for increase in temperature, since diluent also suppresses network crystallization. For non-crystallizable networks, however, neither change is very important, as is illustrated by the results reported for PDMS networks [92].

In the case of such non-crystallizable, unfilled elastomers, the mechanism for network rupture has been elucidated to a great extent by studies of model networks similar to those already described. For example, values of the modulus of bimodal networks formed by end-linking mixtures of very short and relatively long chains as illustrated in Figure 7.4 were used to test the "weakest-link" theory [7] in which rupture was thought to be initiated by the shortest chains (because of their very limited extensibility). It was observed that increasing the number of very short chains did *not* significantly decrease the ultimate properties. The reason [85] is the very non-affine nature of the deformation at such high elongations. The network simply reapportions the increasing strain among the polymer chains until no further reapportioning is possible. It is generally only at this point that chain scission begins, leading to rupture of the elastomer. The weakest-link theory implicitly assumes an affine deformation, which leads to the prediction that the elongation at which the modulus increases should be independent of the number of short chains in the network. This assumption is contradicted by relevant experimental results, which show very different behavior [85]; the smaller the number of short

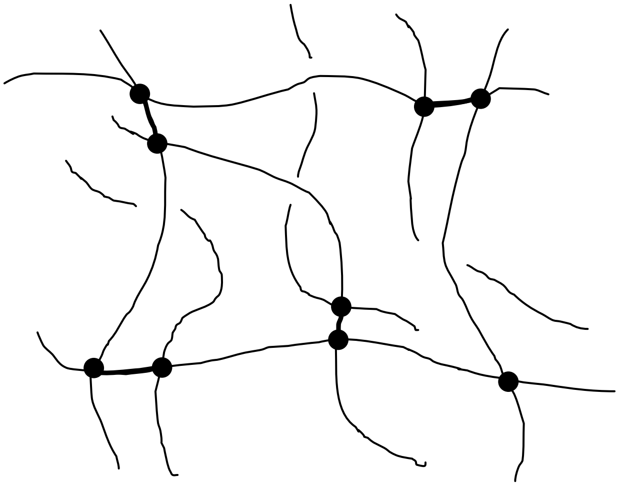

Figure 7.4 Sketch of a network having a bimodal distribution of network chain lengths. The very short and relatively long chains are arbitrarily shown by the thick and thin lines, respectively.

chains, the easier the reapportioning and the higher the elongation required to bring about the upturn in modulus.

7.6 Multimodal Chain-Length Distributions

As already mentioned, there turns out to be an exciting bonus if one forms a multimodal distribution of network chain lengths by end linking a very large number of short chains into a long-chain network. The ultimate properties are then actually improved! Bimodal networks prepared by these end-linking techniques have very good ultimate properties, and there is currently much interest in preparing and characterizing such networks [9,67,74,93–102], and developing theoretical interpretations for their properties [103–108]. The types of improvements obtained are shown schematically in Figure 7.5. The results are represented in such a way that the area under a stress–strain isotherm corresponds to the energy required to rupture the network. If the network consists of all short chains that are brittle, it means that the maximum extensibility is very small. If the network consists of all long chains, the ultimate strength is very low. In neither case the material is a tough elastomer because the areas under the curves are relatively small. As can readily be seen from the figure, the bimodal networks are much improved elastomers in that they can have a high ultimate strength without the usual decrease in maximum extensibility.

A series of experiments were carried out in an attempt to determine if this reinforcing effect in bimodal PDMS networks could possibly be due to some intermolecular effect such as strain-induced crystallization. In the first such experiment, temperature was found to have little effect on the isotherms [77]. This strongly argues against the presence of any crystallization or other type of intermolecular ordering. So also do the results of stress-temperature and birefringence-temperature measurements [77]. In a final experiment, the short chains were pre-reacted in a two-step preparative technique so as to possibly segregate them in the network structure [75,91] as might occur in a network crosslinked by an incompletely soluble peroxide. This had very little effect on elastomeric properties—again arguing against any type of intermolecular organization as the origin for the reinforcing effects. Apparently, the observed increases in modulus are due to the limited chain extensibility of the short chains, with the long chains serving to retard the rupture process. This can be thought of in terms of what executives like to call a "delegation of responsibilities."

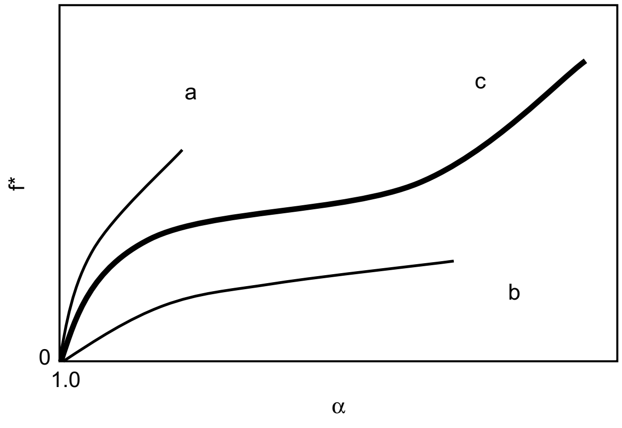

Figure 7.5 Typical plots of nominal stress against elongation for unimodal and bimodal networks obtained by end linking relatively long chains and very short chains. Curve *a* is for a unimodal network of all short chains, curve *b* is for a unimodal network of all long chains, and curve *c* is for a bimodal network of short and long chains. The area under each curve represents the rupture energy (a measure of the "toughness" of the elastomer).

There is an another advantage to such bimodality when the network can undergo strain-induced crystallization; the occurrence of which can provide an additional toughening effect [109]. Decrease in temperature was found to increase the extent to which the values of the ultimate strength of at least some bimodal networks exceed those of the corresponding unimodal ones. This suggests that bimodality facilitates strain-induced crystallization.

In practical terms, the above results demonstrate that short chains of limited extensibility may be bonded into a long-chain network to improve its toughness. It is also possible to achieve the converse effect. Thus, bonding a small number of relatively long elastomeric chains into a relatively hard short-chain PDMS thermoset greatly improves its impact resistance [110].

Since dangling chains represent imperfections in a network structure, one would expect their presence to have a detrimental effect on the ultimate properties and $\alpha_{r,}$ $(f/A^*)_r$ of an elastomer. This expectation is confirmed by an extensive series of results obtained on PDMS networks which had been tetrafunctionally crosslinked using a variety of techniques [111]. The largest values of the ultimate strength $(f/A^*)_r$ were obtained for the networks prepared by selectively joining functional groups occurring either as chain ends or as side groups along the chains. This is to be expected, because of the relatively low incidence of dangling ends in such networks. Also as expected, the lowest values of the ultimate properties generally occurred for networks cured by radiation (UV light, high-energy electrons, and γ radiation) [111]. The peroxide-cured networks were generally intermediate to these two extremes, with the ultimate properties presumably depending on whether or not the free radicals generated by the peroxide are sufficiently reactive to cause some chain scission. Similar results were obtained for the maximum extensibility α_r [111]. These results were supported by more definitive results obtained by investigation of a series of model networks prepared by end-linking vinyl-terminated PDMS chains [111].

7.7 Other Types of Deformation

7.7.1 Biaxial Extension

There are numerous other deformations of interest, including compression, biaxial extension, shear, and torsion [1,2]. Some of these deformations are considerably more difficult to study experimentally than simple elongation and, unfortunately, have therefore not been as extensively investigated.

Measurements in biaxial extension are of particular importance since they are important in packaging applications. This deformation can be imposed by the direct stretching of a sample sheet in two perpendicular directions within its plane, by two independently variable amounts. In the equi-biaxial case, the deformation is equivalent to compression. Such experimental results [112] have been successfully interpreted in terms of molecular theories [7,9].

Biaxial extension studies can also be carried out by the inflation of sheets of the elastomer [2]. Upturns in the modulus [113] were seen to occur at high biaxial extensions, as expected.

7.7.2 Shear

Experimental results on natural rubber networks in shear [114] are not well accounted for by the simple molecular theory of rubber-like elasticity. The constrained-junction theory, however, was found to give excellent agreement with experiment [7]. The upturns in modulus in shear [115] were found to be very similar to those obtained in elongation.

7.7.3 Torsion

Very little work has been done on elastomers in torsion. There are, however, some results on stress—strain behavior and network thermoelasticity [2,116]. More results are presumably forthcoming, particularly on the unusual bimodal networks and on networks containing some of the unusual in situ generated fillers described below.

7.7.4 Swelling

Most studies of networks in swelling equilibrium give values for the crosslink density or related quantities that are in satisfactory agreement with those obtained from mechanical property measurements [1,2].

A more interesting area involving some swollen networks or “gels” is their abrupt collapse (decrease in volume) upon relatively minor changes in temperature, pH, solvent composition, etc. [7,9,117,118]. Although the collapse is quite slow in large, monolithic pieces of gel, it is rapid enough in fibers and films to make the phenomenon interesting with regard to the construction of switches and related devices.

Gels are also formed, of course, when elastomers are used to absorb liquids, e.g. in diapers and in attempts to control oil spills over bodies of water.

7.8 Filler-Reinforced Elastomers and Elastomer-Modified Ceramics

One class of multi-phase elastomers are those capable of undergoing strain-induced crystallization, as was mentioned above. In this case, the second phase is made up of the crystallites thus generated, which provide considerable reinforcement. Such reinforcement is only temporary, however, in that it may disappear upon removal of the strain, addition of a plasticizer, or increase in temperature. For this reason, many elastomers (particularly those which cannot undergo strain-induced crystallization) are generally compounded with a permanent reinforcing filler [5,7,9,119—132]. The two most important examples are the addition of carbon black to natural rubber and to some synthetic elastomers [121,123,133], and the addition of silica to siloxane elastomers [122]. In fact, the reinforcement of natural rubber and related materials is one of the most important processes in elastomer technology. It leads to increases in modulus at a given strain, and improvements of various technologically important properties such as tear and abrasion resistance, resilience, extensibility, and tensile strength [121,123,125,128,134—137]. There are also disadvantages, however, including increases in hysteresis (and thus of heat build-up), and compression set (permanent deformation).

There is an incredible amount of relevant experimental data available, with most of these data relating to reinforcement of natural rubber by carbon black [123,125,134,138]. Recently, however, other polymers such as PDMS, and other fillers, such as precipitated silica, metallic particles, and even glassy polymers, have become of interest [6,39,55,139—174].

The most important unsolved problem in this area is the nature of the bonding between the filler particles and the polymer chains [137]. The network chains may adsorb strongly onto the particle surfaces, which would increase the effective degree of crosslinking. This effect will be especially strong if particles contain some reactive surface groups which may crosslink (or end link) the polymer chains. Chemisorption, with permanent chemical bonding between filler particles and polymer chains, can be dominant, particularly if the filler is precipitated into the elastomer in situ during curing [39,142,143,161]. Another type of adsorption which can occur at a filler surface is physisorption, arising from long-range van der Waals forces between the surface and the polymer. Contrary to chemisorption, this physical adsorption does not severely restrict the movement of polymer chains relative to the filler surface when high stresses are applied. The available experimental data suggest that both chemisorption and physisorption contribute to reinforcement phenomena, and that the optimal degree of chemical bonding is quite low (of the order 0.2 bonding sites per nm^2) [128]. Excessive covalent bonding, leading to immobilization of the polymer at the filler surface, is highly undesirable. A filler particle may thus be considered a crosslink of very high functionality, but transient in that it can participate in molecular rearrangements under strain.

There are probably numerous other ways in which a filler changes the mechanical properties of an elastomer—some of admittedly minor consequence [5,137]. For example, another factor involves changes in the distribution of end-to-end vectors of the chains due to the volume taken up by the filler [136,137,175—178]. This effect is obviously closely related to the adsorption of polymer chains onto filler surfaces, but the surface also effectively segregates the molecules in its vicinity and reduces entanglements. Another important aspect of filler reinforcement arises from the fact that the particles influence not only an elastomer's static properties (such as the distribution of its end-to-end vectors), but also its dynamic properties (such as network chain mobility). More specifically, the presence of fillers reduces the segmental mobility of the adsorbed polymer chains to the extent that layers of elastomer close to the filler particles are frequently referred to as "bound rubber." [179—182]

As is obvious from the above comments, the mechanism of the reinforcement is only poorly understood. Some elucidation might be obtained by precipitating reinforcing fillers into network structures rather than blending badly agglomerated fillers into the polymers prior to their crosslinking. This has, in fact, been done for a variety of fillers, e.g. silica by hydrolysis of organosilicates, titania from titanates, alumina from aluminates, etc. [7,9,141,143,173,174]. A typical, and important, reaction is the acid- or base-catalyzed hydrolysis of tetraethyl orthosilicate:

$$Si(OC_2H_5)_4 + 2H_2O \rightarrow SiO_2 + 4C_2H_5OH \quad (3)$$

Reactions of this type are much used by the ceramists in the new sol-gel chemical route to high-performance ceramics [183—192]. In the ceramics area, the advantages are the possibility of using low temperatures, the purity of the products, the control of ultrastructure (at the nanometer level), and the relative ease of forming ceramic alloys. In the elastomer reinforcement area, the advantages include the avoidance of the difficult, time-consuming, and energy-intensive process of blending agglomerated filler into high molecular weight and high-viscosity polymers, and the ease of obtaining extremely good dispersions.

In the simplest approach to obtaining elastomer reinforcement, some of the organosilicate material is absorbed into the crosslinked network, and the swollen sample placed into water containing the catalyst, typically a volatile base such as ammonia or ethylamine. Hydrolysis to form the desired silica-like particles proceeds rapidly at room temperature to yield the order of 50 wt% filler in less than an hour [7,9,141,143,190].

Impressive levels of reinforcement can be obtained by this in situ technique [7,40,41]. The modulus [f^*] generally increases substantially, and some stress—strain isotherms show the upturns at high elongation that are the signature of good reinforcement. As it generally occurs in filled elastomers, there can be considerable irreversibility in the isotherms, which is thought to be due to irrecoverable sliding of the chains over the surfaces of the filler particles.

If the hydrolyzes in organosilicate-polymer systems are carried out with increased amounts of the silicate, bicontinuous phases can be obtained (with the silica and polymer phases interpenetrating one another) [39]. At still-higher concentrations of the silicate, the silica generated becomes the continuous phase, with the polymer dispersed in it [7,193—207]. The result is a polymer-modified ceramic, variously called an "Ormocer," [193—195] "Ceramer," [196—198] or "Polyceram" [202—204]. It is obviously of considerable importance to determine how the polymeric phase, often elastomeric, improves the mechanical properties of the ceramic in which it is dispersed.

A variety of silica particle shapes can be obtained by biomimicry, using some of the reactions Nature uses in the biosilicification process [208].

In the areas of theory and simulations, there is also considerable interest in obtaining a better molecular understanding of structure—property relationships in this area, particularly the reinforcement of elastomers by filler particles of various types [176,177,209,210].

7.9 Current Problems and Future Trends

There is a real need for more high-performance elastomers, which are materials that remain elastomeric to very low temperatures and are relatively stable at very high temperatures. Some phosphazene polymers, [—PRR'N—] [211—213], are in this category. These polymers have rather low glass transition temperatures in spite of the fact that the skeletal bonds of the chains are thought to have some double-bond character. There are thus a number of interesting problems related to the elastomeric behavior of these unusual semi-inorganic polymers. There is also an increasing interest in the study of elastomers that also exhibit mesomorphic behavior [7].

A particularly challenging problem is the development of a more quantitative molecular understanding [214—217] of the effects of filler particles, in particular carbon black in natural rubber and silica in siloxane polymers [121,123,218,219]. Such fillers provide tremendous reinforcement in elastomers in general, and how they do this is still only poorly comprehended. A related but even more complex problem involves much the same components, namely one that is organic and one that is inorganic. When one or both components are generated in situ, however, there is an almost unlimited variety of structures and morphologies that can be generated [7]. How physical properties such as elastomeric behavior depend on these variables is obviously a challenging but very important problem.

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8 Nanocomposites: Preparation, Structure, and Properties

József Hári [1,2] ***and Béla Pukánszky*** [1,2]
[1] Laboratory of Plastics and Rubber Technology, Department of Physical Chemistry and Materials Science, Budapest University of Technology and Economics, H-1521 Budapest, Hungary
[2] Institute of Materials and Environmental Chemistry, Chemical Research Center, Hungarian Academy of Sciences, H-1525 Budapest, Hungary

8.1 Introduction

One of the buzz words in the technical world including polymer science is nano with all the positive and negative consequences. In recent years practically everything became "nano" even materials which are around for more than a hundred years like carbon black used for the reinforcement of rubbers. Many laboratories launched projects on composites containing particles in the nanometer scale with variable extent of success. The general idea of nanocomposites is based on the concept of creating a very large interface between the nanosized-building blocks and the polymer matrix. However, the properties of nanocomposites are not determined only by the size of the interface, but other factors like structure and interactions also play an important role. Very often already the homogeneous distribution of the nanosized particles is problematic, i.e., the expected large interface cannot be always created, but the adjustment of the proper interaction or coupling of the components presents further problems.

Nanocomposites can be classified in many ways; in this chapter we discuss them according to the dimensionality of the nanosized heterogeneity. The size is in the nanometer range in all three dimensions for particles like silica (SiO_2), titanium dioxide (TiO_2), calcium carbonate ($CaCO_3$), or polyhedral oligomeric silsesquioxane (POSS); nanotubes and fibers are small in two dimensions but can be micrometer long; while the individual platelets of layered silicates are approximately 1 nm thick, their other two dimensions are usually much larger. As mentioned above, nanocomposites often do not meet the expectations and possess much inferior properties than expected. In any composite, the conditions for considerable reinforcement and good properties are the homogeneous distribution of the reinforcing component, high aspect ratio, orientation, and good adhesion. Unfortunately, these conditions are rarely fulfilled—thus the inferior performance should not be surprising. The main problems of nanocomposites are usually the homogeneous distribution of the particles in the polymer matrix and interfacial interactions. Compared to the basic idea behind nanocomposites, interfacial interactions are treated rather superficially—the available information is limited and very often contradictory. Very little unambiguous information exists about the relationships among the interaction of a coated nanoparticle surface, the size and characteristics of the available uncoated area, the strength of interfacial adhesion, and the macroscopic properties of the nanocomposites.

Considering all these aspects, we focus our attention mainly on these issues in this chapter. Unlike many others, we assume that in spite of particular differences, the general rules of heterogeneous materials apply also for nanocomposites, and their properties are determined by the same factors. In several sections we discuss information published in the literature, which are very often misleading, as e.g., miscibility, in our opinion. We also mention some factors, which are largely neglected during the discussion of nanocomposite preparation, structure, and properties. Our views occasionally do not agree with generally accepted beliefs, but we find it important to point out contradictions, to raise doubt, and call attention to questions, which are neglected or not studied in sufficient detail.

8.2 Factors Determining the Properties of Heterogeneous Polymer Systems

As mentioned in the Section 8.1 the same factors determine the properties of all heterogeneous polymers including nanocomposites: the characteristics of the components, composition, structure, and interfacial interactions. All four are equally important and must be adjusted to achieve optimum properties. However, nanocomposites differ somewhat from traditional particulate-filled microcomposites—their structure is often more complicated and interactions are less well defined.

8.2.1 Component Properties

The characteristics of the matrix influence strongly the effect of a filler on composite properties; reinforcement increases with decreasing matrix stiffness both in micro and nanocomposites. In elastomers true reinforcement takes place—both stiffness and strength increase [1]. This effect is demonstrated well by Figure 8.1, in which the stiffness of two

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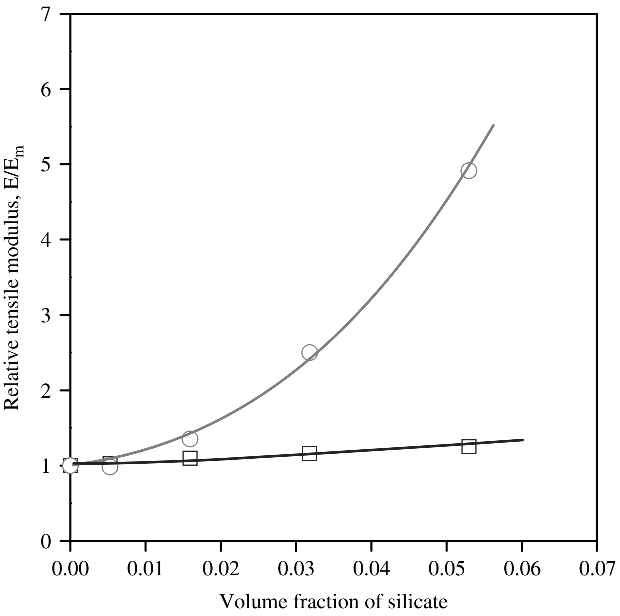

Figure 8.1 Effect of matrix characteristics on the reinforcing effect of layered silicates in epoxy nanocomposites. Symbols: (○) elastomer, (□) glass [2].

epoxy resin nanocomposites is plotted against filler content. The modulus of the elastomer increases significantly, while only moderate reinforcement occurs in the glassy polymer [2]. For the sake of easier comparison the data were plotted on a relative scale—composite stiffness was related to the modulus of the matrix.

The structure of crystalline polymers may be significantly modified by the introduction of fillers. Crystallite and spherulite size, as well as crystallinity, all change as an effect of nucleation [3]. Layered silicates, and especially montmorillonite (MMT), were shown to nucleate polypropylene (PP) quite strongly [4—8]. One study showed that organophilization decreased the nucleating efficiency of MMT assigned to the presence of nonexfoliated stacks or particles [4]. Nucleation increases crystallization temperature that usually leads to the increase of lamella thickness and crystallinity and to the decrease of the size of the spherulites with the result of increased stiffness and decreased impact resistance of the final product [9]. Nucleation may also change the predominant crystal modification of the polymer. In the presence of MMT, polyamide (PA) was shown to crystallize mainly in the γ form [10—16] irrespective of organophilization as shown by Figure 8.2 [17]. Different crystal modifications usually possess dissimilar properties [18].

Numerous filler characteristics influence the properties of composites [19,20]. Chemical composition and especially the purity of the filler have both a direct and an indirect effect on its application possibilities and performance. Traces of heavy-metal contamination decrease stability. Insufficient purity leads to discoloration. Accompanying minerals in layered silicates do not exfoliate, and if their particle size is large, they deteriorate composite properties already at very small filler contents.

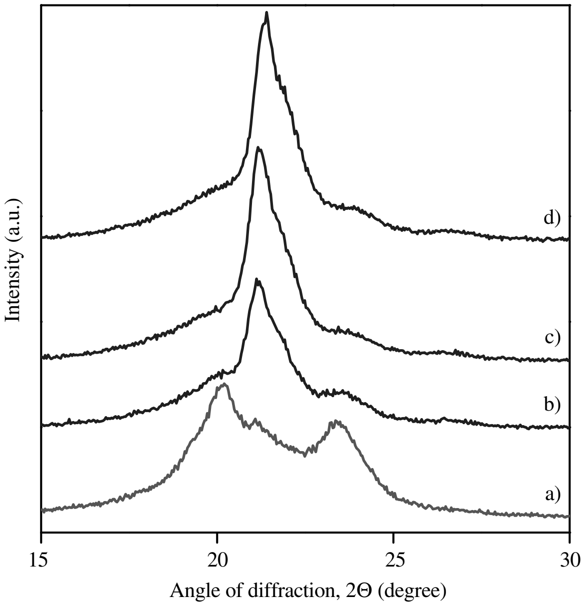

Figure 8.2 Formation of the γ modification in PA/clay nanocomposites. a) PA, b) PA/NaMMT, c) PA/Nanofil 948 (aliphatic amine), d) PA/Nanofil 784 (ω-amino acid). Silicate content 2 vol%.

The mechanical properties of particulate-filled composites are determined mainly by their particle characteristics, i.e., particle size and particle size distribution. Strength, sometimes modulus increase, deformability, and impact strength usually decrease with decreasing particle size. The knowledge of the particle size distribution is equally important [21]. Large particles easily debond from the matrix under loading, while the aggregation tendency of fillers increases with decreasing particle size. This aspect is especially important in nanocomposites containing spherical nanoparticles, nanotubes, and fibers. Extensive aggregation leads to insufficient homogeneity, rigidity, and low impact strength. Aggregated filler particles often act as crack-initiation sites under dynamic loading conditions demonstrated well by Figure 8.3 showing the failure of a large $CaCO_3$ aggregate of nanosized particles formed in a PP matrix. Rather surprisingly, the particle size of the original silicate is almost never considered as a factor during the preparation of layered silicate nanocomposites. The formation of an intercalated or exfoliated structure is claimed practically always [22—25]. However, the kinetics and extent of exfoliation must depend on particle size, on the one hand, while nonexfoliated large particles may deteriorate properties considerably, on the other hand.

The specific surface area of fillers has direct impact on composite properties. Adsorption of both small molecular weight additives and that of the polymer is proportional to the size of the matrix/filler interface [19]. Adsorption of additives may change stability, while matrix/filler interaction significantly influences mechanical properties, first of all yield stress, tensile strength, and fracture resistance [26,27]. The specific surface area of completely exfoliated silicates is extremely

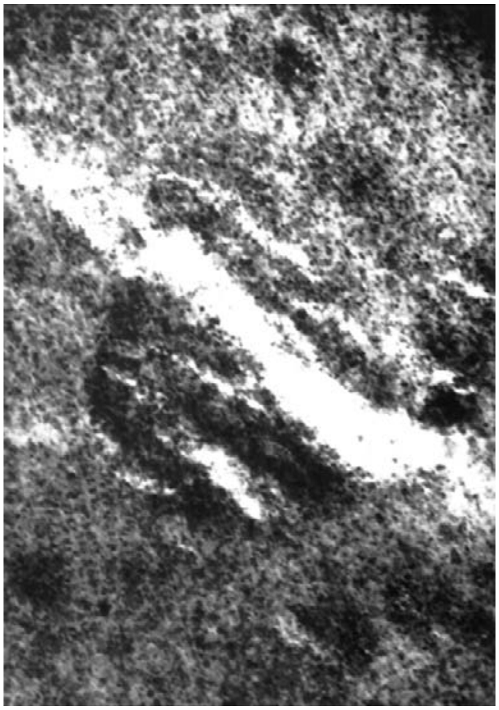

Figure 8.3 Inferior strength and fracture of a $CaCO_3$ aggregate consisting of 80 nm large primary particles under the effect of external load.

large, around 750 m^2/g for MMT [28,29], and that of carbon nanotubes (CNTs) or spherical particles, like carbon black and SiO_2, may be in the same range. Strong interaction of the polymer with this surface would lead to very stiff and brittle composites. However, stiffness and fracture resistance usually stay within acceptable limits that raise some doubts about homogeneous particle distribution, complete exfoliation, and strong interaction.

Anisotropic particles reinforce polymers and the effect increases with aspect ratio. Plate-like fillers reinforce polymers more than spherical fillers and the influence of fibrous reinforcements is even stronger [30]. Anisotropic fillers orientate during processing further enhancing their reinforcing effect, which depends very much also on the distribution of orientation. Completely exfoliated silicates should have an aspect ratio of 100−1000, which would lead to extremely strong reinforcement. Since such an effect is rarely observed, one of the conditions is probably not fulfilled, i.e., exfoliation, orientation, or adhesion. Achieving large extent of orientation is one of the main issues in nanotube- or nanofiber-reinforced composites as well.

Surface free energy (surface tension) of the fillers determines both matrix/filler and particle/particle interaction. The former has a pronounced effect on mechanical properties, while the latter determines aggregation. Both interactions can be modified by surface treatment. The role of surface free energy is especially contradictory in layered silicate nanocomposites. Practically, always organophilic silicates are used in the composites and the number of possible interactions (matrix/silicate, matrix/surfactant, silicate/surfactant, silicate aggregation, edge-to-edge interaction of individual platelets, etc.) is much larger than in traditional microcomposites. Interaction is an important question in other kinds of nanocomposites as well shown also by the numerous attempts to modify or functionalize CNTs.

8.2.2 Composition

Composition, i.e., the filler content of composites, may change in a wide range in microcomposites, but according to the general idea of nanocomposites the amount of nanosized fillers used in them is much smaller. Numerous models are available which describe the composition dependence of various composite properties [20,30−34]. Composite characteristics may be predicted and optimized with the help of these models. In traditional microcomposites the goal of modification is either to decrease price or to improve properties. Nanocomposites differ strongly from these on several points. The price of nanofillers including organophilic silicates and CNTs is high; economy cannot be the goal of their application. The amount used is another question to be considered. Although they are used in relatively small amounts, occasionally even these might be too large. Properties were shown to change or level off below 10 wt% filler content, and interaction of particles was observed already at 0.3 vol% [35]. Finally, most nanofillers are usually added on a weight basis for some reason, although volume fraction determines properties just like in all heterogeneous systems. At least modeling must be done on this basis.

8.2.3 Structure

The structure of particulate-filled polymers seems to be simple, homogeneous distribution of particles is assumed in most cases. This, however, rarely occurs and often special, particle-related structures develop in the composites. The most important of these are aggregation and the orientation of anisotropic filler particles. The structure of layered silicate nanocomposites is also considered to be rather simple—usually the formation of intercalated and/or exfoliated structure is claimed in a large number of papers [22−25, 32,33,36]. However, ample evidence shows that structure is usually much more complicated than assumed and structural units of various length scales might be present simultaneously in the composites [37]. Aggregation is a major issue in composites containing spherical nanoparticles, while both aggregation and orientation must be considered in those prepared with nanotubes or fibers.

8.2.4 Interactions

In composites particle/particle interactions induce aggregation, while matrix/filler interaction leads to the development of an interphase with properties different from those of both components [38,39]. The principles are valid also for nanocomposites. However, interactions are more complicated in layered silicate nanocomposites. In silicate, the considerable amount of surfactant used and the polymer may interact in various extent and ways. Silicate particles and platelets may aggregate, the polymer can dissolve the surfactant, and even chemical reactions may take place in the composite during homogenization. Most of these questions will be addressed in various details in following sections.

8.3 Nanocomposite Structure

Homogeneous dispersion of nanoparticles is the primary condition of the preparation of nanocomposites with acceptable properties. Parallel alignment of the reinforcement with the external load as well as good adhesion are further conditions to be met, if the particles are anisotropic (layered silicates, nanotubes) and the composite is used in load-bearing application. Moreover, extensive exfoliation is a further requirement in layered silicate nanocomposites [32,40−44], which is often difficult to achieve, since the kinetics of exfoliation depends on many factors and the structure formed in the process is usually quite complicated. The complexity of structure and the factors determining it change from one nanocomposite to the other; thus structure is discussed according to the type of reinforcement.

8.3.1 Layered Silicate Nanocomposites

The structure of polymer/layered silicate nanocomposites differs from that prepared with the other two reinforcements discussed here, i.e., CNTs and spherical nanocomposites, in two aspects. In order to prepare layered silicate nanocomposites, the silicate must be exfoliated—the original particles separated to individual layers. The other difference is the complexity of the structure, which may contain several structural entities with different dimensions. Accordingly, the structure of these composites must be considered and studied at a very wide length scale from the nanometer range to microns.

8.3.1.1 Particle structure

The existence of original clay particles is hardly ever mentioned in studies on nanocomposites [45−54]. One may deduce from this fact that particles are not present in the composites; i.e., they break down to smaller units, into intercalated stacks or to individual platelets during mixing. This is not very surprising since mostly X-ray diffraction (XRD) measurements and transmission electron microscopy (TEM) are used for the characterization of the composites and those do not necessarily detect the presence of large particles. The problem regarding the use of XRD is illustrated by Figure 8.4, in which the lower 2θ range of the XRD trace of two PP composites is presented. It is well known that PP nanocomposites cannot be prepared by the simple melt compounding of PP and an organophilic silicate. Exfoliation does not take place in these composites and the silicate is dispersed in the matrix as large particles. In order to facilitate exfoliation a coupling agent, usually maleic anhydride- or acrylic acid-grafted PP (MAPP or AAPP) is added to the combination of PP and organophilized montmorillonite (OMMT) [55,62]. Accordingly, the reflection of the silicate is shown clearly in the XRD trace of the PP/OMMT composite prepared with 2 vol% silicate (modified with stearyl amine, Nanofil 848) without MAPP (trace a). The incorporation of 20 vol% MAPP into the same composite leads to the complete disappearance of the silicate peak (trace b). Based on these results one could claim that the original particles disappeared and the silicate is completely exfoliated. Such conclusions were drawn by some groups from the results of XRD studies based on similar traces [44,56,63,64].

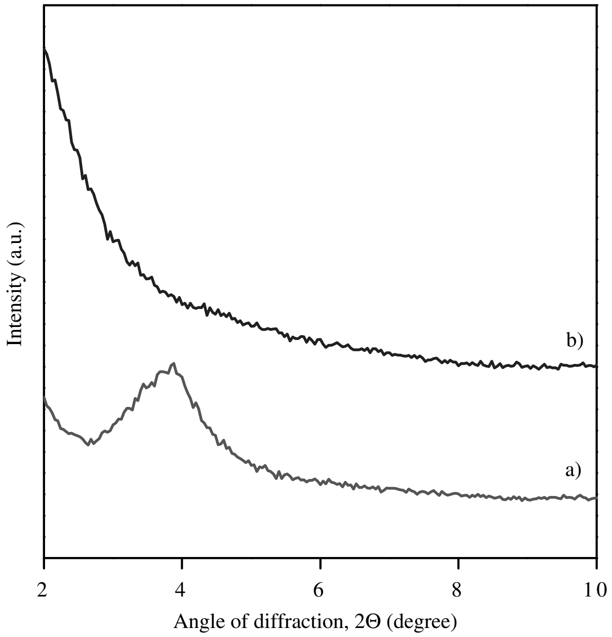

Figure 8.4 XRD traces of PP nanocomposites containing 2 vol% silicate (N848); a) PP/OMMT, b) PP/OMMT/MAPP(20 vol%).

Figure 8.5 completely contradicts the above conclusion drawn from trace b. Scanning electron micrographs (SEM) taken from the etched surfaces of PP/OMMT (Figure 8.5a) and PP/OMMT/MAPP (Figure 8.5b) composites show a distinct particulate structure in both cases. Large particles are dispersed in PP in the PP/OMMT composite not containing any functionalized polymer and also the interfaces are rather distinct; the wetting and/or adhesion of the components seem to be rather poor. The presence of MAPP clearly changes the morphology.

The number of large particles decreases drastically, but a very large amount of smaller particles appears together with one or two larger ones in the 5−10 μm range. The interfaces are much less distinct than in the previous case. Both changing particle size and the modification of the interface

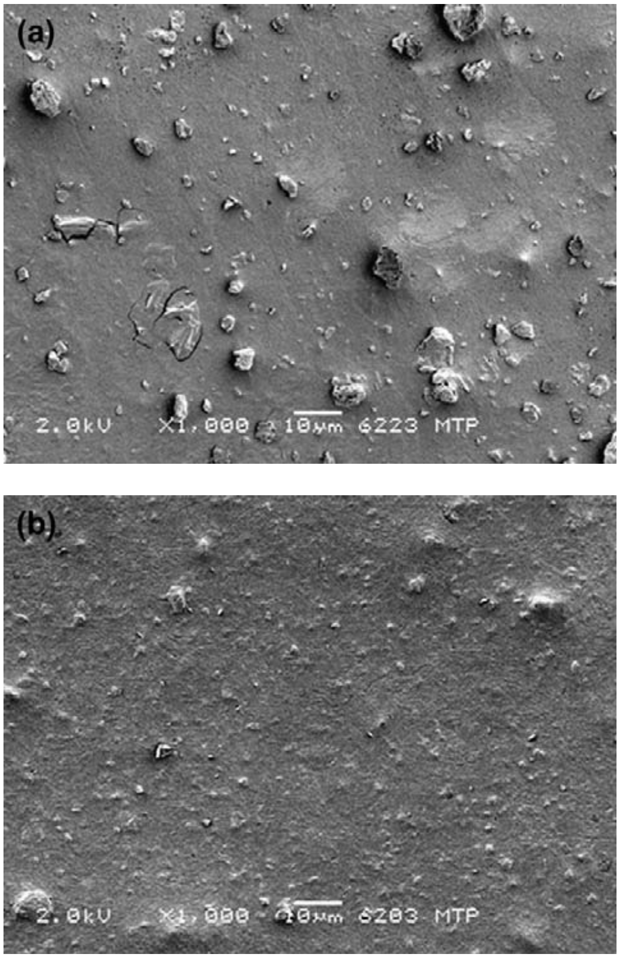

Figure 8.5 SEM micrographs taken from the etched surface of PP nanocomposites containing 2 vol% organophilic clay. a) PP/OMMT, b) PP/OMMT/MAPP(20 vol%).

indicate that MAPP helps to break down particles and modifies interfacial interactions. Nevertheless, it can be safely stated that in spite of the absence of the silicate reflection in the corresponding XRD pattern (Figure 8.4, trace b), complete exfoliation has not been achieved, and clay particles in the length scale of microns are also present in the composite. Their amount and size must strongly influence all properties. Luduena et al [49]. observed similar phenomena in polycaprolactone/OMMT composites; although the silicate reflection disappeared from the XRD pattern, large, micron-sized particles were found in them by SEM.

8.3.1.2 Gallery structure

In most cases not neat sodium montmorillonite (NaMMT), but organically modified silicate is used for the preparation of polymer/layered silicate nanocomposites. Solvated inorganic cations located in the galleries of layered silicates are exchanged to organic cations of long-chain ammonium salts in order to separate the layers [65,66]. Increased gallery distance and decreased surface energy should lead to easier exfoliation. As a consequence, the amount of surfactant located in the galleries and the orientation of the molecules should influence the structure and properties of layered silicate/polymer nanocomposites significantly.

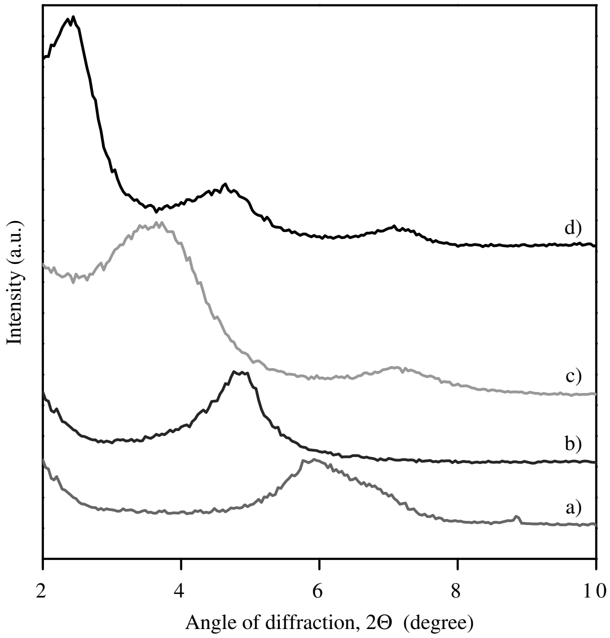

Figure 8.6 XRD traces of four silicates. a) NaMMT, b) Nanofil 848 (stearyl-amine), c) Cloisite 20A (distearyl-dimethyl-ammonium chloride), d) Nanofil 948 (distearyl-dimethyl-ammonium chloride).

The gallery distance of silicates is routinely determined by XRD. Layer distance is inversely proportional to the position of the silicate reflection recorded at low 2θ angles. XRD traces are presented in Figure 8.6 for four commercial silicates. Large differences can be observed in the number, shape, intensity, and location of the silicate reflection. NaMMT produces a low intensity reflection at large 2θ angle (trace a). The position of this peak depends on the water content of the clay, which is usually considerable. The high intensity peak detected at low 2θ angle for Nanofil 948, as well as the two smaller interference peaks, indicates large gallery distance and a high degree of regularity for this silicate (trace d). Interestingly, Cloisite 20A was modified with the same surfactant, but its XRD pattern differs significantly (see trace c) from that of Nanofil 948. Obviously, besides the type of the surfactant some other factor, probably its amount, also influences the gallery structure of the silicate. The gallery distance of the clay organophilized with stearyl amine is smaller than that of the other two OMMTs indicating a different arrangement of this surfactant in the galleries (trace b).

Several studies were carried out to investigate the effect of the type and amount of the surfactant on exfoliation and on the properties of composites [33,44,67,68], but relatively little attention is paid to the gallery structure of the original OMMT. This issue was investigated in a recent study [69].

Table 8.1 Type and amount of surfactant used for the organophilization of several commercial silicates and for the preparation of a laboratory product (CPClMMT)

		Surfactant		
Name	**Abbreviation**	**Chemical Name**	**Composition**	**Amount (wt%)**
NaMMT	NaMMT	–	–	0
OMMT	CPClMMT	*N*-cetyl-pyridinium chloride	$C_6H_5N^+ (CH_2)_{15}CH_3Cl^-$	22
Nanofil 784	N784	12-amino-dodecanoic acid	$NH_2(CH_2)_{11}COOH$	20
Nanofil 804	N804	Stearyl-dihidroxyethyl-ammonium chloride	$CH_3(CH_2)_{17}NH^+(C_2H_4OH)_2Cl^-$	30
Nanofil 848	N848	Stearyl amine	$CH_3(CH_2)_{17}NH_2$	25
Nanofil 919	N919	Stearyl-benzyl-dimethyl-ammonium chloride	$CH_3(CH_2)_{17}N^+(CH_3)_2C_6H_5Cl^-$	35
Nanofil 948	N948	Distearyl-dimethyl-ammonium chloride	$[CH_3(CH_2)_{17}]_2N^+(CH_3)_2Cl^-$	45
Cloisite 20A	C20A	Bis(H[a] tallow alkyl)dimethyl-ammonium chloride	$[CH_3(CH_2)_{13-17}]_2N^+(CH_3)_2Cl^-$	38

[a] *Hydrogenated*

Table 8.2 Gallery structure of the layered silicates listed in Table 8.1

	Gallery Structure		**Surfactant**			
Silicate	**Peak (2θ) (°)**	**Distance (nm)**	**Length (nm)**	**Occupied Surface (nm^2)**	**Thickness (nm)**	**No. of Chains**
NaMMT	9.0	1.0	–	–		0
CPClMMT	5.0	1.8	2.5	1.24	0.43	2
N784	5.2	1.7	2.0	0.86	0.43	2
N804	4.9	1.8	2.7	1.16	0.43	2
N848	4.9	1.8	2.4	1.03	0.43	2
N919	4.4	2.0	2.7	1.16	0.61	2
N948	2.5	3.5	2.7	1.16	2.54[a]	6
C20A	3.3	2.7	2.7	1.16	2.54	4

[a] *In this case, the length of the alkyl chain, which acts as spacer (see Figure 8.7c).*

The type and amount of surfactant used for organophilization is listed in Table 8.1, while the location of the characteristic silicate reflection and the gallery distance calculated from it are summarized in Table 8.2. The data on Cloisite 20A were taken from an even more recent study and added to the table. The layer distance for the completely dry silicate and the corresponding XRD reflection is given for NaMMT in the table. The third column of the table shows gallery distances between 1 and 3.5 nm. Different gallery distances may result from dissimilar amounts of surfactant and/or from the different shape or orientation of the organic molecules located in the galleries [70—72].

In order to obtain some idea about the effect of these factors on gallery distance and about the approximate orientation of the surfactant between the galleries of the clay, their shape and size were calculated by the ChemOffice 2004 software. The results are presented in Table 8.2. The comparison of the thickness of the surfactants to the gallery distances derived from the XRD traces leads to the conclusion that two surfactant molecules lay parallel to the surface in most cases (see last column of Table 8.2) that agrees well with the results of most studies done on organically modified layered silicates [65,66,73]. The orientation of the surfactant depends mainly on the ion density of the clay, which is

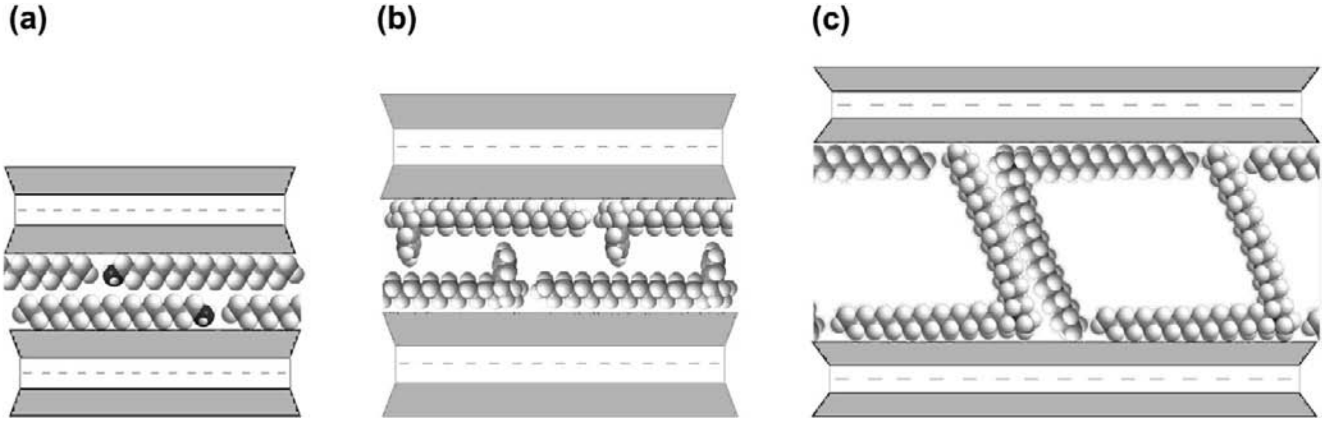

Figure 8.7 Orientation of surfactants among the galleries of montmorillonite. a) Nanofil 848 (stearyl-amine), b) Nanofil 919 (stearyl-benzyl-dimethyl ammonium chloride, c) Nanofil 948 (distearyl-dimethyl-ammonium chloride).

relatively small for MMT [65,66,74], and on the amount of surfactant used. Gallery distance depends on the thickness of the surfactant as shown by Figure 8.7a and b. Naturally, the picture presented here is oversimplified. Detailed measurements and numerical simulation showed that the arrangement of the surfactant molecules is more complicated inside the galleries [70−72]. The actual configuration of the chains depends on several factors including chain length, packing density, and temperature. However, the good agreement between measured gallery distances and the calculated thickness of the chains shows that the assumption of all *trans* conformation of chains gives an acceptable estimate of surfactant orientation within the layers.

The exceptions among the surfactants presented in Table 8.1 are N948 and C20A, in which two aliphatic chains are attached to the nitrogen atom. XRD indicates a larger gallery distance corresponding to the thickness of six aliphatic chains (see Table 8.2) for N948. However, it is improbable that six layers of the surfactant are located between the galleries arranged parallel to each other and with the silicate platelets; the configuration presented in Figure 8.7c may be assumed instead, in which one chain is oriented at an angle to the surface. The length of the chain is almost exactly 6 times of its thickness thus explaining the integer obtained for the number of aliphatic chains arranged parallel to each other. The tilted orientation of the surfactant molecule and the larger gallery distance should lead to easier intercalation and exfoliation of this clay in most polymer matrices. However, these speculations are contradicted by the characteristics of the Cloisite 20A silicate, the surface of which was modified with a similar surfactant (see Table 8.1). The only reasonable explanation we found for the different gallery structure was mainly the dissimilar amount of surfactant used for modification (Table 8.1), but the composition of the ditallow surfactant (65 wt% C18, 30 wt% C16, and 5 wt% C14) might also play a role. The smaller surface coverage and varying chain length lead to smaller tilt angles and to a less regular structure. The explanation is strongly supported by the smaller gallery distance and the wider diffraction peak of this silicate compared to Nanofil 948 (see traces c and d in Figure 8.6).

Several groups studied the effect of the chemical structure of the surfactant on exfoliation, composite structure, and properties, as mentioned above. Reichert et al. [44] found in PP/OMMT composites that large extent of exfoliation cannot be achieved if the length of the aliphatic chain is ≤ 8; large, micron-sized particles were found in the composite in these cases. Better dispersion was obtained at chain lengths of 12−18 carbon atoms, but the functionality of the coupling agent used (MAPP) also influenced exfoliation. Fornes et al. [33] investigated in detail the effect of the amount and type of surfactant used for organophilization, i.e., gallery structure, on the structure and properties of PA nanocomposites. They showed that surfactants with two long tails (see Figure 8.7c) are less advantageous than those having a single aliphatic chain attached to the nitrogen atom (Figure 8.7a and b); smaller head groups lead to increased exfoliation compared to large ammonium cations, and excess surfactant is disadvantageous for exfoliation, structure development, and properties. They obtained similar results also in thermoplastic polyurethane matrices [67]. Similarly, Vaia et al. [68] have shown that gallery structure strongly influences intercalation in polystyrene (PS) nanocomposites. However, contrary to Fornes et al. [33], he found that head groups do not influence intercalation and two long aliphatic chains are more advantageous than one. These contradictions clearly prove that unambiguous, general correlations have not been established yet among the gallery structure of the silicate, interactions, and composite properties.

8.3.1.3 Exfoliation

Exfoliation is usually studied by TEM, which is able to detect also individual silicate layers [75]. Very few publications present micrographs in which only individual silicate layers are dispersed in the polymer for any matrix and especially for polyolefins. Usually, intercalated stacks or tactoids with a range of gallery distances form in the composites and such tactoids appear in the micrographs. "Very good" composites with a high degree of dispersion may contain stacks of silicates with 3−10 layers [33,36], but even this can be achieved only with the proper selection of components and processing conditions.

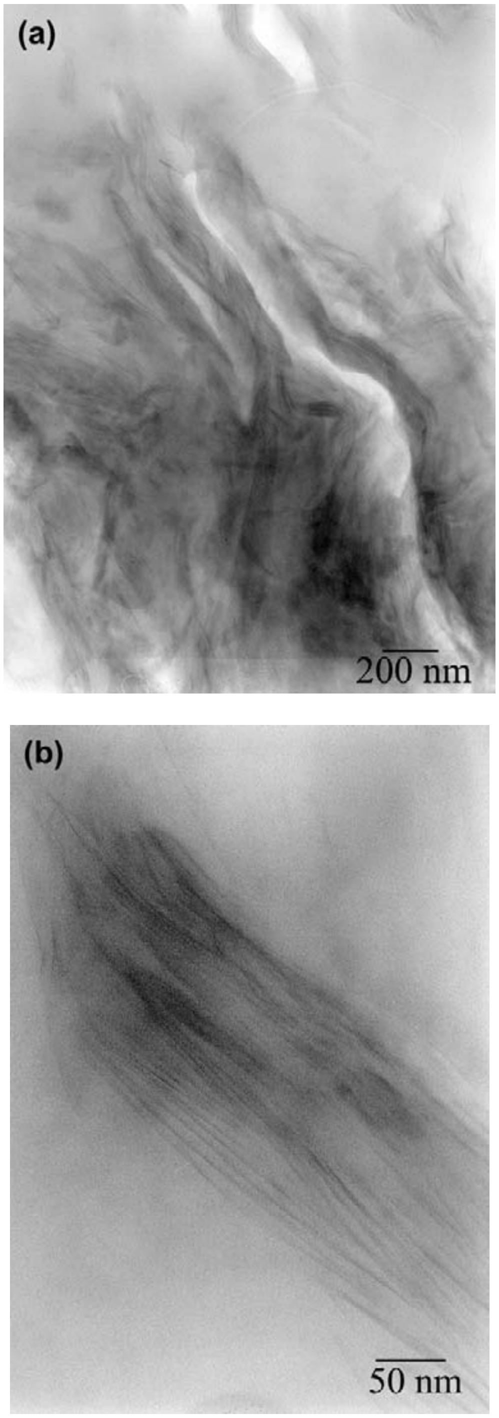

Figure 8.8 TEM micrographs taken from PP/OMMT/MAPP nanocomposites. a) 3 vol% silicate, 20 vol% MAPP, b) 2 vol% silicate, 30 vol% MAPP.

A variety of structural units were detected in PP/MMT composites. Two micrographs are presented in Figure 8.8, which demonstrate the wide scale of structures found in PP/OMMT/MAPP composites. A very large and compact clay particle is shown in Figure 8.8a detected in a composite with 3 vol% silicate and 20 vol% MAPP content. Obviously, disintegration and intercalation are at the preliminary stages for this particle. Nevertheless, it possesses a relatively wide range of gallery distances. A looser structure is presented in Figure 8.8b. Besides larger layer distance, the stack contains smaller number of platelets and more individual layers can also be detected in the micrograph. The structure observed in the TEM micrographs obviously depends on composition, but also on sampling, i.e., on the choice of the location from which the slice was taken. Processing conditions were the same in both cases.

Figure 8.9 offers a further example of the variety of structures found in a composite. Besides individual platelets, a larger silicate unit is shown in the composite containing 0.5 vol% silicate and 60 vol% MAPP. The particle is in the process of intercalation and complete exfoliation. Several layers peeled already off from the particle and the extent of intercalation, i.e., gallery distance, changes along its length. The micrograph indicates that intercalation and exfoliation proceed simultaneously in the investigated nanocomposites. The evidence presented above proves that a wide range of structural units may form not only in PP/silicate, but also in other composites; similar structures were detected in PA/MMT composites as well [76].

Figure 8.9 TEM micrograph showing the peeling off of layers from a silicate particle in a PP nanocomposite, changing gallery distance and varying extent of intercalation. Composition: 0.5 vol% silicate, 60 vol% MAPP.

8.3.1.4 Silicate network

TEM definitely confirmed the presence of individual silicate layers in PP nanocomposites containing also MAPP. Exfoliated silicate platelets were shown to interact with each other in water suspension and the type as well as the extent of interaction depended on the pH of water and on the amount of clay [77]. Face-to-face interaction leads to aggregation, while edge-to-face orientation results in the formation of a silicate network structure. Both phenomena have been observed also in polymer composites [31,44,78].

Although quite a few papers mention the formation and existence of such a network as a possibility [7,44,45,56, 79−82], relatively few papers focus on the determination of the conditions, which would yield such structures or on the characterization of the network itself [79,81]. The formation of the network is usually detected by TEM [7,44,79] or by the analysis of the results of rheological measurements, from the linear viscoelastic properties of nanocomposite melts [45,56,80]. TEM micrographs published are usually not very convincing, but the low-frequency range of complex viscosity or *G'*, as well as the appearance of a yield stress, clearly indicates considerable changes in the structure of the melt, and in all probability refers to the formation of a silicate network [83]. In polyvinylidene fluoride (PVDF)/clay/poly(ethyl methacrylate) (PMMA) composites, Moussaif and Groeninckx [82] observed a considerable increase of storage modulus in the low-frequency range with increasing intercalation and/or exfoliation and explained the phenomenon with the formation of a silicate network. They also found that network formation increases stiffness considerably in the rubbery plateau region.

Although TEM cannot and does not supply unambiguous proof for the formation of the silicate network, large extent of exfoliation occurs at very small silicate and large MAPP content, and occasionally overlapping of the silicate layers may be observed as a result as shown in Figure 8.10. In spite of the convincing micrograph, TEM alone is not sufficient to prove the formation of the silicate network, but together with rheology it may supply sufficient evidence for it. Moreover, such micrographs offer indirect evidence that considerable exfoliation takes place during the processing of these materials, since only highly exfoliated stacks or individual layers may form the network. Exfoliation and network formation obviously depend on component properties, composition, and processing conditions.

As mentioned above, the presence of the silicate network is usually detected by the increase of storage modulus and complex viscosity with decreasing frequency, in the small frequency range of the spectrum [83]. Earlier studies of materials in which internal processes are accompanied by the loss of energy (dielectric polarization, mechanical deformation) showed that plotting the two components of dynamic viscoelastic characteristics (dielectric permittivity, viscosity, modulus) against each other yields an arc-shaped curve if the process can be described with a single relaxation time (Cole-Cole plot) [84,85]. If the material possesses a relaxation time spectrum, the arc transforms to a semicircle or a skewed semicircle [85,86]. If more than one process with different relaxation times occur simultaneously, the so called Cole-Cole plot is further modified; i.e., a new semicircle or a tail appears [87,88]. The formation of a network structure leads to the increase of the elastic component of modulus and viscosity, and the network obviously deforms with different relaxation times than the homogeneous melt; thus we expect a correlation deviating from a semicircle in the above-mentioned representation.

Figure 8.10 Interaction of silicate layers in a PP nanocomposite at small clay (0.5 vol%) and large (60 vol%) MAPP content; possible network formation of the silicate sheets.

The Cole-Cole plots of composites containing 2 vol% silicate and various amounts of MAPP are shown in Figure 8.11. The deviation from a skewed semicircle is clearly visible at large MAPP contents. The change in the shape of the plots indicates the appearance of a new relaxation process, probably the formation of the silicate network. The critical MAPP content, at which this change occurs, is relative large; it is around 20 vol%, since a relatively large degree of exfoliation is needed to form the network at this silicate content. The change in shape depends on MAPP and silicate content. Not only does the shape of the traces change, but the absolute value of viscosity also increases considerably with silicate content. Larger numbers of silicate particles increase the probability and the efficiency of exfoliation and promote the formation of the silicate network. The critical amount of MAPP, at

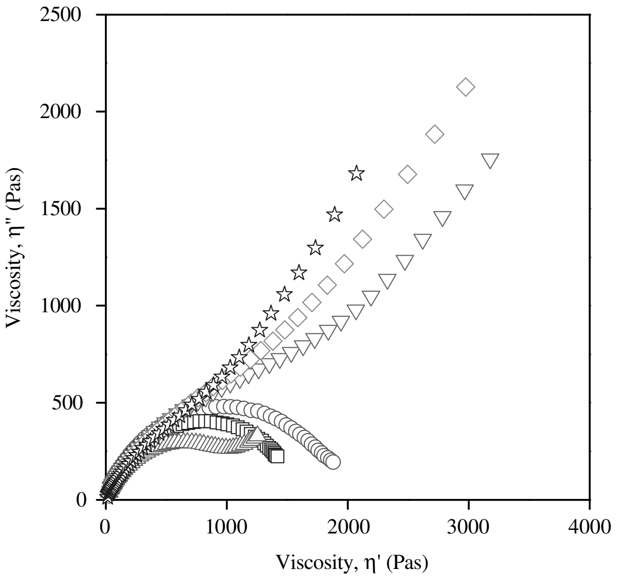

Figure 8.11 Cole-Cole plots obtained for PP/OMMT/MAPP nanocomposites at 2.0 vol% clay and various MAPP contents. Symbols: (–) 0, (□) 10, (△) 20, (X) 30, (M) 40, (☆) 50 vol% MAPP.

which the network appears, is plotted against silicate content in Figure 8.12. Two series of experiments were carried out to check the effect of composition on network formation. Although the two sets of values differ slightly from each other, the agreement between them is quite reasonable.

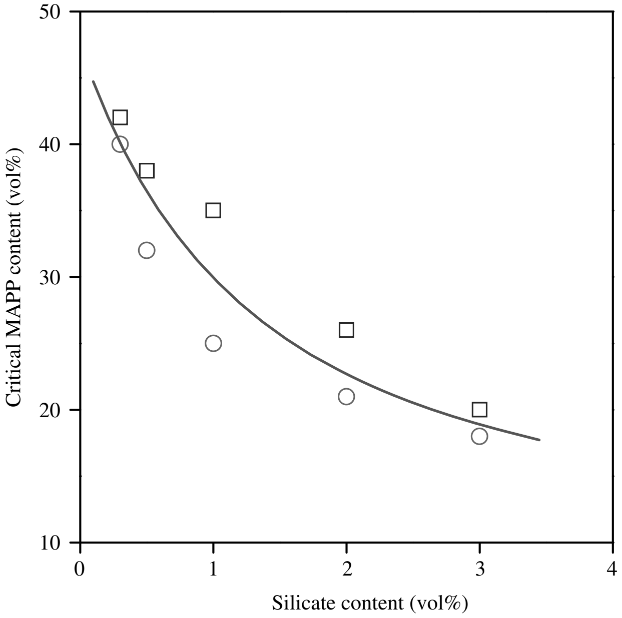

Figure 8.12 Dependence of the critical MAPP content at which the silicate network forms on the amount of organophilic silicate. (○) series 1, (□) series 2.

8.3.2 Carbon Nanotubes

Nanotubes and nanofibers have two dimensions in the nanometer range; they are usually micrometer or even millimeter long. They attracted the interest mainly because of their exceptional mechanical [89] and electrical properties [90]. Theoretical and experimental investigations proved that CNTs have Young's modulus in the range of 1.2 TPa, but they are also flexible [91]. The extremely high stiffness would make these materials ideal reinforcements for composites. Ideally, the ultimate goal of composite preparation, i.e., producing materials with high stiffness and toughness at low reinforcement content, could be achieved with nanotubes. However, as mentioned before, efficient reinforcement has three conditions: sufficient aspect ratio, alignment parallel to the direction of the load, and good stress transfer from the matrix to the fibers. The first is usually satisfied, but the other two are difficult to achieve. CNTs form bundles and they are usually twisted. Separation of the individual tubes, their homogeneous distribution, and parallel alignment are problems to be solved in order to prepare CNT nanocomposites successfully.

8.3.2.1 Dispersion

The properties of polymer/CNT composites depend on many factors including the technology of preparation and purification, the type and amount of residual contaminations, the structure of the nanotube (single- or multiwall), diameter, the length and aspect ratio of the tubes, as well as their association or aggregation (individual tubes, bundles). Numerous methods are used for the preparation of polymer/CNT composites and their main goal is practically always the achievement of homogeneous dispersion.

Solvent-assisted techniques are frequently used for the preparation of CNT nanocomposites. The approach has several advantages including its small scale and efficiency. The nanotubes are first dispersed in the solvent and then the solution of the polymer is added. Unfortunately, good dispersion is difficult to achieve even at small CNT content especially for single wall nanotubes. Dispersion is aided by stirring, the use of surfactants, and other surface modification techniques including functionalization and ultrasound-assisted homogenization. Although ultrasound efficiently improves dispersion, considerable fiber attrition takes place; the length of the tubes was found to be inversely proportional to the time of ultrasound treatment [92]. Besides the fact that it is difficult to find an appropriate medium for dispersion, another disadvantage of the technology using ultrasound is the limited stability of the suspension. Nanotubes reorganize relatively fast to aggregates during the evaporation of the solvent that leads to inhomogeneity in the final product. After achieving the necessary dispersion, either the polymer is precipitated from the mixture or a film is cast with the difficulties and dangers mentioned above.

Homogenization by melt mixing is one of the most frequently used techniques for the preparation of CNT composites. The approach has the advantage of using traditional plastic processing technology and equipment but requires relatively large amounts of material. The technique proved to be generally less efficient than the solvent-assisted method and it can be used only at small CNT content, since the viscosity of the polymer increases significantly with increasing nanotube concentration. The approach was used for the production of composites from polycarbonate (PC) [93], PA6 [94], PP [95], and from several other polymers [96,97]. Processing technology must be optimized to achieve acceptable dispersion of the nanotubes in the polymer matrix. Pegel et al. [98] carried out a series of experiments to produce PC/CNT nanocomposites. They found that at 250 °C and 50 rpm the homogeneity was much better after 15 minutes mixing time than at 300 °C (see Figure 8.13a and b). They reprocessed the materials at higher temperature (300 °C) and determined dispersion again. The homogeneous sample was processed at 50 rpm, while the one with inferior dispersion at 250 rpm. Homogeneity changed drastically and aggregates formed in the

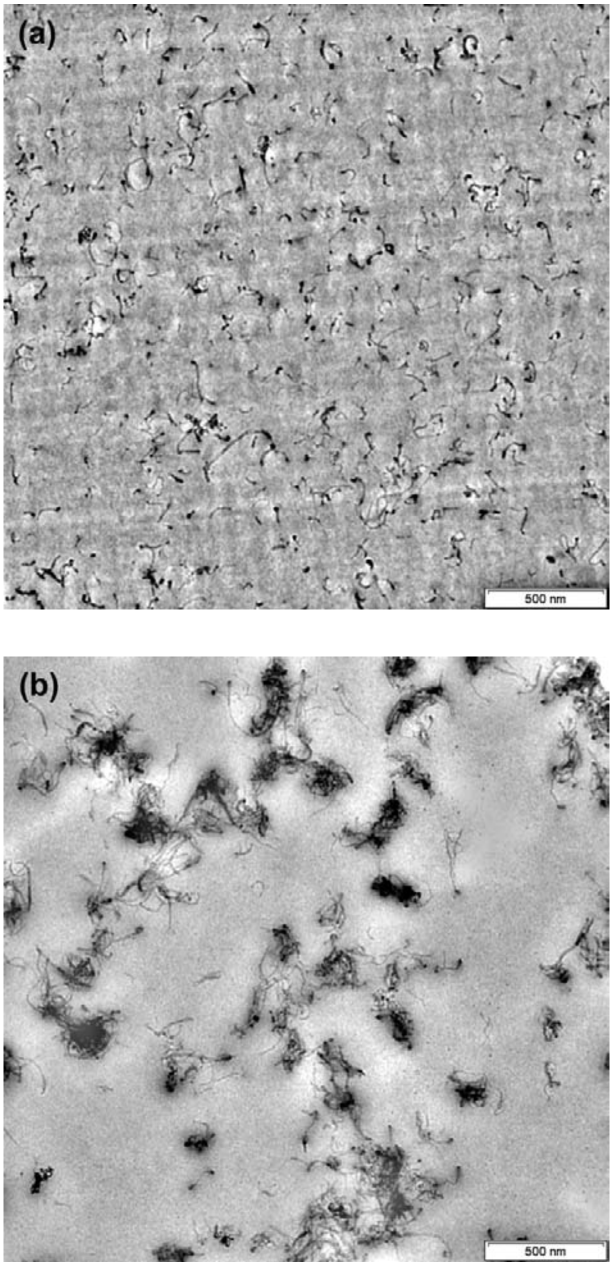

Figure 8.13 Aggregation in PC/CNT nanocomposites; effect of processing conditions on dispersion. a) rotor speed 50 rpm, processing temperature 250 °C b) rotor speed 50 rpm, processing temperature 300 °C c) rotor speed 50 rpm, reprocessing temperature 300 °C d) rotor speed 250 rpm, reprocessing temperature 300 °C

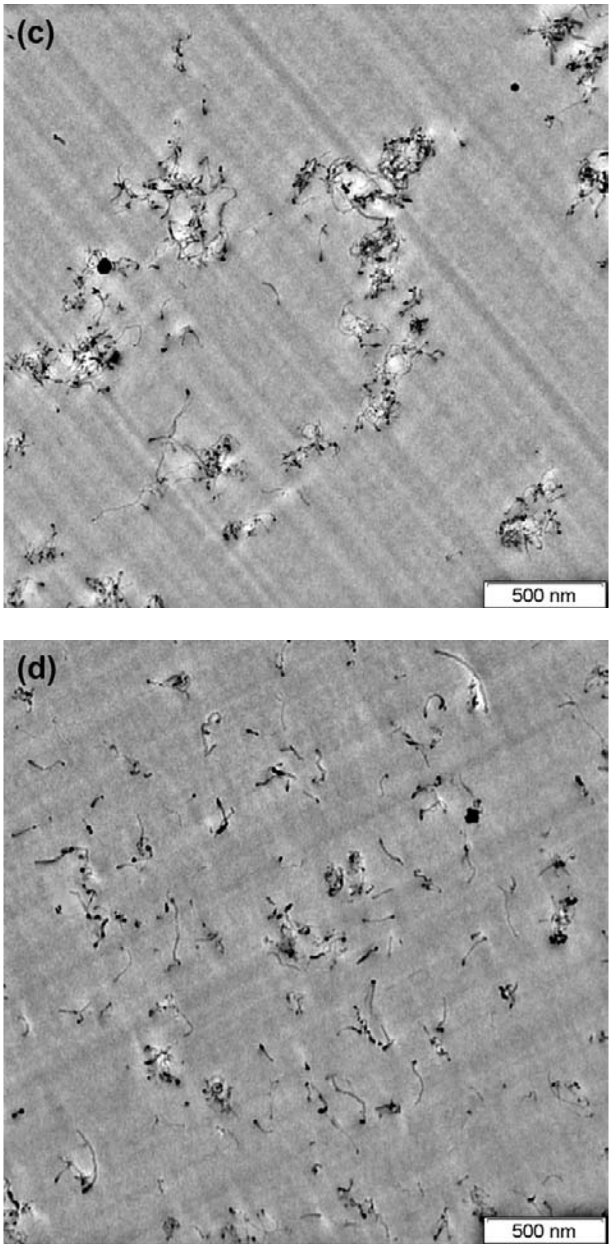

Figure 8.13 *—Cont'd*

previously homogeneous sample, while dispersion improved in the other (see Figure 8.13c and d). The authors drew the conclusion from their results that the relative magnitude of adhesion and shear forces determine the homogeneity of the composites. However, the possibility to increase shear forces is limited since fiber attrition or even the degradation of the polymer may take place at very large shear rates.

In situ polymerization is another, if not very convenient method for the preparation of homogeneous CNT composites. First, the nanotubes are dispersed in the monomer followed by polymerization. Functionalization of the tubes improves dispersion also in this case. The initiator or catalyst is often deposited onto the surface of the nanotubes before polymerization. Epoxy/CNT nanocomposites are often produced by this approach [99,100].

8.3.2.2 Orientation

As mentioned above, the inherent stiffness of CNTs is extremely large, around 1.2 TPa [91]; thus using them as reinforcement in polymers seems to be obvious. However, besides good dispersion and strong adhesion, the tubes must be oriented in the direction of the external load, which is at least as difficult to achieve as to meet the other two conditions. Several approaches were tried to align the fibers parallel to each other. These can be divided into two main classes. The first group includes those techniques in which the fibers are orientated before embedding them into the polymer. Raravikar [101] and Feng [102] used this approach to produce PMMA and polyaniline nanocomposites, respectively. In the first case the nanotubes were impregnated with the monomer and then the composite was prepared by in situ polymerization, during which the orientation of the tubes did not change significantly. Polymerization can also be carried out in a magnetic field which orientates the tubes into the desired direction. The extent of orientation is influenced significantly by the viscosity of the suspension in this case. The discontinuous technology and the nonconventional method make these techniques rather cumbersome and disadvantageous. More attempts are made to orientate the fibers during processing or by stretching the extruded product [103], by fiber spinning from the melt [104] or by electrospinning [105]; the largest extent of orientation is achieved by the last two methods. Nevertheless, the orientation and dispersion of CNTs remain the main obstacles before using them routinely as reinforcements in polymer composites. These difficulties are demonstrated well by Table 8.3 presenting the stiffness of various CNT composites. The increase in modulus is very moderate in all matrices except maybe in the thermoplastic polyurethane composite [106]. However, one should treat these results with the utmost care, and the validity of the values might be doubted somewhat, since thermoplastic polyurethane (TPU) polymers rarely have a stiffness of 7.7 GPa, especially at 850% elongation and 8.4 MPa tensile strength. Similarly, a modulus of 0.4 GPa for PA6 is unusually small [94].

8.3.3 Spherical Nanoparticles

Numerous attempts have been made to distribute spherical nanoparticles in a polymer matrix with the most different

Table 8.3 Mechanical properties of selected polymer/carbon nanotube composites at 0.5 wt% CNT content

Composite				
Matrix	**Reinforcement**	**Stiffness (GPa)**	**Tensile Strength (MPa)**	**Reference**
Epoxy	–	2.60 ± 0.08	63.8 ± 1.1	307
Epoxy	Carbon black	2.83 ± 0.06	65.3 ± 0.8	307
Epoxy	DWCNT	2.79 ± 0.03	67.7 ± 0.5	307
Epoxy	DWCNT–NH_2	2.98 ± 0.02	69.1 ± 0.2	307
Epoxy	MWCNT	2.61 ± 0.01	61.5 ± 0.2	307
Epoxy	MWCNT–NH_2	2.82 ± 0.02	64.3 ± 0.3	307
TPU	–	7.70 ± 1.00	12.4 ± 4.5	106
TPU	SWCNT	14.50 ± 3.40	13.3 ± 4.0	106
PA6	–	0.40 ± 0.04	–	94
PA6	MWCNT	0.77 ± 0.05	–	94
PP	–	0.86	30.8	308
PP	Carbon black	0.89	35.9	308
PP	SWCNT	1.10	32.3	308

methods, since aggregation is the major issue in these composites. One approach is the use of traditional thermoplastic or thermoset technologies to homogenize the previously prepared particles into the matrix polymer. Carbon black, precipitated $CaCO_3$, and SiO_2 are the most frequently used representatives of this class of materials, but nanoparticles are prepared from almost all inorganic compounds. Interaction and its control is the key for success in the application of these materials, but particle—particle interactions are usually more important than polymer—filler adhesion. It has been shown earlier that the occurrence and extent of aggregation depend on the relative magnitude of adhesion and shear forces [107], just like in composites prepared with CNTs. The ratio of the two forces depends on interfacial adhesion, shear forces, and the size of the particles. The aggregation tendency of fillers increases strongly with decreasing particle size. Since in nanocomposites particles are very small, aggregation is practically unavoidable and the formed structure governs properties. The size and interaction of the particles determine also the strength of the aggregates, which can be large like in some SiO_2 composites or relatively weak, like for $CaCO_3$ as shown in Figure 8.3, where fracture is initiated inside the aggregate leading to the premature failure of the composite. Shear forces can be changed in a limited range; thus the main factor to control aggregation is the surface characteristics of the filler. Various treatments and modification techniques are used to control them, like the surface grafting of the SiO_2 [108,109], but aggregation can be rarely avoided. We can hope only for a decrease in its extent at the most.

The simultaneous formation of the particles and the polymer matrix, usually in sol—gel technology, seems to have much more potentials. The interest in organic—inorganic hybrids dates back to the 1980s and several reviews are available in this field summarizing the technical possibilities, structure, properties, and potential applications of these materials [110—112]. Usually silicate chemistry is used to produce particles of different sizes [113] or organic—inorganic networks [114]. The size of the particles can be changed from 10 to 500 nm by modifying the conditions of polymerization, hydrolysis, and condensation of the SiO_2-precursors [113]. The homogeneity of the composite is much better in these materials, although depending on chemistry aggregates can form even in this case [113].

8.4 Interfacial Interactions

Nanocomposites are expected to have very large interfaces, which are supposed to generate their exceptional properties. The specific surface area of totally exfoliated silicates, e.g., is around 750 m^2/g; thus the surface characteristics of the filler, interactions, and interphase formation must influence composite properties considerably. Surface characteristics are rarely determined and only limited information is published about them, but they are especially important in polymer/layered silicate nanocomposites, since organophilization of the clay is a prerequisite for the successful preparation of such composites in most cases. Accordingly, we focus our attention mainly on layered silicates in this section and pay less attention to the other two nanofillers, nanotubes, and spherical nanoparticles.

8.4.1 Surface Characteristics

Layered silicate nanocomposites can be rarely prepared from neat, unmodified silicates like NaMMT; thus organophilic silicates are used practically always for the preparation of nanocomposites. Organophilization modifies drastically the surface free energy of the silicate, which, in view of the extremely large interface supposedly forming, must influence properties significantly. However, in spite of its importance, organophilization and its effect are usually treated in very general terms and the surface characteristics of silicates are rarely investigated in detail. The majority of papers published on polymer/layered silicate nanocomposites containing an organophilic silicate claim that surface modification renders the hydrophilic silicate hydrophobic, decreases its polarity, facilitates intercalation and exfoliation, improves wetting and the compatibility of the phases, and results in advantageous properties [22—24,44]. Unfortunately, this explanation does not agree with the fact that nanocomposite cannot be prepared from organophilic silicates and PP without an additional compatibilizer, although both are hydrophobic [44,57,63]. Moreover, apart from nanocomposites prepared from PA, the properties of most polymer/layered silicate nanocomposites are relatively poor, but they definitely do not reach the expected values or those predicted on the basis of the principles mentioned above (extensive exfoliation, large interfaces) [24,41].

It is completely true that the treatment of silicates renders them hydrophobic and decreases their polarity. However, the claim that decreased polarity leads to better compatibility and wetting is not true. Organophilization decreases the surface free energy of the silicates leading to the decrease of the strength of interaction between the filler and the polymer, as was shown many times before [115]. The interaction of the silicate and the polymer, both neat and organophilic silicates, is an adsorption process. The strength of adsorption can be characterized by the reversible work of adhesion [116,117], which considerably decreases upon treatment with an organic substance. Strong polarity of the neat silicate helps adsorption and increases the strength of interaction, while organophilization has the opposite effect.

Wetting of the silicate by polymers is also claimed to improve upon organophilization. Wettability is usually characterized by the thermodynamic quantity

$$S_{mf} = \gamma_f - \gamma_m - \gamma_{mf} \qquad (1)$$

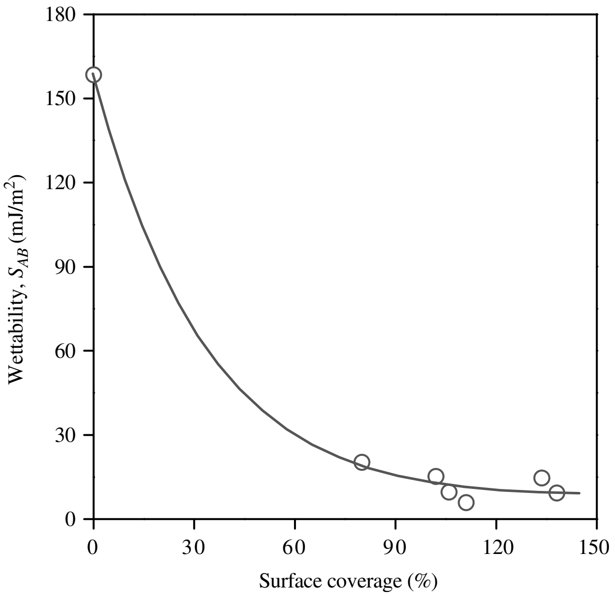

Figure 8.14 Influence of surface coverage on the wettability of organophilic silicates in PP nanocomposites.

where γ_f and γ_m are the surface tension of the filler and the matrix polymer, respectively; γ_{mf} is the interfacial tension, and $\gamma_f > \gamma_m$. Accordingly, wettability decreases on organophilization due to the drastic decrease of the surface tension of the filler. The correlation is demonstrated by Figure 8.14 where S is plotted against the surface coverage of OMMT in PP composites [69]. Wettability improves with increasing S, and in the case of negative values definite contact angle develops (partial wetting).

The question arises, what are the factors improving intercalation and exfoliation, if not changing polarity and wetting. Organophilization leads to the increase of gallery distance and to the decrease of interaction between the individual silicate layers, which facilitates exfoliation under certain conditions. However, these changes do not result in even partial exfoliation as the example of PP/OMMT composites shows. Interaction must be decreased further by additional measures, like the addition of solvents [118], or coupling agent (MAPP) must be added [55–62] in order to achieve intercalation and/or exfoliation.

Besides the orientation of surfactant molecules in the galleries, the amount used for organophilization is also important in the determination of surface characteristics and behavior. A small amount does not cover the entire surface, leaves high energy surface uncovered, and results in large surface tension, while excessive amounts may dissolve or disperse in the polymer leading to inferior properties. The amount of surfactant used for the treatment of the silicates listed in Table 8.1 was given by the producer and it is shown in column 3 of Table 8.4.

This amount covers a relatively wide range from 20 to 45 wt%. The organic content of the silicates was checked also by thermogravimetric analysis (TGA) and the results are presented in Table 8.4, too. The agreement between the two sets of data is excellent. Surface coverage was calculated from the ion-exchange capacity of the silicate, which was taken as 120 meq/100 g [22]. The results of the calculation are summarized in Table 8.4 (column 5). The data indicate that the silicates used in the study are usually coated near to 100 % of their capacity, which leads to monolayer coverage. N919 and N948 were treated with an excess of surfactant, while N784 and CPClMMT contain somewhat less organic compound. Nevertheless, we can conclude that the silicates are covered practically completely with the surfactant.

Inverse gas chromatography (IGC) is frequently used for the surface characterization of particulate fillers [119–123] and also silicates [124]. The dispersion component of the organophilic silicates listed in Table 8.4 was determined at 100 °C according to the Dorris–Gray [125] approach. Because of its large value, the surface tension of the neat, uncoated MMT could be determined only by extrapolation from measurements done at higher temperatures. We obtain a very high value, 260 mJ/m^2, for the dispersion component of NaMMT that is larger than the total surface energy of

Table 8.4 Surface coverage and surface tension of selected layered silicates

Silicate	Water (wt%)	Surfactant Amount (wt%)		Coverage (%)	Surface Tension, γ_s^d (mJ/m^2)
		Nominal	Measured		
NaMMT	6.8	0	0	0	257
CPClMMT	1.7	22	25.9	100.0	32
N784	4.2	20	19.0	96.9	48
N804	0.9	30	31.9	99.8	36
N848	1.2	25	22.3	103.3	35
N919	1.1	35	36.6	120.0	32
N948	1.6	45	44.7	124.0	31
C20A	0.9	38	37.8	95.0	33

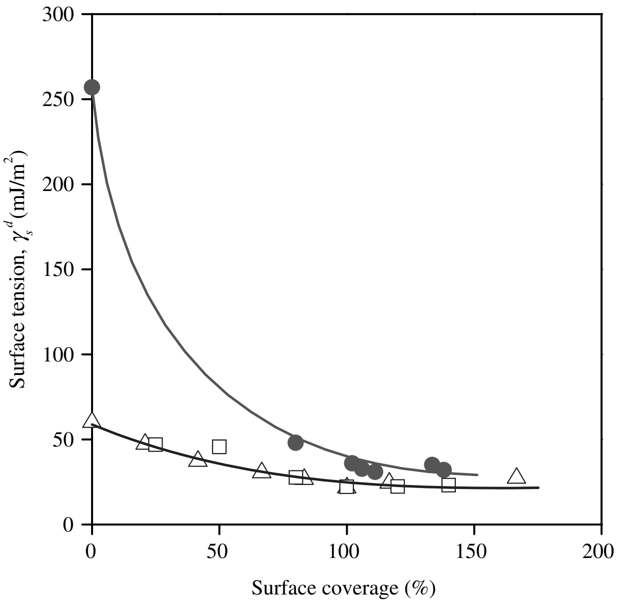

Figure 8.15 Effect of surface coverage on the surface tension of layered silicates (●); comparison to $CaCO_3$ coated with stearic (△) and lauric (□) acid.

205 mJ/m^2 determined by Helmy et al. [126]. Nevertheless, we can conclude that the surface energy of neat layered silicates is large that explains the strong surface activity of the clay and the need for organophilization before composite preparation.

Earlier studies carried out on other fillers showed that the coating of inorganic fillers with an organic compound, usually a surfactant, leads to the decrease of surface tension, and the surface free energy of the coated filler depends on surface coverage [127−130]. The correlation of surface tension and coverage is plotted in Figure 8.15 for the studied silicates. Similar values obtained on $CaCO_3$ are presented for comparison. The character of the correlation is the same in the two cases, but the surface tension of neat NaMMT is much larger than that of $CaCO_3$. It is interesting to note that the surface free energy of the coated fillers is very similar to each other, irrespectively of filler type (clay, $CaCO_3$) or the chemical composition of the surfactant used for treatment.

The results presented above have serious consequences for composite properties. Although IGC probably measures only the external surface of the particles, surface characteristics must be the same even after exfoliation, with the consequence that interaction between the silicate and the polymer decreases proportionally with surface tension. As a consequence, we cannot expect large improvement in mechanical properties, i.e., increase in strength, which agrees well with current experience and published results [24,40,41]. On the other hand, these observations are in contradiction with the fact that often considerable improvement in properties is reported when organically modified silicates are used for the preparation of nanocomposites [124]. However, such improvement may result from a number of changing factors including, structure, interactions, and deformation mechanisms.

8.4.2 Interactions

Strong interactions are essential when composites are used in load-bearing applications. Interactions usually influence also dispersion as mentioned above during the discussion of dispersion in polymer/CNT composites. The role of interactions and their modification is relatively simple in CNT and spherical nanoparticle modified polymers and very similar to other heterogeneous polymer systems in spite of the nanometric dimensions of these reinforcements. Surface is modified by surfactants or by coupling and the consequences are similar—only the increased role of particle−particle interactions must be considered additionally. On the other hand, the role of interactions is much more complicated in layered silicate nanocomposites, since it influences exfoliation and structure, but the number of possible interactions can also be much larger in them than in composites containing the other two reinforcements.

8.4.2.1 Layered silicates

The thermodynamics of exfoliation and component interactions was considered by several groups. Vaia et al. [68] developed a mean-field lattice model for the description of the thermodynamics of polymer melt intercalation into organically modified layer silicates. The model considers a single gallery of the organophilic silicate in which the surfactant molecules are tethered to the surface and the polymer molecules diffuse into the gallery among these tethered chains. Both entropy and internal energy change with increasing gallery distance during intercalation. New interactions between the polymer the tethered chains and the silicate determine changes in the internal energy of the system. The aliphatic chains of the surfactant can form only weak van der Waals type interactions with all components and thus they are regarded as “unfavorable” dispersive interactions. Intercalation and the final structure of the nanocomposite are usually determined by the “favorable” polymer/silicate interactions. The model was compared to experimental data obtained in static melt intercalation experiments with various organophilic silicates and neat, as well as functionalized, PS. Good qualitative agreement was found between experimental results and predictions in various organophilic silicate/PS systems [131]. Balazs et al. [132−134] also proposed various thermodynamic models for the prediction of the intercalation of polymers into organophilic silicates, but their conclusions do not agree with those of Vaia or with experience.

Both of the approaches discussed above use the terminology of polymer blends, which we find confusing and misleading. The term compatibility is not defined sufficiently and it is very difficult to understand. Immiscible polymer/

Table 8.5 Interactions in PA nanocomposites as determined with molecular dynamics calculations by Sikdar et al. [136]

Component 1	Component 2	Interacting Site	Interaction Energy (kcal/mol)
Clay	Surfactant	Functional group	−330
Clay	Surfactant	Backbone	−217
Clay	Polymer	Backbone	−108
Polymer functional group	Surfactant	Functional group	−143
Polymer functional group	Surfactant	Backbone	−23

silicate composites are simple particulate-filled polymers, while miscible ones are exfoliated nanocomposites. However, they differ considerably from miscible blends, since in the latter the units occupying lattice sites are about 3−5 orders of magnitude smaller than the silicate platelets, which have dimensions of 500−1000 nm or larger even if they are only 1 nm thick in the ideal case. Accordingly, the properties of nanocomposites are determined by the same factors as those of the traditional microcomposites. Nevertheless, the Vaia et al. [68,131] approach is useful, because it points out the most important factors influencing intercalation and exfoliation and shows that interactions determine the structure and properties of layered silicate nanocomposites.

The interaction of the silicate layers must be overcome to achieve exfoliation [135]. Alexandre and Dubois [22] claim that the forces which hold the stacks together are relatively weak and the intercalation of small molecules is easy. However, experience shows that the forces among silicate platelets are so strong in the polymer melt that the high shear of processing often cannot separate them even if the silicate is treated with a surfactant. Organophilization separates the layers and decreases the forces between them. Ion-exchange capacity, surface coverage, and layer distance determine the forces acting between the silicate platelets [135] and these factors must be optimized to achieve exfoliation.

The interactions in layered silicate PA nanocomposites were analyzed by molecular dynamics modeling by Sikdar et al. [136] and they proved that the strongest interaction forms between the silicate layer and the ammonium ion, but the backbone of the surfactant also interacts with the silicate rather strongly (Table 8.5). Further interactions develop between the polymer and the silicate, the various functional groups of the polymer and the surfactant, and the presence of additional components like solvents, additives, and compatibilizers increases the number of possible interactions even more. Obviously, various groups of the components compete for active sites on the silicate surface, but also interact with each other, and these competitive interactions determine the extent of exfoliation, the developed structure, polymer/silicate interaction, and finally the properties of the composites. Quite a few of the interactions mentioned above are ignored completely, but they are definitely not investigated in sufficient detail.

Besides interactions created by secondary forces, chemical reactions may also occur during the preparation of nanocomposites, and they are also neglected in most cases. Maleic anhydride groups on the compatibilizer, e.g., are much more reactive than the amide group of PA and they may react with the functional group of the surfactant. Model experiments carried out with hexadecylamine (HDA), often used for the organophilization of silicates, and MAPP proved that the two components react with each other under the conditions of melt intercalation [137]. The same results were obtained in further experiments with HDA-modified silicate and MAPP. Although the functionalized polymer may interact with the silicate surface directly as suggested by some authors [57,63], chemical reactions undoubtedly occur because of the high reactivity of MAPP and they strongly influence the interaction of the components, as well as the structure of the composite. Numerous other reactions may also take place during the preparation of layered silicate nanocomposites. Direct evidence shows that the surfactant with rather basic character accelerates the degradation of PVC [138]. Liu and Wu [139] prepared PP nanocomposites by swelling OMMT with an acrylate, which contained also a peroxide. The decomposition of the peroxide created radicals from PP, which reacted with the acrylate leading to significantly modified matrix properties and interaction. Yuan et al. [140] swelled their silicate with poly(ethylene glycol), PEG, before adding it to polyethylene terephthalate (PET). The results indicate that glycolysis or transesterification takes place during the processing of the composites resulting in a matrix with smaller molecular weight and modified properties. The deintercalation of silicates in rubber composites vulcanized with sulfur [141,142] can be mentioned as a further example where chemical reactions change the structure and properties of nanocomposites.

8.4.2.2 Other nanofillers

The relative magnitude of adhesion and shear forces is important for dispersion, but strong interactions are needed to achieve stress transfer in CNT-reinforced composites. Although experiments directed toward the determination of interfacial fracture energy in multiwalled CNT-reinforced

Table 8.6 Surface tension of carbonaceous reinforcements

Reinforcement	Components of Surface Tension, γ (mJ/m^2)			References
	Dispersion, γ_s^d	Polar, γ_s^p	Total, γ_s	
MWCNT	18.4	26.9	45.3	309
MWCNT	17.6	10.2	27.8	310
Carbon nanofiber	18.4	21.8	40.3	309
Carbon fiber	18.3	27.5	45.9	309
Carbon fiber	35.8	4.5	40.3	311

composites indicated the existence of a "relatively" strong interface [143], whatever that means, interfacial adhesion is insufficient in most cases in spite of the small diameter of the fibers. CNTs have a very regular structure almost exclusively consisting of carbon atoms. The surface free energy of the tubes is low and they do not contain reactive groups necessary for coupling. This statement is strongly supported by Table 8.6 listing the surface tension of CNTs, nanofibers, and carbon fibers. Although polar and dispersion components may differ considerably depending on the source, total surface tension is between 30 and 45 mJ/m^2 in each case. This is rather small compared to the dispersion component of NaMMT that is around 250 mJ/m^2 at 100 °C (see Table 8.4).

The surface of CNTs is modified by two approaches to control dispersion and improve interactions. Several groups use surfactants to facilitate the dispersion of the tubes [144—147]. This approach is based on physical adsorption; the surface of the nanotubes is covered with a polymer or a surfactant. The modifiers are attached to the surface by van der Waals and/or π bonds. The advantage of the approach is that it improves processing but does not disrupt the conjugated electron system of the tubes. Most often surfactants are added to a waterborne suspension of the nanotubes [148—149] to create a coating of surfactant micelles around the nanotubes. The strength of adsorption increases if the surfactant contains aromatic groups. The strength of adsorption depends on the length of the alkyl chain of the surfactant, the size of the ionic group, as well as on its charge density. References can be found for the use of anionic, cationic, and nonionic surfactants. The most often used anionic detergents are sodium dodecyl sulfate, SDS [144,150—152], and sodium dodecylbenzene sulfate, SDBS [153,154]. The dispersion of CNTs can be assisted by polymers both in water [155] and in organic solvents [156]. A wrapping mechanism is assumed in this case which claims the encapsulation of the tubes by the polymer molecules through the formation of a supramolecular complex [157,158]. As an example for the use of surfactants, Gong et al. [100] applied a surfactant processing aid to improve the properties of a CNT/polymer composite. They could increase the glass transition temperature, T_g, of the polymer and its stiffness in this way. Although a surfactant may improve homogenization, it is difficult to see how it can improve interfacial adhesion between the fiber and the polymer matrix. Moreover, Bryning et al. [146] found that the heat conductivity of composites containing nanotubes modified with a surfactant was significantly smaller compared to that of composites not containing the additive.

The surface of nanotubes can be modified chemically in order to improve interfacial adhesion by the functionalization of the tubes. An improvement of properties was reported invariably as an effect of such modification, as expected [159,160]. Chemical reactions may occur between the reactive group of the coupling agent and the π electron system of the nanotube. However, the chemical modification of the fibers changes their structure, decreases regularity, modifies properties and usually decreases conductivity. CNTs can be chemically modified by a direct reaction with the wall of the tubes or by a preceding oxidation that creates carboxyl or hydroxyl groups on the surface. Carboxyl groups can be formed by oxidation in air or oxygen, in concentrated sulfuric or nitric acid, hydrogen peroxide, or in a mixture of various acids. The number of functional groups as well as the ratio of —COOH/—OH groups depends on the type and conditions of oxidative treatment, as well as on reaction time and temperature [161,162]. Carboxyl groups are very advantageous since they are very reactive and may react with a large number of compounds [163,164]. CNTs were successfully functionalized with thiocarboxyl and dithiocarboxyl esters which help the formation of crosslinks among nanotubes [165]. Single-walled CNTs can be also halogenated with fluor at various temperatures [166]. The solubility of a CNT modified in this way is better in alcohol compared to the neat tube [167], which facilitates the reaction with Grignard reagents or with alkyl lithium [168,169]. CNT was also reacted directly with nitrenes or carbenes to improve solubility [170] and aryl groups were also formed on the surface of nanotubes [171,172].

Besides the functionalization of the surface with a well-defined compound or group, polymers are also often grafted to the surface. Grafting to has the advantage of using a polymer with well-defined molecular weight, polydispersity, and structure, but this polymer must be prepared separately and sterical effects decrease grafting efficiency.

Table 8.7 Selected surface modification approaches for carbon nanotubes

Nanotube	Method	Modifier	References
SWCNT	Surfactant	Anionic (SDBS)	150, 152
SWCNT	Surfactant	Anionic (SDS)	151
SWCNT	Surfactant	Nonionic (Triton X-100)	144
SWCNT	Surfactant	Cationic (DTAB)	144
SWCNT	Surfactant	Fluorene-based polymer	157
SWCNT	Surfactant	Amylose	158
MWCNT	–	Thiokarboxylic ester	165
SWCNT	–	Elemental fluorine	166
SWCNT	Grignard synthesis	Alkanes	168
SWCNT	Grafting from	PMMA	169
SWCNT	[2+1] Cycloaddition	Nitrenes	170
SWCNT	Nucleophilic addition	Carbenes	170
SWCNT	Grafting to, ultrasonication	PMMA	312
SWCNT	Grafting to	Amine-terminated polyimide	313
SWCNT	Grafting to	PEG	175
MWCNT	Grafting to	PLA	176
MWCNT	Grafting from, ATRP	PS	178, 314
MWCNT	Grafting from, ATRP	PMMA	178, 314
SWCNT	Grafting from, anionic	PA 6	315
SWCNT	Grafting from, free radical	Poly(4-vinylpyridine)	315

Nanotubes were successfully modified with PS [173], PVOH [174], PEG [175], and PLA [176] in this way. The tubes can be modified also by the grafting from approach. In this case larger grafting density can be achieved, but the reaction is more sensitive to the composition of the mixture and to conditions. Nanotubes grafted with PS [177], PMMA [178], and PA6 [179] were prepared with this technique. A randomly selected list of techniques used for the modification of the surface of CNTs is compiled in Table 8.7.

In spite of huge efforts and intensive study, CNT-reinforced composites do not meet expectations yet, their performance is moderate at most, especially if we compare it to their price. A possible way to overcome the difficulties caused by the shape and conformation of nanotubes might be the use of nanofibers produced by electrospinning. According to Dzenis [180] these fibers are superior to nanotubes in many respects, although the way to control interfacial interactions is unclear also in this case.

The methods used for the surface modification of CNTs can be and are applied also to spherical nanofillers. The surface of the particles is modified either by surfactants or by the proper reactants to introduce functional groups to the surface of the filler [181–185]. These groups can react with the polymer during polymerization or crosslinking. This technology may lead to nanocomposites with controlled structure and interfacial adhesion; thus materials with tailor-made properties can be produced for the most diverse applications. POSS is a modifier having great potentials. Sometimes it is regarded as a molecule, while others treat it as a nanofiller. Possible applications are catalysis, precursors to silicates, preparation of copolymers, and hybrid networks. Interest and the intensity of research increased further by the commercial availability of the material. POSS cages (Figure 8.16) can be functionalized by various methods like grafting groups onto preformed clusters or particles, or by the formation of functional groups during particle formation [112]. Nanocomposites with a wide variety of structures can be formed in this way. POSS can be built into the chains, can be attached to them by a spacer, can form networks, etc. Besides POSS, other hybrid organic–inorganic supermolecular assemblies can also be prepared, e.g., from butyltin oxo-hydroxo nanobuilding blocks and dicarboxylates, as well as by related chemistry [186]. Although the chemistry is not simple, the potentials of the approach are large and homogeneity, as well as interactions can be kept under control relatively easily, at least compared to traditional homogenization technologies.

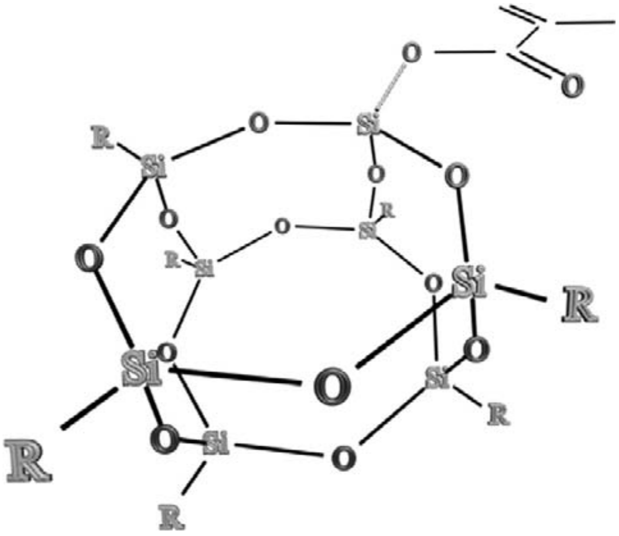

Figure 8.16 An acrylate functionalized POSS cage.

8.4.3 Interphase Structure and Properties

The formation of an interphase in heterogeneous polymers is a well-accepted fact [38,39,187,188] and interphase volume, thickness, and characteristics considerably influence composite properties. Large interfaces and a significant interphase volume should form in composites containing fillers or reinforcements with dimensions in the nanometer range. The importance of the interphase was emphasized in composites containing spherical nanoparticles [189], but interphase formation has not been mentioned yet practically at all in layered silicate nanocomposites. It is also quite surprising that the formation of an interphase and its properties are not considered even when polymeric compatibilizers are added to the composite, which are assumed to interact strongly with the silicate [55,56]. In such cases an interphase should definitely form between the silicate surface and the matrix.

The detection and analysis of the interphase is difficult both by direct and by indirect methods. First of all the interphase cannot be present in sufficient amounts to detect it—if the extent of exfoliation is small that happens quite frequently. Spectroscopy cannot see changes in properties in the absence of chemical reactions. The only possibility for the detection and analysis of an interphase is to follow changes in molecular mobility by nuclear magnetic resonance spectroscopy (NMR) [190], dielectric spectroscopy [190], or by changes in the dynamic mechanical spectra of the composites. The latter do not show much change in most cases. However, NMR and dielectric spectroscopy indicated an increase in the mobility of polymers confined in the galleries of layered silicates and the appearance of a second, lower glass transition temperature for the interphase than for the bulk material [190] that could explain the less than expected reinforcement in several nanocomposites. These results also indicate that the polymer interacts mainly with the surfactant and not with the silicate surface and only weak interactions form, which do not decrease mobility.

The results and conclusions described in the previous paragraph are contradicted by the measurements and calculations of Utracki et al. [191—193]. The authors prepared various polymer/layered silicate nanocomposites, determined their PVT behavior, and applied the Simha—Somcynsky [194] equation of state for the determination of the free (hole) fraction of the materials. The model could be applied only if the adsorption of the polymer was assumed on the clay surface resulting in clay platelets covered by a 6 nm layer of solid like matrix and an interphase of 100—120 nm thickness with changing properties. The results showed that free volume decreases by 4—16 % depending on the system studied. The adsorption and the decrease of free volume indicate the formation of a hard interphase. Unfortunately, none of the parameters derived from the model correlated with the actual mechanical properties of the composites. Much more attention must be dedicated to the study of interphase formation and to its effect on composite properties than has been done up to now.

8.5 Nanocomposite Preparation

Many ways and approaches have been published on the preparation of layered silicate nanocomposites. The methods can be classified in different ways, but the classification will be always arbitrary. The review paper of Alexandre and Dubois [22] distinguishes four, while the one written by Sinha Ray and Okamoto [23], three categories in their classification of nanocomposite preparation techniques. Our classification is similar to this second approach and discusses solvent-assisted methods, in situ polymerization, and melt compounding. Because of its practical importance we pay our attention mostly to the last technique and we must emphasize that the three techniques are used in different extents for the preparation of the three composites discussed here, i.e., for layered silicate, CNT-, and spherical nanoparticle-reinforced composites. The combination of monomers, polymers, solvents and other compounds, as well as the type and amount of silicate modification used are practically unlimited. The two review papers mentioned above list tenths or hundreds of references on the preparation of polymer/layered silicate composites by the various methods. It is impossible and superfluous to give a similar overview here, but we try to select representative examples and call attention to correlations between preparation technology, structure, and properties.

8.5.1 In Situ Polymerization

This technique was mentioned already in relation with the homogenization of CNTs (Section 3.2.1) and spherical particles (Section 3.3). The method is used also for the preparation of layered silicate composites and it consists of the intercalation of a monomer or a prepolymer into the galleries of the silicate and then the initiation of polymerization by heat or radiation. The initiator or catalyst can be diffused into the galleries of the silicate or fixed through cationic exchange to the layers before swelling them by the monomer. The method can be used for the production of thermoplastic or thermoset composites. Mostly epoxy [195,196], polyurethane [197,198], and polyester [199,200] composites were prepared in the latter class with this method. Methyl methacrylate [201−203] and styrene [204,205] are the most often used monomers for the preparation of thermoplastic nanocomposites by this approach, but many other monomers have been tried as well [206]. The polymerization itself can be done in bulk [197−200,207], solution [205], emulsion [203,204,206], or suspension [204]. Occasionally solvents are used to assist the intercalation of the monomer into the galleries of the silicate even when suspension or emulsion polymerization is used. The technique and the conditions depend very much on the components. The key factor is the separation of the silicate into individual layers and the prevention of their aggregation after the completion of polymerization. The preparation of composites in aqueous media is relatively easy, since layered silicates exfoliate in water. Accordingly, composites can be efficiently produced from NaMMT, but solvents and other swelling agents must be used when organophilic silicates are used in the process.

One of the first composite, in fact the one that triggered the revival of interest in layered silicate nanocomposites, was prepared by in situ polymerization from PA by the Toyota group [208,209]. MMT modified with 12-aminolauric acid and 1-caprolactam was mixed in a mortar. The mixture was heated first at 100 °C for 30 minutes and then at 250 °C for 6 hours. The cooled and solidified product was grinded, washed with water at 80 °C, and then dried. Exfoliated or exfoliated/intercalated structure was obtained depending on the composition of the reaction mixture. A detailed study of the product showed that the $-NH_2$ end groups of the PA interact with the cations of the silicate. Several attempts were made to prepare PP and PE nanocomposites by using metallocene [210], palladium [211], or Ziegler-type catalysts [212]. In one approach neat MMT and hectorite were first treated with trimethylaluminum-depleted methylaluminoxane before being contacted with a Ti-based, constrained geometry catalyst [212]. The nanocomposite was formed by the addition and polymerization of ethylene. Ultrahigh molecular weight polyethylene was produced in the absence of chain-transfer agent. The tensile properties of these nanocomposites were poor and essentially independent of the nature and content of the silicate. Upon hydrogen addition, the molecular weight of the polyethylene decreased with a corresponding improvement in mechanical properties. Considering the experimental difficulties of the preparation and the moderate properties achieved, we may expect that the role of in situ polymerization will remain limited in the production of nanocomposites. It is surprising though, that complete exfoliation is rarely achieved even with this technology.

8.5.2 Solution Mixing

In situ polymerization has the advantage that monomers diffuse into the galleries of the silicate more efficiently than high molecular weight polymers. The use of monomers and occasionally solvents offers the additional possibility of adjusting the competitive interactions among the components in a way, which makes possible intercalation and hopefully results in exfoliation. Polymerization involves chemical reactions. Solution mixing tries to apply the same principles, but without the difficulties of initiation or catalysis reactions, which are very sensitive to numerous factors. Many attempts have been made to prepare polymer/layered silicate nanocomposites by solution blending.

Water-soluble polymers, like poly(ethylene oxide), poly(vinyl alcohol), poly(vinylpyrrolidone) and poly(acrylic acid) can be used with high efficiency in this approach. Neat, unmodified layered silicates exfoliate relatively easily and almost quantitatively in water; thus the mixing of the solution made from the polymer with the slurry of the silicate is relatively easy. Unfortunately, the result of competitive interactions is rather difficult to predict. Occasionally homogeneous, stable colloidal distribution of the silicate layers prevails in the mixture [213] and a good quality film can be prepared under mild drying conditions. On the other hand, reaggregation of the silicate layers may also occur like in poly(vinylpyrrolidone) [214] and poly(ethylene oxide) [213]. Organic solvents must be applied when the polymer does not dissolve in water. Usually organophilic silicates are used as reinforcements in such cases. Nanocomposites can be prepared with a wide variety of solvents. A good example is supplied by the study of Li and Ishida [215] who compared the solution intercalation of PS and PMMA in eight different solvents. Based on their results they concluded that polymer−surfactant, solvent−surfactant, and polymer−solvent interactions play important roles in the solution intercalation of polymers. The importance of competitive interactions is shown also by the frequent use of solvent mixtures as well; a wide variety of combinations are used for the most diverse polymer/silicate pairs [216,217]. Interestingly, a hybrid technology was used by Adhikari et al. [218] who first prepared a film from OMMT and a styrene−butadiene−styrene (SBS) copolymer by solution mixing, then grinded the film, and processed the material in a twin-screw mini-extruder to improve homogeneity further.

The solution mixing of the components of layered silicate nanocomposites called attention to the importance of competitive interactions. This aspect is further emphasized by the use of swelling agents in several studies in which homogenization occurs by melt compounding. Zhang et al. [219,220] swelled OMMT with maleic anhydride and an acetic ester (no further definition given) coswelling agent in order to improve intercalation and exfoliation. They claimed complete exfoliation as a result of their process.

8.5.3 Melt Compounding

Previous sections have shown that the degree of exfoliation depends on the properties of the components, competitive interactions, and preparation conditions. A high degree or complete exfoliation is very difficult to achieve even when in situ polymerization or solution mixing is used; the result often does not justify the complications related to these methods. No one should be surprised as a consequence that the large majority of polymer/layered silicate nanocomposites are produced by melt compounding and considerable effort is dedicated to use the technology also for the preparation of other nanocomposites. The technique is simple, all available equipment can be used for processing, and composites can be prepared from practically every thermoplastic polymer. The number of papers published on the melt compounding of nanocomposites is enormous—their comprehensive discussion is impossible. Only a few examples are mentioned randomly here. Among others, layered silicate nanocomposites were prepared by this route from styrenic polymers [221,222], natural rubber [223], PA [40,224–228], and very many from polyolefins, especially from PP [229–233]. The approach is especially useful for polyolefins, since both in situ polymerization and solution-blending techniques are overly complicated for these polymers. The equipment used for the production of the composites also covers a wide range from two roll mill [230] and internal mixer [231–233] to twin-screw extruder [225,229]. One group [222] attempted even the direct compounding of the clay with the polymer in an injection molding machine. Further processing to specimens or to a final product can also be done by any technology like compression [230], injection molding [228, 229,231], or extrusion [224].

The results presented in the two previous sections indicated that the extent of exfoliation is influenced by many factors and the prediction of the final result is extremely difficult. The controversy related to the various factors is demonstrated well by the contradictory results of two groups mentioned already. Fornes et al. [33] investigated PA nanocomposites and based on the results they claimed that surfactants with two long tails (see Figure 8.7c) are less advantageous than those having a single aliphatic chain attached to the nitrogen atom (Figure 8.7a and b); smaller head groups lead to increased exfoliation compared to large ammonium cations, and excess surfactant is disadvantageous for exfoliation, structure development, and properties. On the other hand, Vaia et al. [68] found that the head groups do not influence intercalation and two long aliphatic chains are more advantageous than one. The same controversy applies to the effect of processing conditions. Poisson et al. [224] found that processing conditions did not influence significantly the studied properties of single- and multilayer blown films prepared from PA6/nanoclay composites, and Yilmazer and Ozden [234] came practically to the same conclusion during their study on PS composites. On the other hand, Fornes et al. [225] found that the molecular weight of PA6 used for the preparation of nanocomposites influenced considerably exfoliation; better exfoliation was achieved with the polymer of larger molecular weight. They explained this result by the larger shear stresses developed during the processing of this polymer compared to its small molecular weight counterpart. Wang et al. [233] came practically to the same conclusion when they found that the temperature of mixing must be adjusted according to the viscosity of the composite in order to achieve sufficiently high shear stresses leading to acceptable degree of exfoliation. Artzi et al. [235] showed changes in the structure and properties of ethylene vinyl alcohol copolymer/OMMT nanocomposites as a function of mixing time, i.e., processing conditions.

Although the dispersion of organophilic silicates is claimed to be relatively easy in PA, only a relatively few papers discuss the effect of processing conditions in this polymer. Among other questions Garcia-Lopez et al. [236] studied also the effect of processing conditions on the dispersion and exfoliation of the silicate in three component PA6/EPDM/clay blends with maleated ethylene-propylene diene rubber (MAEPDM) compatibilization. They compared one-step mixing in a corotating twin-screw extruder to a two-step method, in which the blend was prepared first and then the silicate was added in a second step. Compounding was carried out at two different rates in this second step. The authors found that processing conditions influence structure and properties considerably. Large shear stress facilitates silicate dispersion in the PA6 matrix thus improving reinforcement. The two-step process proved to be more efficient than the simultaneous feeding of the components.

The most thorough study on the effect of processing conditions on silicate exfoliation and dispersion was carried out by Paul and coworkers [237–239]. In their first two studies [237,238] the authors compared the effect of various processing equipment and conditions on the dispersion of two organophilic silicates with different surface modifications at 5 wt% silicate content in a PA6 matrix. They used a single-screw and three twin-screw extruders. The latter included a corotating intermeshing, a counter-rotating intermeshing, and a counter-rotating nonintermeshing machine. They studied the effect of different screw configurations offering dissimilar levels of shearing from high, through medium to low. They found that the degree of exfoliation depends both on clay treatment and on processing conditions. Both the level of shear and residence time influenced the structure and properties of the composites. Residence time increases exfoliation generally, but both back mixing and shear intensity have an optimum. Too high values of these latter variables lead to poorer delamination and dispersion.

As mentioned earlier, practically all polyolefin/layered silicate nanocomposites are prepared by melt compounding [32,43,56,240,241]. Functionalized polymers, i.e., maleinated

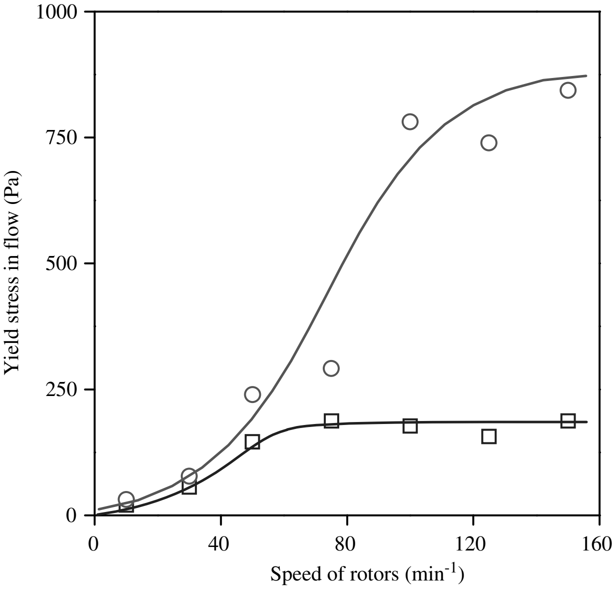

Figure 8.17 Changes in the yield stress of the melt of PP/OMMT/MAPP composites with the intensity of mixing and MAPP content. Silicate content: 5 wt%, MAPP content: (□) 15 wt%, (○) 30 wt% [83].

polyethylene or PP, are used to promote exfoliation and dispersion practically always. For example, a series of very thorough experiments were done by Lertwimolnun and Vergnes [83,242,243] on the effect of processing conditions on the structure and properties of PP/layered silicate nanocomposites. They prepared their composites from a PP homopolymer, Cloisite 20A organophilized clay (see Tables 8.1, 8.2, and 8.4) and a maleic anhydride modified PP compatibilizer (Orevac CA 100). Their first study was carried out in an internal mixer [83]. They used XRD, TEM, and rheology for the characterization of the composites. They found that the rate of processing, as well as the amount of MAPP, considerably modifies structure and properties. The gallery distance of the silicate did not change much in the experiments, but the yield stress in flow detected by rotational viscometry increased considerably as a function of these two variables. They identified yield stress as a measure of the extent of exfoliation. The correlation is presented in Figure 8.17 showing considerable differences in yield stress as a function of both mixing rate and MAPP content. Their further study focused on the effect of processing conditions [242] and screw geometry [243] on the structure and properties of PP/OMMT composites. They came to the same conclusions as before, i.e., layer distance does not change, but the extent of exfoliation characterized by the yield stress of flow depends strongly on the conditions of processing.

In spite of controversies, the majority of results published in the literature indicate that processing conditions considerably influence the structure of polymer/layered silicate nanocomposites. It is not surprising, as a consequence, that many attempts are made to find techniques in order to improve the extent of exfoliation. One approach was explored by Isayev and his group [244–246]. They found that the use of ultrasound considerably facilitates and increases the rate of intercalation even in the absence of a coupling agent. Comparison of several technologies indicated that ultrasound has a larger effect than the type of equipment or screw configuration [245,246]. Another method to improve clay dispersion is the preparation of a masterbatch and the production of the composite in a two-step process. Although Yilmazer [234] found the approach to be less efficient than in situ polymerization for PS composites, the technique seems to work in PP nanocomposites [247,248]. Both Li et al. [247] and Treece et al. [248] found that the preparation of a masterbatch improves clay dispersion and the properties of PP/silicate nanocomposites. Although the proper selection of processing conditions may increase the extent of exfoliation considerably, complete exfoliation rarely occurs in most composites. As a consequence, we may conclude again that the structure of polymer/clay composites is complex and contains simultaneously several structural units in different amounts. Moreover, competitive interactions of the components must be always considered, if we want to achieve large extent of exfoliation and good properties.

8.6 Composite Properties

Review papers and books [22,23,25,249] offer a detailed account on various properties of polymer nanocomposites prepared from the most diverse matrices and reinforcements. As a consequence, we refrain from the listing of further papers and discussing property changes merely as a function of composition but focus more on the effect of structure and interfacial interactions. Unfortunately, this is not easy, since very limited information is available on the correlation of structure, interactions, interphase formation, and properties.

8.6.1 Stiffness

Stiffness is the most often measured, modeled, and discussed property of nanocomposites [32,34,250–254]. Percentage increase in modulus is often used to prove the exceptional properties of this class of materials [255–258] and also the high degree of exfoliation in layered silicate nanocomposites. Large increase in stiffness is observed in elastomers, indeed, but much more moderate in glassy or crystalline polymers, as shown in Figure 8.1 [2,259,260]. PA is one of the exceptions in which considerable increase of stiffness can be achieved by silicate modification as shown by Fornes and Paul in their paper [33]. Based on data taken from the literature they argue that layered silicates offer exceptional reinforcement at very small filler content. However, data are available which show that CNTs reinforce PA even more [94] (see Figure 8.18), although some doubts might

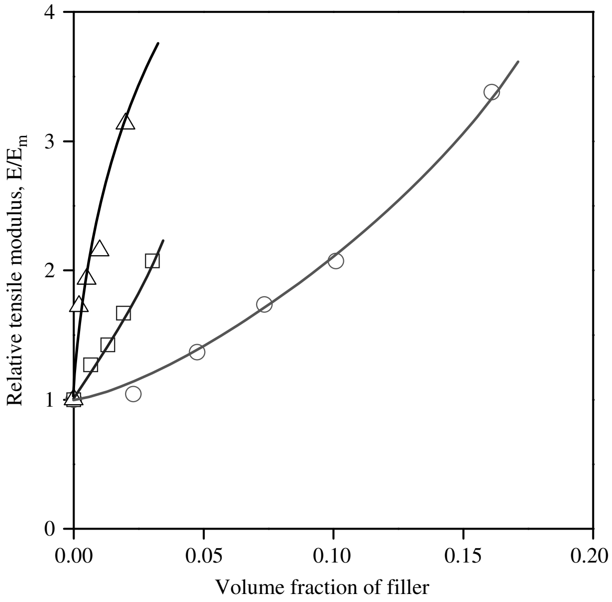

Figure 8.18 Exceptional reinforcing effect of a layered silicate compared to traditional glass fiber reinforcement in PA composites [33]. Symbols: (□) layered silicate [33], (○) glass fiber [33], (△) MWCNT [94].

arise about the reliability of the latter values (small stiffness of PA, see Section 3.2.2 and Table 8.3). Most of the stiffness values are generated by dynamic mechanical measurements and papers often include also a few spectra to demonstrate the benefit of nanoreinforcement.

Because of its assumed importance, the stiffness of nanocomposites is modeled quite frequently. Molecular dynamics [261] and continuum mechanical models [33,255] are used for the analysis and prediction of elastic properties. In a recent paper Valavala and Odegard [261] compare the theoretical background, advantages, and drawbacks of the various approaches. Usually the composition dependence of stiffness is modeled by continuum mechanical models developed for traditional composites. The Halpin–Tsai [262] and the Mori–Tanaka [263] models are the most frequently used [32–34,251,255,264–267], but other micromechanical models are also applied or developed occasionally [34,251,268]. Although the papers usually claim good agreement between measured and predicted properties, the general validity of the conclusions is limited for several reasons. Various assumptions are used during the development of these models, like the linear elasticity of the components, homogeneous distribution of the reinforcement in the matrix, its unidirectional alignment, as well as the perfect adhesion of the phases. Most of these assumptions are not realistic and the conditions are difficult to satisfy in layered silicate nanocomposites—thus the validity of the models is questionable.

One encounters enhanced difficulties during modeling in layered silicate nanocomposites because of their complicated structure. Many of the models use various assumptions for structure and try to account for the structural diversity of layered silicate nanocomposites [34,251,264,268]. Structure is usually simplified in the calculations, i.e., particles and silicate network are neglected and only individual layers and tactoids are considered. In spite of such simplifications the proper accommodation of the varying degree of exfoliation and changing orientation within the composite into the model presents serious difficulties. Fornes and Paul [33] showed that very tedious and meticulous procedure is needed to obtain acceptable data for model calculations. Accordingly, most of the modeling efforts are focused around assumptions concerning the structure of the composite and most output information is related to structure as well. The resulting characteristics are, e.g., the number of platelets per stack or the aspect ratio of the dispersed clay units. However, Osman et al [32]. expressed their doubts about the validity of such estimates based on the argument that composite modulus depends also on particle orientation and on the Poisson's ratio of the matrix. Based on the analysis of their results, they came to the conclusion that the aspect ratio of the inclusions cannot be estimated from the Halpin–Tsai equation for layered silicate nanocomposites [32].

8.6.2 Strength, Reinforcement

The basic condition of efficient reinforcement is strong adhesion between the matrix and the reinforcing component. Good adhesion usually results in large stiffness and strength at the same time. Strength or yield stress can be small due to weak interaction or the formation of a soft interphase, but considerable reinforcement cannot be achieved in either case. Modulus always increases in the presence of hard inclusions and specific surface area has only a moderate effect on it. Stiffness is not very sensitive to interactions or structure either. The composition dependence of strength or yield stress gives more accurate information about interfacial interactions and reinforcement in all heterogeneous polymer systems, including nanocomposites, than modulus [26,27,31].

The effect of interfacial interaction depends on its strength and on the contact surface between the phases. Interaction is often claimed to be strong in polymer/layered silicate composites in spite of the fact that the surface of the silicate is covered with a surfactant that decreases interaction significantly as shown in Section 4.1. However, the interface between the phases can be extremely large in nanocomposites, e.g., the specific surface area of completely exfoliated silicate is around 750 m^2/g [24,28,29] compared to the 3–5 m^2/g value of usual particulate fillers [107,269,270].

The composition dependence of the tensile yield stress of heterogeneous polymer systems can be described by the following simple equation [26,27,115]:

$$\sigma_{\mathrm{y}} = \sigma_{\mathrm{y}^0} \frac{1-\varphi}{1+2.5\varphi} \exp(B\varphi) \qquad (2)$$

where σ_y and σ_{y0} are the yield stress of the composite and the matrix, respectively; φ, the volume fraction of the filler in the composite; and B is related to the load carried by the dispersed component—i.e., it depends on interaction [26,27,31,129,271]. The term $(1-\varphi)/(1+2.5\varphi)$ expresses the effective load-bearing cross-section of the matrix. At zero interaction all the load is carried by the polymer and the load-bearing cross-section decreases with increasing filler content. The same correlation can be used to describe the composition dependence of tensile strength, if the elongation of the composite is small, usually <100% [27].

The value of parameter B depends on all factors influencing the load-bearing capacity of the filler, i.e., on the strength of interaction and the size of the contact surface. The effect of these factors on B is expressed as:

$$B = \left(1 + A_f \rho_f \ell\right) \ln \frac{\sigma_{yi}}{\sigma_{y0}} \tag{3}$$

where A_f is the specific surface area of the filler (contact surface), ρ_f is its density, while ℓ and σ_{yi} are the thickness and the corresponding property of the interphase forming spontaneously in all heterogeneous polymer systems. These two parameters were shown to depend on the strength of matrix/filler interaction [272,273]. The load carried by the second component depends also on the properties of the matrix; the extent of reinforcement is larger in a softer than in a stiffer polymer (see e.g., Figure 8.1). The validity of the model has been demonstrated for various heterogeneous systems from particulate-filled polymers to blends and short fiber-reinforced composites [26,27,274–276].

If the model is valid, we should obtain linear correlation when the natural logarithm of reduced yield stress eliminating the influence of effective load-bearing cross-section is plotted against filler content. Linearity is a necessary, but not sufficient, condition to prove the validity of the model. However, linearity of the correlation in a large number of various composites as well as the dependence of B on the factors indicated by Eq. (3) sufficiently validated the approach. It is easier to compare composites with different matrices, if we normalize reduced strength by the matrix value.

$$\ln \sigma_{yrel} = \ln \frac{\sigma_y}{\sigma_{y0}} \frac{1 + 2.5\varphi}{1 - \varphi} = B\varphi \tag{4}$$

In the representation of Eq. 4 the yield stress of composites should fall on a straight line with zero interception and with slopes proportional to the extent of reinforcement (B).

PA nanocomposites are undisputedly the reference materials in which layered silicates exert the largest reinforcing effect [40,277]. Extensive exfoliation and strong reinforcement are almost invariably assumed and expected in PA/layered silicate composites [225,250,278–280]. However, if we thoroughly examine and compare published data, we find that the properties of these materials may vary in a very wide range and occasionally the silicate has only a very moderate reinforcing effect. The tensile yield stress of six composites is plotted against silicate content in Figure 8.19, in order to support our statement; the yield stress of the composites covers a very wide range, indeed.

The composition dependence of the yield stress of the composites of Figure 8.19 was analyzed by the model presented above. The logarithm of relative yield stress is plotted in Figure 8.20 as a function of silicate content. Straight lines are obtained in all cases; the deviation from the lines is negligible. The slopes of the lines differ considerably from each other indicating widely differing reinforcing effects. Rather surprisingly very small B values of about 4 or 5 are obtained in some cases even when OMMTs were used, in spite of the general belief that silicates exfoliate in a large extent in PA and properties improve tremendously [41,64]. We must call attention here to the fact that most of the silicates were treated with aliphatic amines and not with an ω-amino acid [281]. While the latter creates covalent bond and strong adhesion to the matrix, the former decreases interfacial interaction, results in poorer stress transfer as well as in weaker reinforcement [280]. Without exception all composites containing a silicate with aliphatic amine treatment have small B values, i.e., limited reinforcement. We must also mention here that the authors of the composite with the largest B value of 22.9 do not supply any information about the composition of their material. We may conclude from these results that interfacial interactions play an

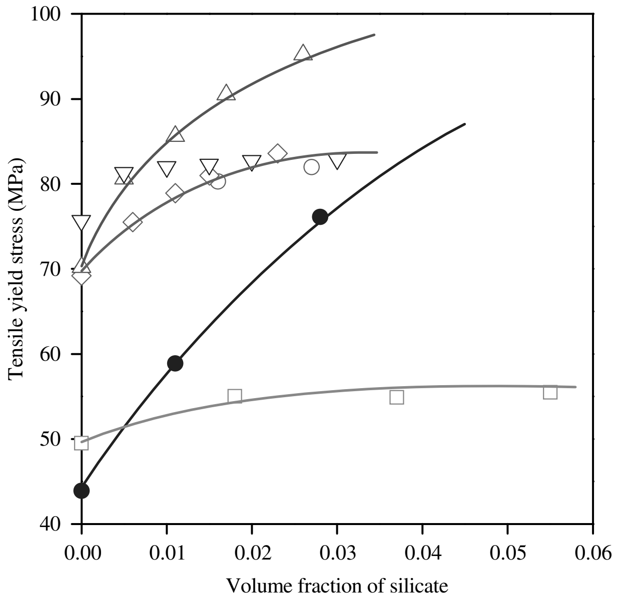

Figure 8.19 Wide range of absolute values and different composition dependence of tensile yield stress in PA/layered silicate nanocomposites. Symbols: (□) Liu [280], (▽) Rácz [282], (○) Fornes [252], (◇) Fornes [227], (△) Fornes [227], (●) Shelly [281].

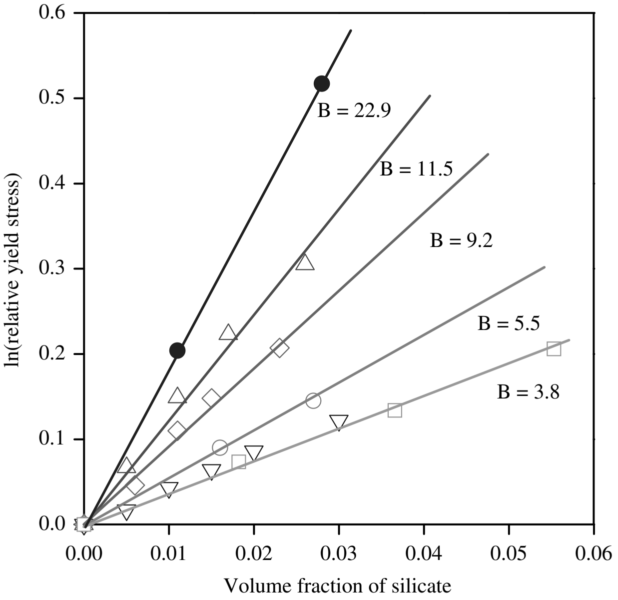

Figure 8.20 Relative tensile yield stress of the PA/OMMT composites of Fig. 19 plotted as a function of silicate content. Symbols are the same as in Fig. 19.

important role in the determination of the properties of layered silicate nanocomposites.

The determination of *B* values offers the possibility to estimate also the extent of exfoliation in these composites. We assume that NaMMT does not exfoliate at all, while the specific surface area of completely exfoliated silicate is known to be about 750 m^2/g [24,28,29]. These two cases represent the boundaries for zero and maximum reinforcement. *B* depends linearly on specific surface area if all other factors including interaction are the same (see Eq. 3). Using PP/$CaCO_3$ composites as reference, we obtain the results listed in Table 8.8. This shows that *B* values of about 200 should be obtained if exfoliation were complete down to individual silicate layers. The largest *B* value calculated for the PA composite of Shelley [279] corresponds to a specific surface area of about 90 m^2/g. This indicates the formation of stacks containing approximately 10 silicate layers in the average. This result agrees well with the experience that complete exfoliation is very difficult to achieve and nanocomposites always contain different structural formations including individual silicate platelets, intercalated stacks, but sometimes even large particles.

We must call attention here to the significance of the results and to the complexity of the correlation between structure, interaction, and properties. Although *B* measures reinforcement properly, its value is influenced by several factors. *B* can be used for the estimation of the extent of exfoliation only in the case of good adhesion and in the absence of platelet orientation in a particular direction. Although this latter condition might be fulfilled in many cases, since published TEM micrographs usually show random orientation of the platelets, the adhesion between the matrix and the polymer may vary considerably from one composite to the other. We may assume good adhesion in PE, PP, and in some of the PA composites because of the use of functionalized polymers or ε-caprolactam as a coupling agent, respectively. In these cases, *B* is probably related to the degree of exfoliation. Interaction is weak in PA composites containing silicates treated with aliphatic amines as shown by the small *B* values obtained in such cases and also by previous results [280]. Because we cannot control or even characterize structure with sufficient precision, the estimation of the strength of interfacial interactions as well as the existence and properties of an interphase cannot be estimated with any model calculations.

8.6.3 Other Properties

Modification, i.e., the introduction of fillers or reinforcements, changes all properties of polymers in smaller or larger extent. Modification usually targets a specific property, very often stiffness, strength, or toughness, which improves indeed, but other properties may deteriorate at the same time. As a consequence, properties must always be optimized to obtain the required performance. Nanocomposites are frequently intended for structural applications and the main goal of the modification is the improvement of mechanical properties; as a consequence, much attention is paid to the study and modeling of the latter. Other characteristics of the composites are investigated much less and relatively few attempts are made to describe their composition dependence by models.

Table 8.8 Estimation of the extent of exfoliation from parameter *B* determined in PP composites

Filler	Parameter *B*	Specific Surface Area (m^2/g)	Extent of Exfoliation (%)	References
$CaCO_3$	1.5	3.3	0	129
NaMMT	1.8	26.0	0	316
OMMT	195[a]	750	100	24,28,29
OMMT	22.9	91.0[b]	11.7	279

[a] *Calculated from published specific surface area assuming complete exfoliation.*

[b] *Calculated from the largest B value published.*

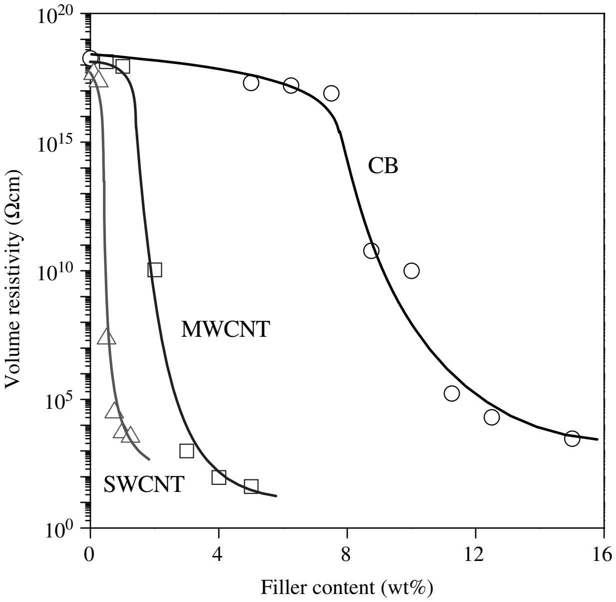

Figure 8.21 Comparison of the effect of carbon black (CB), multiwalled (MWCNT) and singlewalled carbon nanotubes (SWCNT) on the conductivity of polycarbonate composites. Data were provided by Petra Pötschke, IPF Dresden, Germany.

One of the characteristics mentioned quite frequently in relation to layered silicate nanocomposites is heat deflection temperature (HDT). This property is closely related to stiffness and changes with composition in a similar way. Cost is an important attribute of every engineering material and it decreases with increasing filler content in traditional composites but usually increases in nanocomposites. Moreover, decreasing polymer prices and increasing compounding costs make any composite competitive only if their technical benefits are utilized to their full extent. The introduction of any reinforcement may change the appearance of the product (color, surface) or influence the stability of the compound. Heat capacity, heat conductivity, shrinkage, and dielectric properties can be described quantitatively by models used for the description of the composition dependence of modulus. Fillers and reinforcements influence the barrier properties of polymers; the permeation of gases and vapors decreases with increasing filler content. Layered silicates are expected to improve this property exceptionally, and one of their potential applications is thought to be packaging— the production of materials with improved barrier properties. Models exist for the description of this phenomenon [282−286], which take into account the tortuosity of the diffusion path.

Two properties must be specifically mentioned here. The inherent flammability of plastics is one of their major drawbacks and the use of flame retardants is required today in most applications, especially in construction or transportation. Traditional halogen/antimony flame retardants are very efficient, but their use will be banned in the near future because of environmental and health considerations. Both layered silicates and CNTs were shown to decrease the flammability of plastics. Although they cannot provide the specification of V0 to the polymer as a single additive, they increase flame retardancy considerably in combination with traditional flame retardants [287,288].

Polymers are basically insulators with surface resistivity of around $10^{14}-10^{18}$ Ωcm. Applications exist which require a certain conductivity, like air ducts in mines, pipes for solvent transport, electromagnetic interference (EMI) shielding, and some other areas. Conductivity is usually achieved by the introduction of conductive fillers. Traditionally special conductive carbon blacks or metal fillers, particles, or flakes are used in such applications, but recently intensive research is going on to use carbon nanofibers or nanotubes for this purpose [289,290]. Conductivity increases stepwise at a certain additive content, and the percolation threshold is claimed to be much smaller, around several tenth of a weight percent [289,290], for nanofillers than for traditional fillers. This claim is strongly supported by the results of Pötschke et al. [289,290] presented in Figure 8.21. The percolation threshold of the special conducting carbon black is around 8 wt% in PC, while that of single-walled nanotube is <1% in the same polymer, indeed. Such behavior can be described and the composition dependence of conductivity can be modeled with percolation theories [291,292].

8.7 Possible Applications

One of the first target areas for both layered silicate and CNT composites was their use as load-bearing parts utilizing the large stiffness and aspect ratio of these reinforcements. Serious obstacles were met during the production of parts with the desired properties for reasons described in previous sections, i.e., difficulties with the control of structure, dispersion, orientation, adhesion and last, but not least, price. Although GM announced in 2004 that it uses 270,000 lb nanocomposites that year, recalculation of this large number results in about 300 tons [293] which is negligible, if we compare it to the capacity of a single PE plant of 400,000 ton/year. Nanocomposites can be used as structural elements in certain areas, but the real potentials of these materials are in special, niche application. In previous sections we mentioned already their use as additives in flame-retardant packages or as conductive fillers to render plastics antistatic or conductive. We mention three potential areas in this section: gas permeation and membrane technology, biomedical applications, and electronics.

Gas barrier properties of polymers can be modified significantly through the introduction of layered silicates. The general idea is that individual silicate layers with large aspect ratio increase the diffusion path of gases considerably especially if they are oriented parallel to each other. Based on this idea several models have been developed to describe the permeability of nanocomposite films [294]. Several groups observed significant decrease in the oxygen permeability of PET/layered silicate nanocomposites produced by in situ polymerization [294,295]. Brulé et al. [296] prepared blown films from PA6/polyolefin/silicate nanocomposites and found that their permeability for styrene decreased in the presence of the silicate. The main field of application for these materials is packaging where the targeted combination of properties is achieved with the preparation of coextruded films. One solution already introduced into practice is the PA6 based-Imperm nanocomposite offered by Nanocor for the production of multilayer films and for bottles used in the packaging of soft drinks [297].

In the last decades significant progress was made in the production of polymer-based membranes. One limiting factor in increasing the performance of these membranes is that selectivity decreases with increasing permeation and productivity decreases with increasing temperature [298]. One way to circumvent these problems is the preparation of nanocomposite membranes, which show improved permeation and selectivity at the same time [299−301]. Nanocomposite membranes are used already in fuel cells as well. In these cells oxygen is reduced on electrodes containing carbon black and nanosized platinum particles. The performance of the electrodes could be improved, when CNTs were used instead of carbon black [302]. The diffusion of methanol is one of the main problems in methanol fuel cells decreasing efficiency considerably. Nanocomposite membranes decrease methanol permeation thus improving the performance of these cells [303].

Nanotechnology and nanocomposites play an increasing role in many biomedical applications; in fact they form a new discipline: nanomedicine. One important application is the production of networks from nanofibers for cell and tissue growth [304]. Antibacterial effects are achieved with nanosized silver, silver oxide, or other silver salt containing composites for dendrimer-based drugs [305]. Gelatin containing hydroxyapatite particles as well as other nanocomposites prepared with this filler are used as protheses [306]. Controlled drug release and targeted drug delivery are other promising fields in which nanocomposites may play a role in the future. Nanoparticles are used in increasing quantities also in various drug formulations; the particles are thought to slow down and regulate drug release. Iron oxide particles were used in several experiments targeting controlled drug release, and they were used as MRI contrast materials or immunoassay materials. The number of potential applications is probably unlimited in this area.

The third area discussed here is electronics where size reduction requires the use of nanotechnology. The size of active electronic parts is already in the nanometer range in most devices. Both the type and application of nanocomposites are very diverse in this field. Light sensors, photo diodes, super condensers, other sensors, LEDs, and transistors are produced from composites containing CNTs [253]. The electric conductivity of nanotubes is used in various shielding applications as well as in diverse transparent conductive coatings [99]. Sensors are prepared from conjugated polymers and nanoparticles, but metal oxide nanofibers, CNTs, gold, silver, platinum, and palladium nanoparticles are also used in various electronic applications. The potentials of these materials are extremely large,

Table 8.9 Application of nanocomposites in industrial practice, areas and products

Matrix	Nanofiller	Targeted Property	Application Area, Product	Company
PA6	Layered silicate	Stiffness	Automotive, engine room	Toyota, Ube
TPO	Layered silicate	Stiffness, strength	Automotive, body elements	General Motors
Epoxy	Carbon nanotube	Stiffness, strength	Tennis racket	Babolat
Epoxy	Carbon nanotube	Stiffness, strength	Ice hockey stick	Montreal
Various matrices	Multiwalled nanotubes	Electric conductivity	Antistatic painting	Hyperion catalysis
Various matrices	Multiwalled nanotubes	Electric conductivity	Antistatic protection	Hyperion catalysis
Nylon MXD6	Layered silicate	Barrier property	Food packaging	Nanocor
Unknown	Silver particles	Antimicrobial effect	Wound dressing	Beiersdor, Elastoplast
Unknown	Unknown	Decreased gas permeability	Food packaging	InMat, Nanolok

but progress toward practical applications is slower than expected. Nevertheless, nanocomposites found application in several areas and Table 8.9 gives an overview of selected products used in industrial practice already.

8.8 Conclusions

Nanocomposites are heterogeneous materials—thus their properties are determined by the same factors as in traditional composites, i.e., component properties, composition, structure, and interfacial interactions. On the other hand, their structure is usually more complicated than that of microcomposites, and that is especially valid for polymer/layered silicate nanocomposites. Besides the usually assumed individual silicate platelets and tactoids, layered silicate nanocomposites may contain also large particles and a silicate network can also form in them at large extent of exfoliation. Aggregation and orientation are the most important structural phenomena in CNT-reinforced composites, and aggregation dominates also in composites prepared with spherical particles. Interfacial interactions should play an increased role in nanocomposites compared to traditional composites because of the assumedly very large interfacial area developing in them. Surprisingly, the surface characteristics of nanofillers are rarely determined or known. The surface of these reinforcements is modified practically always. The goal of the modification is to improve dispersion and/or adhesion in CNT- and spherical particle-reinforced composites and to help exfoliation in layered silicate nanocomposites. Unfortunately, modification decreases surface energy in the latter case leading to decreased interaction with the matrix. Very limited information exists about interphase formation and the properties of the interphase in nanocomposites, although they might influence properties considerably. All kinds of nanocomposites can be prepared with in situ polymerization, solvent-assisted methods, and melt homogenization. Because of its practical relevance, the latter technique is used most frequently, but dispersion and homogeneity are major issues in all three technologies. The properties of nanocomposites are usually far from the expectations, the main reason being insufficient homogeneity, lack of sufficient orientation, and improper adhesion. In spite of considerable difficulties nanocomposites have great potentials especially in specific, niche applications. Several nanocomposite products are already used in industrial practice.

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Part II: Biobased Polymers and Recycling

9 Biodegradable and Biobased Polymers

Long Jiang and Jinwen Zhang
Composite Materials and Engineering Center, Washington State University, WA 99164, USA

9.1 Introduction

Since the subject of biodegradable polymers caught wide notion in the early 1970s, biodegradable polymers have received extensive investigations from academia and industry and experienced several important stages of development. Since plastics account for a significant portion (~21% by volume in the United States) of the municipal waste, degradable or biodegradable plastics were initially intended to address the issue of "landfill crisis," with the anticipation that some landfill space would be freed if the waste plastic materials can be biodegraded. Therefore, the first generation of degradable plastics did not put the consideration of biodegradability and environmental footprint in priority but focused only on landfill space saving. Most of these products are based on the compounds of conventional resins such as polyolefins filled with starch or activated with metal oxide or transition melt salt, which only disintegrate into small pieces over time due to the biodegradation of the starch ingredient or catalyzed photodegradation of the polyolefins. Later on, a series of petroleum-based synthetic polymers, which can be termed as the second-generation degradable plastics and are truly biodegradable, have been developed and entered the marketplace with an insignificant share. These biodegradable polymers mainly include aliphatic polyesters such as polycaprolactone (PCL), poly(butylene succinate) (PBS), poly(butylene succinate-*co*-adipate) (PBSA), and other aliphatic copolyesters and aliphatic—aromatic copolyesters such as poly(butylene adipate-*co*-terephalate) (PBAT). Meanwhile, researchers also devoted tremendous effort in developing biodegradable polymers and plastic materials from renewable resources such as starch, soy protein (SP), cellulose, and plant oil. Starch and SP can be thermoplasticized under heat and mechanical agitation in the presence of appropriate processing agents. Thermoplasticized starch and SP can be effectively blended with other thermoplastic polymers to form biodegradable polymer composites. Cellulosic fiber can be directly used as reinforcement fiber in fiber-reinforced polymer composites. It can also be dissolved using appropriate solvents and then shaped into "regenerated cellulose" products such as fibers and sheets. Polylactic acid (PLA) and polyhydroxyalkanoates (PHAs) represent the two most important biodegradable polymers derived from renewable resources. They are thermoplastics and show mechanical properties and processability similar to that of some petroleum-based polymers. The advent of PLA and PHAs is a great leap forward in the development of biodegradable polymers.

Historically, the research interest and effort on biodegradable and biobased polymers has been up and down, in accordance with the cycle of oil price. The most recent oil price spike and national energy policy shift will definitely promote the already intensive research on alternative energy and renewable materials. With the tremendous interests and efforts being put in this area, new progress and achievements are made continuously as evidenced by the increasing numbers of publications. This chapter summarized contemporary research achievements and situations in biodegradable and biobased polymers. In the following sections, we first discussed naturally occurring biodegradable polymers, and then the biodegradable polymers derived from renewable resources and the biodegradable polymers based on petroleum. Finally, we briefly discussed several biobased polymers which may not be biodegradable.

9.2 Naturally Occurring Biodegradable Polymers

The utilization of natural polymers for non-food uses can be traced back far to ancient time. Skin and bone parts of animals, plant fibers, starch, silk, etc. are typical examples of the natural polymers used in different periods of the human history. In the last century, the development of natural polymers was significantly hindered due to the advent of low-cost petrochemical polymers. It was only about two decades ago that intensive research on natural polymers was revived, primarily due to the issues of environment pollution and the depletion of fossil oils. Modern technologies provide new insights of the synthesis, structures, and properties of the natural polymers. These new findings have enabled developments of natural polymers with novel processing characteristics and properties which can be used for many more advanced applications. This section deals with three major natural polymers: starch, cellulose, and SP. All of them are primarily used as human and animal foods in the history. New developments have allowed them to be used as a material component in polymer blends and composites to make biodegradable products.

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9.2.1 Starch

Starch is traditionally the largest source of carbohydrates in human diet. Being polysaccharide polymers, starch has been intensively studied in order to process it into a thermoplastic polymer in the hope of partially replacing some petrochemical polymers. Starch is a mixture of linear (amylose) and branched (amylopectin) poly-(1, 4)-α-glucose (Figure 9.1) and exists in the form of discrete granules. Amylose has a typical molecular weight of several hundred thousands, whereas the molecular weight of amylopectin is much higher and is in the order of tens of millions. Depending on the botanic origin of starch, the ratio of amylose is typically around 20—35%. Some so-called "waxy" starch has very low amylose content. For example, waxy maize starch contains less than 2% amylose. Starch granules are semicrystalline, containing both ordered structure (mainly double helices of amylopectin short chains) and amorphous structure (amylopectin long chains and branch points and amylose) [1].

In its natural form, starch is not meltable and therefore cannot be processed as a thermoplastic. However, starch granules can be thermoplasticized through a gelatinization process. In this process, the granules are disrupted and the ordered crystalline structure is lost under the influence of plasticizers (e.g., water and glycerol), heat, and shear. The resultant melt-processable starch is often termed thermoplastic starch (TPS). Since the advent of TPS, numerous studies have been conducted to explore its use as a thermoplastic polymer by overcoming its inherent drawbacks including low strength, high moisture sensitivity, and brittleness caused by starch retrogradation and gradual loss of the plasticizers.

To destruct the crystalline structure of starch and allow flowability, large contents of plasticizers are used in the preparation of TPS. Depending on the amount of plasticizers used, TPS materials range from glassy to rubbery state. Their stress—strain behaviors are dependent on the content of the plasticizers. Being hydrophilic, TPS is susceptible to moisture attack during storage or service. The increase in water content decreases glass transition temperature (T_g) of TPS and subsequently reduces its tensile strength. It was found that T_g of starch—glycerol—water blends depended linearly on the water content [2]. Glass transition temperature decreased from −53 to −105 °C when the water content increased from 2% to 30%. A small amount of glycerol also caused a large decrease in T_g of the blends, but further addition of glycerol only slightly affected T_g [2]. Besides the strength and T_g, TPS's susceptibility to water also leads to poor dimensional stability of its final products.

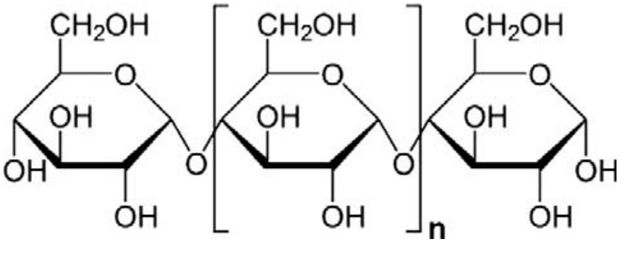


Figure 9.1 Chemical structure of starch.

On the other hand, when humidity and temperature are constant, mechanical properties of TPS depend on the storage or service time of the products [3]. The tensile strength of TPS increased and the elongation degreased after the product was stored for 5 weeks at constant humidity and temperature [2]. This was due to time-dependent retrogradation (post-crystallization) of starch in the presence of water and glycerol.

The time-dependent properties of TPS are a combined result of starch retrogradation, water content fluctuation, and plasticizer (e.g., glycerol) diffusion. These factors are difficult to be controlled during the storage and service life of TPS. As a result, TPS is rarely used alone but is often blended with hydrophobic thermoplastic polymers to form starch-containing polymer blends so that the mechanical performance, moisture resistance, and dimensional stability of TPS can be improved.

In the early years of starch-containing polymer blends, dry starch granules were directly used in the blends as a filler [4]. Since most polymers are hydrophobic, hydrophilic starch is thermodynamically immiscible with these polymers and consequently resulted in weak interfacial bonding between the starch and the polymer matrix. This in turn led to poor mechanical properties of the blends, e.g., low tensile strength, low elongation, and brittleness. In view of this, compatibilization between the starch granules and the polymer matrix was carried out. Maleic anhydride (MA) is the most commonly used and is also one of the most effective coupling agents for the starch-containing blends. In the literature, both biodegradable polymers, e.g., ethylene vinyl acetate (EVA), low-density polyethylene (LDPE), and high-density polyethylene (HDPE), and non-biodegradable polymers, e.g., PBS, PCL, and PLA, were functionalized by MA and used as compatibilizers in the corresponding starch—polymer blends. Remarkable strength increase was realized after the addition of the compatibilizers. The modulus and elongation of the blends were relatively less affected [5—7].

Compared to granular starch, TPS offers a great advantage in material processability and morphology control as the TPS can be deformed and dispersed to a much finer state than the dry native starch. Property-enhancing microstructures such as co-continuous structure can be formed during melt blending. The polymers used to blend with TPS included LDPE [8], polystyrene (PS) [9], and most often biodegradable polymers such as poly(hydroxyl ester ether) [10], castor oil-based polyurethane (PU) [11], poly(ester amide) [12], PCL [13], and poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV) [14—16]. In general, the typical disadvantages of TPS such as moisture susceptibility, brittleness, and low strength were reduced to various degrees by blending with these polymers. However, mechanical properties of these blends still decreased as the TPS content increased. This limited the contents of TPS in the blends if the strength of the matrix needed to be maximally maintained. The reports on compatibilization between TPS and the polymer matrix are surprisingly scarce. Using a twin-screw extruder, Huneault and Li [16] first grafted MA to PLA by free radical grafting and then allowed the resultant MA-*g*-PLA to react with TPS. In the PLA-g-MA TPS extrudates, TPS was shown to be dispersed in a much finer state than in the PLA/TPS blend without MA grafting. The tensile strength and modulus showed no obvious variation with or without MA grafting. However, the elongation was significantly increased when PLA-g-MA was used.

Besides being used as a dispersed component in polymer blends, TPS was also used as a matrix polymer and was reinforced by natural fibers. TPS/sisal fiber composite prepared by compression molding exhibited improved tensile strength. The strength increased from 4 MPa (neat TPS) to 8 MPa at 10% fiber content [17]. Ma *et al.* [18]. prepared TPS/winceyette fiber composite by extrusion. The composite exhibited a tensile strength of 15 MPa at 20% fiber content, tripling the strength of the unreinforced TPS. Using a starch-based emulsion-type resin, Ochi prepared unidirectional continuous hemp fiber-reinforced starch composites [19]. A tensile strength of 365 MPa was obtained at the highest fiber content of 75%.

In recent years, nanoclay has also been studied for its effects on mechanical and barrier properties of TPS and TPS/polymer blends. For example, Wilhelm *et al.* reported a 70% increase in tensile strength of TPS/hectorite nanocomposite films at a 30% clay level [20]. Avella *et al.* also reported increased mechanical properties of potato starch/montmorillonite (MMT) nanocomposite films [21]. Especially, Huang *et al.* observed an increase of 450% and 20% in tensile strength and strain, respectively, after the addition of 5% clay to corn starch/MMT nanocomposites [22]. Most recently, Tang *et al.* reported significantly increased tensile strength (up to 92% higher) and reduced water vapor permeability (up to 67% lower) of TPS/MMT films prepared by melt extrusion and subsequent casting [23].

Starch could also be foamed by water vapor to make compostable packaging foams [24]. To provide water resistance, acetylated starch, which was a less polar material and was more water resistant, could be used as the foaming material [25]. For the same purpose, TPS was also first blended with hydrophobic polymers (e.g., PHBV, PCL, PBS, PVA, and PLA) and subsequently foamed [26–28]. Besides water vapor, CO_2 was also used as the foaming agent in TPS/PLA foams [29].

9.2.2 Cellulose

Cellulose is the most abundant renewable biopolymer on earth. About 33% of all plant matter is cellulose. The purest natural cellulose form is cotton (~90%). Wood contains about 50% of cellulose [30]. Cellulose can also be synthesized by some bacteria. Cellulose is a polysaccharide, having a molecular structure similar to starch. However, the D-glucose units are linked by β-glycosidic bonds in cellulose (Figure 9.2) instead of α-glycosidic bonds in starch. Due to this β-glycosidic bond, cellulose molecules adopt an extended and stiff rodlike conformation. The multiple hydroxyl groups from one chain form hydrogen bonds with oxygen molecules on another chain, holding the chains firmly together side by side and forming elementary crystallites (cellulose nanowhiskers (CNWs)) with exceptional high tensile strength. These nanowhiskers, embedded in amorphous hemicellulose and liglin, form microfibrils and further the cell wall of plant cells.

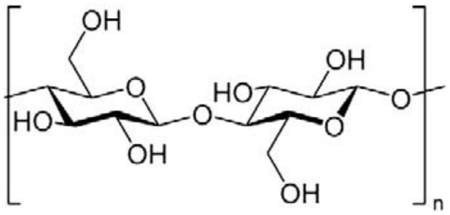


Figure 9.2 Chemical structure of cellulose.

Cellulosic natural fibers (e.g., abaca, bamboo, jute, flax, and hemp) have long been used as load-bearing materials to reinforce polymer matrix. Compared to traditional reinforcement fibers, e.g., glass fibers and carbon fibers, cellulosic fibers show the advantages of low material cost, low environmental impact (renewability and carbon dioxide neutral, i.e., no excess carbon dioxide is returned to the environment when composted or combusted), and competitive strength/density ratio [31]. Cellulosic fibers are almost nonabrasive to processing equipment, which contributes to substantial reduction in production cost. They are also safer to handle compared to man-made fibers.

A major disadvantage of cellulosic fibers is their hydrophilicity due to the existence of large amounts of hydroxyl groups in polysaccharide molecules. When blending with hydrophobic matrix polymers, this leads to serious dispersion and interface problems which often result in poor mechanical properties. Other drawbacks of using cellulosic fibers include limited processing temperature (<200 °C), high moisture absorption and swelling, non-uniform dimensions and properties, and low microbial resistance and product durability (if this is needed). However, many of these disadvantages can be reduced or even eliminated by appropriate fiber treatment and composite processing.

One of the most promising uses of cellulosic fibers is the development of fully biodegradable "green" composites using biopolymers as the matrix. The "green" composites should be environmentally friendly, biodegradable, and sustainable. The disposal of the composites at the end of their service poses no harming to the environment. For example, Plackett *et al.* prepared PLA/jute fiber mat composite by film stacking technique [32]. Tensile strength of the composite was significantly increased when the composite was pressed within the 180−220 °C temperature range. Interfacial bonding between the hydrophilic fibers and the hydrophobic polymers can be improved by compatibilization. Lee and Wang studied the effects of coupling agent (lysine-based diisocyanate) on the properties of bamboo fiber (BF) composites [33]. They found that tensile strength, water resistance, and interfacial bonding were all improved for the PLA/BF and PBS/BF composites after the addition of coupling agent. Jiang *et al.* prepared PHBV/bamboo pulp fiber (BPF) composites by melt compounding and injection molding [34]. Tensile strength and modulus, flexural strength and modulus, impact strength, and crystallization rate were all substantially increased by the addition of BPF. Tensile and flexural elongations were also moderately increased at low fiber contents (<20 wt%). When PHBV8-g-MA was used as the compatibilizer, the strength and modulus were further increased due to improved polymer/fiber interfacial bonding. However, the toughness of the composites was substantially reduced due to the hindrance to fiber pullout, a major energy dissipation source during the composite deformation. Cellulosic fibers were also used in SP plastics as reinforcing agents. Lodha and Netravali investigated ramie fiber [35] and flax yarn [36] -reinforced SP isolate (SPI) resin. They found that stearic acid modified SPI (MSPI)/ramie fiber composites showed significantly higher mechanical properties compared to SPI/ramie fiber composites. A poly-carboxylic acid-based modifier (Phytagel®) also considerably improved mechanical and moisture properties as well as thermal stability of SPI/flax yarn composites.

The elementary crystallites of cellulose, CNWs, exhibit a Young's modulus of over 100 GPa and a surface area of several hundred square meters per gram [37]. They have the potential to significantly reinforce polymers at low volume ratios as being realized by other nanomaterials such as carbon nanotubes (CNTs) and nanoclays. CNWs can be separated from cellulosic fibers by acid hydrolysis. Oksman's group has performed extensive research on the production of CNW and the processing of various polymer/CNW nanocomposites by both solution casting and extrusion blending [38−45]. Homogeneous dispersion of the whiskers posed a great challenge in CNW nanocomposite processing due to hydrogen bonding-induced agglomeration of the whiskers. This was especially true when the freeze-dried whisker powder and polymers were compounded by extrusion. Good dispersion of CNW in polymer matrix was obtained by solution casting [43] or by directly pumping whisker suspension into the extruder during the extrusion compounding process [45,39,40]. Dispersion agents/compatibilizers were found to improve the dispersion of CNW [45,40,41,43]. Composites obtained without good dispersion showed insignificant effects on the properties of the composites. Various degrees of success have also been made by other researchers on cellulose whisker-reinforced polymer composites prepared by solution casting [46−48].

Besides being directly used as reinforcement fiber, cellulose was also chemically treated to form cellulose derivatives and then dissolved in appropriate solvents (or directly dissolved in suitable solvents) to produce highly viscous cellulose derivative (or cellulose) solutions. This process imparted flowability to cellulose and thus enabled its processing using traditional polymer-processing equipment. Cellulose was regenerated when the solutions were passed through a coagulation bath. The most widely known "regenerated cellulose" are cellophane, a thin transparent film, and rayon and lyocell, which are both cellulose fibers. The production of lyocell is more eco-friendly than that of rayon and cellophane because the former does not use hazardous CS_2 to form cellulose derivative and its solvent can also be fully recycled and reused.

9.2.3 Soy Protein Plastic

Similar to starch and cellulose, SP is an abundant, low-cost, and renewable biopolymer which shows great potential in polymer industry as a replacement for petrochemical polymers in many applications. SP is commercially available in three different SP concentrations: soy flour (SP concentration ~54%), SP concentrate (65−72%), and SPI (~90%). The rest of SP is primarily carbohydrates. SP is made from dehulled, defatted soybean meal. The concentration of protein is achieved by removing (e.g., water/acid/aqueous alcohol wash, precipitation, and centrifuge) most of the soluble non-protein compounds, including mainly soluble carbohydrates, some nitrogenous substances, and minerals. SP molecules comprise 20 different amino acids with strong inter- and intramolecular interactions. These interactions make SP unmeltable, and therefore it is impossible to process SP as a thermoplastic polymer, unless enough amount of plasticizers, e.g., water, glycerol, ethylene glycol, sorbitol, etc., are applied [49]. Other processing agents, such as sodium tripolyphosphate for interrupting SP ionic interactions [50], or sodium sulfite as a reducing agent to break the disulfide bonds [51], are also used. The use of a significant amount of plasticizers results in low mechanical properties of SP plastics. On the other hand, when the plasticizers migrate away from the SP plastics during storage or service, the materials become very brittle. Moreover, the hydrophilicity of SP and the plasticizers leads to low moisture resistance of SP plastics.

Blending SP plastics with biodegradable polymers is a natural choice to overcome the aforementioned drawbacks of SP plastics. PCL [52,53], PLA [54], PBSA [55], and poly(tetramethylene adipate-*co*-terephthalate) (PTAT) [56] were used to blend with SP. These polymers were hydrophobic and therefore could not establish strong interfacial bonding with SP. As a result, their blends with SP showed inferior properties. On the other hand, poly(hydroxyl ester ether) could form strong hydrogen bonding with SP. Therefore, its blends with SP exhibited better properties [57]. John and Bhattacharya [55] showed that using a small amount of MA-grafted biopolyesters, mechanical properties, moisture resistance, and processing conditions of SP/biopolyester composites can be improved due to enhanced interfacial interactions. Zhong and Sun found that methylene diphenyldiisocyanate (MDI) was an effective compatibilizer to increase the tensile strength of SP/PCL blends [58]. Zhang *et al.* compared the different morphologies and properties between SPI/PLA and SPC/PLA blends [54]. SPC/PLA showed finer phase structures and higher mechanical properties than SPI/PLA due to SPC's higher compatibility with PLA. Co-continuous structure was realized in the SPC/PLA blends in a broad composition range. Moreover, after applying poly(2-ethyl-2-oxazoline) (PEOX) as a compatibilizer to both SP blends, the phase structure, mechanical properties, and water resistance of both blends were all improved. Very recently, by introducing urethane and isocyanate groups to PBS, Li *et al.* obtained SPI/PBS blends with substantially improved phase structures and mechanical properties [59]. The authors attributed the compatibility to the hydrogen bonding between the urethane groups ($-$OCONH$-$) in PBS and the amide groups ($-$CONH$-$) in SPI. The residual NCO groups in isocyanate-containing PBS could also react with NH_2 groups in SPI, which further strengthens interfacial bonding between the two phases.

The low strength of SP plastics can also be remedied by cellulosic fibers and nanosized reinforcing fillers. Liu *et al.* found that raw grass fibers could improve mechanical (tensile, flexural, and impact) and thermal properties of SP plastics [60,61]. Alkali pretreatment of the raw grass fibers removed hemicelluloses and lignin, which resulted in larger length/diameter ratio of the fibers and better fiber dispersion. This in turn led to even higher mechanical and thermal properties of the SP/treated grass composites. SP plastics were also reinforced by CNWs. Wang *et al.* prepared SP/nanowhisker composites by solution dispersion, freeze drying, and hot pressing [62]. The composites showed increased tensile strength and modulus and improved water resistance and thermal stability. The authors ascribed these properties to the crosslink network caused by intermolecular hydrogen bonds between the cellulose whiskers and the SPI matrix. Chen *et al.* prepared SP/MMT nanocomposites by combined aqueous dispersion and melt extrusion method [63]. MMT was shown to be highly exfoliated in the SP matrix at low MMT concentrations ($<$12 wt%). Above this range, MMT was intercalated. The mechanical strength and thermal stability of the SPI/MMT composites were significantly improved due to the fine dispersion of the MMT layers and the strong restriction effects on the interfaces, which was created by the surface electrostatic interaction between the positive charge-rich domains of SP and the negatively charged MMT layers as well as the hydrogen bonding between the $-$NH and Si$-$O groups. SP was also blended with another important category of nano-reinforcement agents, CNTs, for property improvement [64]. Multiwalled CNTs (MWCNTs) of different sizes were compounded with SP in solution, freeze dried, and pressed into sheets. Various degrees of improvement on tensile strength, modulus, elongation, and water resistance were observed for the composites with different sizes and concentrations of MWCNTs. Optimal nanotube size and concentration were identified. Depending on the size (internal and external diameters of MWCNTs), the authors hypothesized two SP-MWCNT microstructures: SP molecules wrapping on MWCNTs (small nanotubes) and SP molecules penetrating the internal channels of MWCNTs (large nanotubes).

9.3 Biodegradable Polymers Derived from Renewable Resources

Unlike the aforementioned natural polymers which can be harvested directly from the nature, some polymers are not available (or available in meaningful quantity) from the nature but can be produced with human intervention from naturally occurring bio-sources. PLAs and PHAs are the two most important polymers within this category. They have received intensive research interests in the past two decades and are finding more and more applications due to their unique combinations of properties.

9.3.1 Polylactic Acid

PLA is a synthetic biodegradable polyester with its monomer, lactic acid, derived from natural resource. Lactic acid is made by bacterial fermentation of carbohydrates such as corn, sugarcane, potatoes, and other biomass. High-molecular-weight PLA can be synthesized using three different routes: direct condensation polymerization, azeotropic dehydrative condensation, and ring-opening polymerization of lactide. The last route was patented by Cargill in 1992 [65] and is the most commonly used method (Figure 9.3). Direct condensation polymerization is the least expensive method, but it can only obtain low-molecular-weight PLA because it is difficult to remove water completely from the reaction mixture.

PLA is well known for its biocompatibility and biodegradability. Moreover, PLA is a thermoplastic polymer and can be conveniently processed using existing polymer-processing equipment and techniques. PLA can be processed into fiber, film, sheet, and 3D articles by fiber drawing, film blowing, extrusion, and injection molding. With the continuous drop of resin price, PLA is gradually gaining the market share. Its clarity makes it suitable for biodegradable packaging, such as bottles, food containers, and wrappers. It has also been used for food service ware, lawn and food waste bags, coatings for paper and cardboard, and fibers for clothing, carpets, sheets and towels, and wall coverings. In biomedical

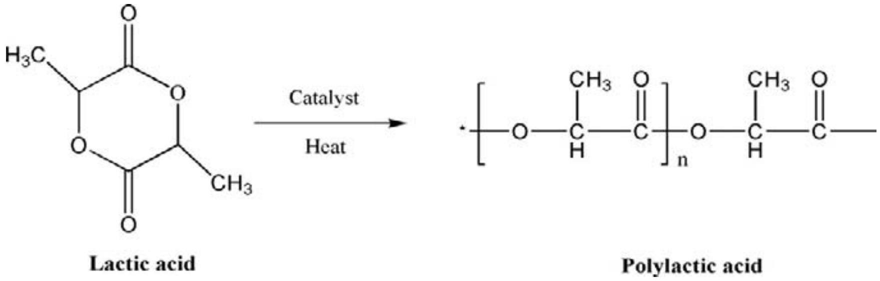


Figure 9.3 Synthesis of PLA.

applications, it is used for sutures, stents, prosthetic materials, dialysis media, and drug delivery devices. PLA degrades primarily by hydrolysis through a two-stage process. First, random chain scission of the ester groups of PLA reduces its molecular weight. The speed of chain scission depends on the pH value, temperature, and moisture levels of the environment [66]. Embrittlement of the polymers occurs with the reduction of its molecular weight. Second, low-molecular-weight PLA is metabolized by microorganisms, yielding carbon dioxide, water, and humus [67].

The properties of PLA can be quite different because of the presence of the pendent methyl group on the alpha carbon atom. L-, D-, and DL-lactide isomers exist due to this structure. L-Lactide is produced by most microorganisms. DL-Lactide is the synthetic blend of D-lactide and L-lactide. The homopolymer of L-lactide (PLLA) is a semicrystalline polymer with a typical melting point (T_m) of 160–180 °C and a glass transition temperature (T_g) of 55–65 °C. It possesses high tensile strength/modulus and low elongation, making it suitable for load-bearing applications such as in orthopedic fixation and sutures. Poly(DL-lactide) (PDLLA) is an amorphous random copolymer of L-lactide and D-lactide. It has lower tensile strength, higher elongation, and a much more rapid degradation time, making it more attractive as a drug delivery system. PLLA is a slow-crystallizing material, and its crystallinity significantly depends on processing conditions such as cooling rate and annealing status. For instance, PLLA products produced by injection molding show minimum crystallinity due to the fast cooling in the mold [68]. Annealing the products above its T_g considerably increases their crystallinity. Higher annealing temperature and time resulted in more perfect, higher melting crystals [69]. General purpose PLLA exhibits much higher strength (~60 MPa) and modulus (~3 GPa) than many other commodity fossil oil-based plastics. For instance, HDPE has a typical strength and modulus of 20 MPa and 1 GPa, while polypropylene (PP) shows a typical strength and modulus of 30 MPa and 1.5 GPa. On the other hand, PLA is a brittle polymer, exhibiting a typical tensile strain at break of less than 6%. This brittleness significantly limits PLA's use in many applications. As a result, PLA toughening has received intensive research interests and a number of toughening strategies have since been developed.

First, PLA can be toughened by copolymerizing lactides with other monomers. For instance, the copolymers of lactide/caprolactone were found to be increasingly rubbery when the caproyl units in the copolymers increased from 5% to 20% [70]. When 50% of trimethylene carbonate (TMC) was copolymerized with lactide, elongation of the copolymer increased to 900%, whereas tensile strength decreased 10-fold to 5 MPa [71]. Second, lowering T_g of PLA by adding miscible plasticizers is another important method to toughen PLA. Lactide monomer and oligomer are natural PLA plasticizers. At ~20 wt% of LA monomer or oligomer, the elongation at break of PLA was increased to larger than 200% [72,73]. Other plasticizers such as poly(ethylene glycol) (PEG) [74] and triethyl citrate [75] were also used.

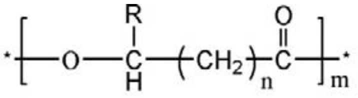
Blending PLA with ductile polymers is probably the most convenient and therefore the most studied route for PLA toughening. To maintain biodegradability of the final blends, ductile biodegradable polymers are often used to blend with PLA. Among these polymers, PCL received the most research interests. PCL is a biodegradable polymer which is flexible at room temperature due to its low T_g. Blending PLA with PCL resulted in significantly improved ductility and toughness [76,77]. PLA was also toughened by other biodegradable polymers such as PBAT [68,78] and PBS [79].

The aforementioned three toughening routes, e.g., copolymerization, plasticization, and blending, can significantly increase the elongation of PLA. However, the strength and modulus of PLA are substantially decreased at the same time. Polymers toughened by rigid particles were shown to be able to maintain or even increase their strength and modulus. A recent study on MMT toughening of PLA showed that PLA could be reinforced and toughened simultaneously when MMT concentration was low (<2.5 wt%) [80]. Furthermore, Chen *et al.* prepared a PLA/PBS/MMT ternary blend by melt blending [81]. When MMT was epoxy-functionalized, the ternary blend showed similar modulus to the neat PLA (1990 vs. 2215 MPa) and significantly increased the elongation at break (118.1 vs. 6.9%).

9.3.2 Polyhydroxyalkanoates

Unlike PLA whose production involves designed chemical reactions, PHAs are biodegradable polyesters directly produced by bacterial metabolism. PHAs are synthesized and accumulated by bacteria as carbon and energy storage materials under the condition of limiting nutrients in the presence of excess carbon source [82,83]. More than 250 species of bacteria have been reported to produce PHAs. The polymers are stored in the cells as discrete granules with sizes between 0.2 and 0.5 μm. The stored PHAs are degraded by depolymerases and metabolized as carbon and energy source as soon as the supply of the limiting nutrient is restored [82]. Depending on the species of bacteria and their growth condition, molecular weight of PHAs is in the range of 2×10^5 to 3×10^6 Da.

PHAs include a family of polyesters with different side groups and different numbers of carbon atoms in the repeating units (Figure 9.4). The most studied PHAs are poly(3-hydroxybutyrate) (PHB) and its copolymer PHBV. The homopolymer PHB is a highly crystalline thermoplastic with a T_m around 175 °C. It possesses several physical properties, e.g., T_m, T_g (15 °C), crystallinity (80%), and tensile strength (40 MPa), similar to those of PP. However, PHB is significantly more brittle than PP (strain at break 6 vs. 400%). With the introduction of 3-hydroxyvalerate (3HV) units to PHB, the regular structure of PHB is disrupted and therefore its crystallinity, crystallization rate, T_g, and T_m decrease as the content of HV increases [84]. As a result, PHBV becomes tougher and more flexible at higher HV percentages. Table 9.1 compares several physical properties of PHB and PHBV with different mole ratios of HV.



$*\!\left[O-\underset{H}{\overset{R}{\underset{|}{\overset{|}{C}}}}-(CH_2)_n-\overset{O}{\overset{\|}{C}} \right]_m\!*$

n = 1	R =	hydrogen	poly(-3-hydroxypropionate)
		methyl	poly(-3-hydroxybutyrate)
		ethyl	poly(-3-horoxyvalerate)
		propyl	poly(-3-hydroxyhexanoate)
		pentyl	poly(-3-hydroxyoctanoate)
		nonyl	poly(-3-hydroxydodecanoate)
n = 2	R =	hydrogen	poly(-4-hydroxybutyrate)
n = 3	R =	hydrogen	poly(-5-hydroxyvalerate)

Figure 9.4 General structure of PHAs.

PHAs can be consumed by microorganisms as an energy source. Therefore, they are readily biodegradable in microbially active environments such as compost [86]. The enzymes secreted by the microorganisms break down PHAs into monomers. The monomers are then used up by the cell as a carbon source for biomass growth. Many factors, e.g., surface area, microbial activity, pH, temperature, and moisture, affect the degradation rate of PHAs. The end products of PHA degradation in aerobic environments are carbon dioxide and water, while methane is also produced in anaerobic conditions. The degradation rate of PHAs varies with environmental conditions. For instance, PHBV completely degrades after 6, 75, and 350 weeks in anaerobic sewage, soil, and sea water, respectively [84]. However, PHAs do not degrade under normal conditions of storage [87].

With their inherent biocompatibility and biodegradability, PHAs have found important applications in medical and pharmaceutical areas, including wound management (e.g., sutures, skin substitutes, nerve cuffs, and staples), vascular system (e.g., heart valves, cardiovascular fabrics, and vascular grafts), orthopedics (e.g., scaffold, spinal cages, bone graft substitutes, and internal fixation devices), and drug delivery systems [88]. PHAs are also finding more and more applications in packaging, single-use, and disposable items, housewares, appliances, electrical and electronics, consumer durables, agriculture and soil stabilization, adhesives, paints, and coatings, and automotive parts. In the United States, PHAs are commercially produced by Metabolix through the fermentation of enzyme-thinned starch, plant sugars, and oils using microbial biofactories. A series of PHAs, including homopolymers, copolymers, and terpolymers, are produced under the brand name of Mirel™. This wide range of PHA structures has allowed a broad property envelope of PHAs, from rigid thermoplastics to thermoplastic elastomers and adhesives.

PHAs have been blended with many biodegradable and non-biodegradable polymers to improve their properties and lower material costs. Miscibility, crystallization behavior, and biodegradability of the blends are the main topics of the published articles on PHA blending. PHB was found to be

Table 9.1 Thermal and mechanical properties of PHB and PHBV [85]

Polymer	T_g (°C)	T_m (°C)	Modulus (GPa)	Strength (MPa)	Strain at Break (%)
PHB	9	175	3.8	45	4
PHBV (11%HV)	2	157	3.7	38	5
PHBV (20%HV)	−5	114	1.9	26	27
PHBV (28%HV)	−8	102	1.5	21	700
PHBV (34%HV)	−9	97	1.2	18	970

miscible with poly(ethylene oxide) (PEO), poly(vinyl acetate) (PVAc), poly(*p*-vinylphenol), poly(vinylidene fluoride), and poly(methyl methacrylate) (PMMA) to various degrees under different component ratios and temperatures. PHB is not miscible or only partially miscible with poly(-vinyl acetate-*co*-vinyl alcohol), PCL, PLA, poly(oxymethylene), ethylene–propylene rubber, EVA copolymer, and epichloridrin elastomers. The reports on mechanical properties of the blends are limited. Parulekar and Mohanty toughened PHB using epoxidized natural rubber with maleated polybutadiene as the compatibilizer [89]. The toughness of PHB was increased by 440%. PHB was also toughened by poly(*cis*-1,4-isoprene) (PIP) and PIP-*g*-PVAc, respectively [90]. It was found that the tensile properties and impact strength of the PHB/PIP-*g*-PVAc blends were superior to the PHB/PIP blends due to the former's higher compatibility. Li *et al.* prepared PHB/PEO blends by solvent casting [91]. They found that when the molecular weight of PEO was low (0.3×10^6), the blends exhibited very poor properties. When the PEO with a molecular weight of 5×10^6 was used, synergism occurred and the tensile strength, modulus, and elongation of the blends all increased to be significantly higher than those of the component materials.

Properties of PHAs were also modified by natural fibers. It has been shown that the addition of natural fibers increased modulus, T_g, and heat distortion temperature (HDT) of PHB (or PHBV) composites [92,93]. Nevertheless, the improvements in tensile strength and toughness were found to be difficult and to depend on many factors such as fiber length and aspect ratio, interfacial bonding, fiber sources, fiber treatments, and fiber forms (single fiber/fabrics). The studies on the composites of PHB/PHBV with flax [92], recycled cellulose fiber [93], wood fiber [94], and pineapple fiber [95] have shown that the tensile strength and toughness were not improved or were even decreased by the addition of short or flour-type natural fibers. Very recently, Jiang *et al.* reported a PHBV/BPF composite with substantially increased tensile strength, modulus, and toughness [34]. They also found that using PHBV-g-MA as a compatibilizer, the strength and modulus were further improved and the impact strength was decreased, due to the increased interfacial bonding between PHBV and BPF. CNWs were also used to reinforce PHBV [96]. PHBV/CNWs composites were prepared by solvent casting and melting compounding, respectively. Homogeneous dispersion of CNWs was achieved and the composites exhibited improved tensile strength and modulus and increased T_g in the solvent-prepared composites. By contrast, the composites prepared through melt process showed decreased strength and constant T_g due to CNW agglomeration.

PHAs have also been spun into fibers for use in textile products. Commercially available Biopol® PHBV fibers were reported to have a tensile strength of 183 MPa [97]. Iwata *et al.* spun ultra-high-molecular-weight PHB fibers with a tensile strength of 1.3 GPa by a combination of cold-drawing and two-step-drawing methods [98]. Using commercial PHBV, Tanaka *et al.* produced high strength fibers (1.1 GPa) using room temperature drawing after isothermal crystallization at the glass transition temperature (T_g) of PHBV [99]. This strength is comparable to that of common polymer fibers such as polyethylene (PE) and poly(ethylene terephthalate) (PET).

9.4 Biodegradable Polymers Derived from Petroleum

Biodegradable polymer can be derived not only from renewable bio-resources but also from petroleum. Some synthetic aliphatic polyesters have been known to be biodegradable for decades. Petroleum-based biodegradable polyesters are synthesized by polycondensation reaction between aliphatic diacids and aliphatic diols or by ring-opening polymerization of lactones. Aliphatic acids and terephthalic acids can also be used together to react with aliphatic diols to produce biodegradable aliphatic–aromatic copolyesters. Typical synthetic aliphatic polyesters include PCL, PBS, and their copolymers. The most widely used aliphatic–aromatic copolyester is PBAT produced by BASF (Ecoflex®), DuPont (Biomax®), and Eastman Chemical (Eastar Bio®).

9.4.1 Polycaprolactone

PCL is a semicrystalline aliphatic polyester synthesized by ring-opening polymerization of caprolactone (Figure 9.5). It is completely degradable through enzyme activities [100].

Depending on its molecular weight, PCL can be a waxy solid (Mw below several thousands) or a solid polymer (Mw above 20,000). The waxy PCL is usually used as additives or co-component. High molecular weight PCL polymer has mechanical properties similar to PE, possessing a tensile stress of 12–30 MPa and a break extension of 400–900%. Table 9.2 provides several properties of PCL with different molecular weights [101]. It is obvious that all the properties are strongly molecular weight dependent.

PCL shows high-molecular-chain flexibility and outstanding processability. It can be spun into fibers or blown films under 200 °C without thermal degradation. The drawback of PCL is its low melting point (~60 °C) and low glass transition temperature (~−60 °C), which prohibited its applications at elevated temperatures [102]. Therefore, PCL is often blended with other polymers, such as PP,

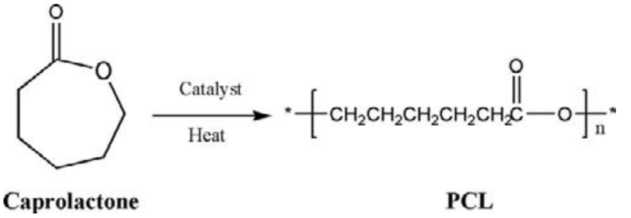


Figure 9.5 Synthesis and structure of PCL.

Table 9.2 The properties of PCL with different molecular weight

Properties	PCL 1	PCL 2	PCL 3
Molecular weight	37,000	50,000	80,000
Melting point (°C)	58–60	58–60	60–62
Tensile stress (kg/cm^2)	140	360	580
Elongation at break (%)	660	800	900

polycarbonate (PC), polyethylene oxide (PEO), and starch, to produce composites with desired properties [103,104]. Major PCL producers include Dow Chemical in the United States, Solvay in Europe, and Daicel Chemical Industries in Japan. Commercialized with the trade name "TONE" and "CAPA," PCL is extensively used in food packaging and tissue engineering. For instance, microcellular PCL foams are used for tissue regeneration and cell transplantation.

9.4.2 Poly(butylene succinate)

PBS is one of the most important biodegradable polyesters synthesized by polycondensation between succinic acid and butanediol. The reaction proceeds in two steps. First esterification occurs between the diacid and the diol, and then polycondensation takes place under high temperature to form high-molecular-weight PBS (Figure 9.6).

Showa Highpolymer (Japan) synthesized various aliphatic copolyesters (PBS and PBSA) based on succinate, adipate, ethylene glycol, and 1,4-butanediol which were synthesized and commercialized them under the trade name "Bionolle." [105] These polyesters exhibit melting temperature >100 °C and thermal degradable temperature >300 °C and other properties similar to LDPE, HDPE, and PP (Table 9.3) [106]. They can be processed by injection molding, extrusion, and film blowing using conventional equipment. Therefore, they are considered to be the potential alternatives to petrochemical polyolefins.

9.4.3 Poly(butylene adipate-co-terephalate)

PBAT is an aliphatic–aromatic copolyester which shows higher chain stiffness than entirely aliphatic polyesters such as PCL and PBS due to the inclusion of terephthalic groups in the molecules. The chemical structure of PBAT is shown in Figure 9.7.

PBAT can be synthesized by conventional bulk polycondensation techniques. It degrades completely in soil, in aqueous environment, and under composting and anaerobic conditions within varying time periods, depending on the average chain length of the aromatic blocks [108–111]. Table 9.4 lists the properties of three commercial biodegradable

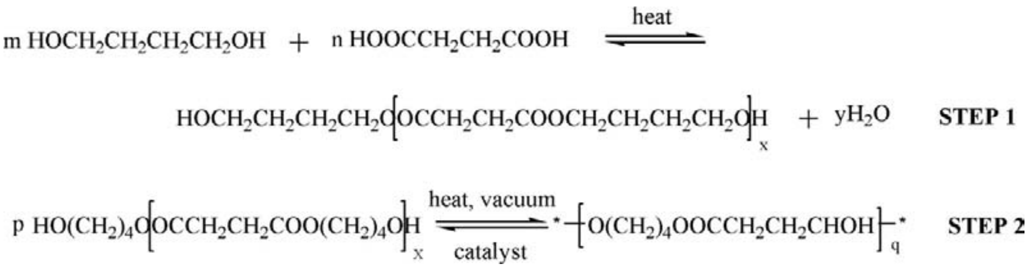


Figure 9.6 Synthesis and structure of PBS.

Table 9.3 Comparison of the properties of Bionolle and LDPE, HDPE, and PP

Properties	Bionolle (#1001)	Bionolle (#3001)	LDPE	HDPE	PP
Glass transition (°C)	−32	−45	−120	−120	5
Melting point (°C)	114	94	110	129	163
HDT (°C)	97	69	88	110	145
Tensile strength (MPa)	57	47	35	39	44
Yield strength (Mpa)	32	19	12	27	31
Flexural modulus (MPa)	656	323	176	1070	1370
Strain at break (%)	700	900	400	650	800
MFR at 190 °C (g/10 min)	1.5	1.4	2	2	4

Data adapted from http://www.shp.co.jp/en/bionolle_data1.htm [107].

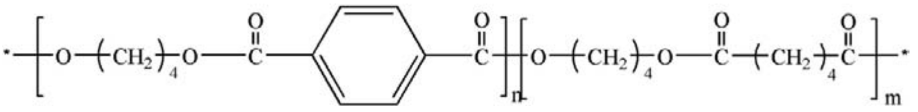


Figure 9.7 Chemical structure of PBAT.

Table 9.4 Properties of three biodegradable aliphatic–aromatic polyesters

Trade name	**Ecoflex**	**Eastar**	**Biomax**
Producer	BASF, Germany	Eastman, USA	DuPont, USA
Raw materials	1,4-Butanediol, adipic acid, terephthalic aicd	1,4-Butanediol, adipic acid, terephthalic aicd	PET with aliphatic dicarboxylic acid
Density (g/cm^3)	1.25–1.27	1.22	1.35
Melting point (°C)	110–115	108	200
Tensile strength (MPa)	32–36	20–22	15–50
Strain at break (%)	580–800	700–730	40–500
Modulus (MPa)	–	106–107	60–2100

Data adapted from R.J. Müller, *Handbook of Biodegradable Polymers*, Rapra Technology Limited, 2005, Chapter 10, p. 303 [112].

aliphatic–aromatic polyesters. Currently, these materials are mainly used in packaging and agricultural applications.

9.5 Biobased Polymers Derived from Plant Oil

Plant oils, including soybean oil, vegetable oil, corn oil, etc., are important raw materials for biobased polymers due to their triglyceride structure and fatty acid chains. Triglyceride contains reactive groups, such as carbon–carbon double bond, and allylic and ester groups which make it possible to introduce polymerizable groups into triglyceride molecules using common synthetic techniques (Figure 9.8). Before they can be used as monomers for high-molecular-weight polymeric materials, all plant oils need to be functionalized by modifying these active sites.

9.5.1 Functionalization of the Carbon–Carbon Double Bond in Triglycerides

The double bonds in triglycerides cannot be used for polycondensation reaction to produce high-molecular-weight polymers without proper modification. Four types of modified triglycerides are shown in Figure 9.9 [113–116]. For compounds 1, 2, and 3, free radical polymerization can proceed through the introduced double bonds. For compound 4, the introduced epoxy group can go through ring-opening or condensation polymerization. Wool *et al.* have conducted intensive research on synthesis of biobased polymers using modified plant oils [116–120]. From compound 1, they synthesized a thermosetting resin by free radical polymerization or copolymerization with reactive diluents such as styrene [117]. The resulting resin exhibited mechanical properties similar to that of commercial polyester and vinyl ester resins. The epoxidized plant oil has been extensively used in surface coating, in ink, and as the major composition of several resins [114].

9.5.2 Modification of the Ester Group

Another important modification to plant oils is to convert triglyceride to monoglyceride or diglyceride through glycerolysis reaction. The conversion reaction can be carried out by heating the triglycerides and glycerol at 220–230 °C with $Ca(OH)_2$ as a catalyst, and the resulting mixture product (containing diglyceride and monoglyceride) was reacted with methacrylic anhydride [120] or MA [121] to obtain other

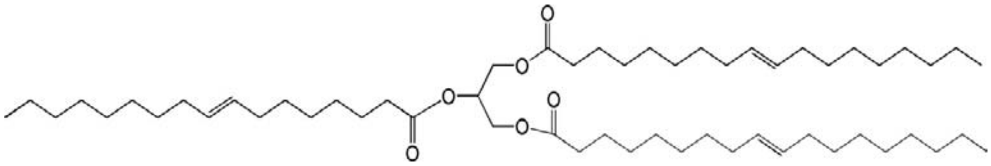


Figure 9.8 Typical structure of plant oil.

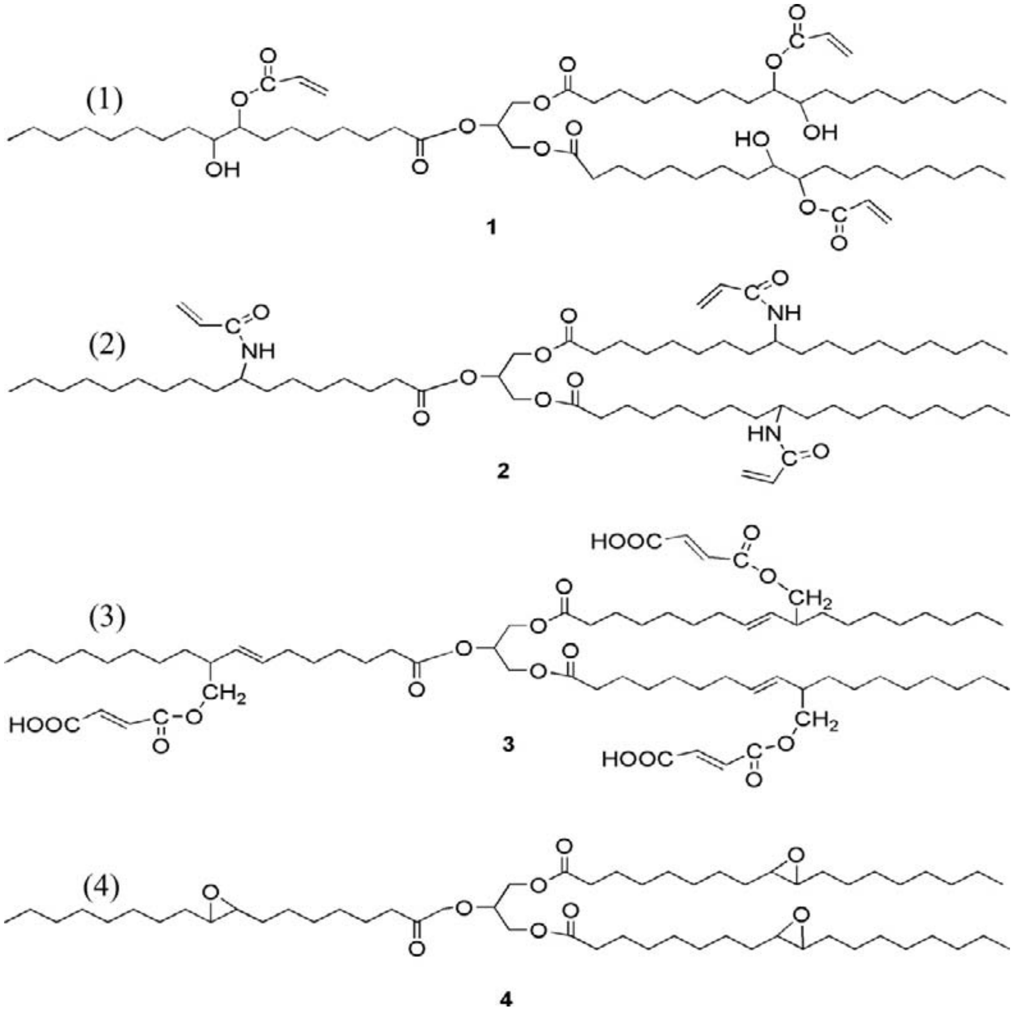


Figure 9.9 Several typical compounds derived from triglyceride [113−116].

triglyceride-based monomers. By this method, several plant oil-based unsaturated polyesters with the melting points in the range of 60−70 °C have been synthesized by Wool's group. On the other hand, using the monoglycerides and diglycerides derived from plant oils, some biobased PUs with excellent chemical and physical properties including increased thermal stability have been synthesized [122,123]. In addition, waterborne PUs and PU/acrylic hybrid latex were made from soybean oil-based polyols [124].

9.6 Concluding Remarks

Biodegradable polymers could be either natural or synthetic polymers and they could be derived from either renewable or non-renewable resources. Non-biodegradable polymers could also be derived from renewable feedstock, e.g., Dupont's Sorona®, which is poly(trimethylene terephthalate) using the corn-derived 1,3-propanediol as the diol monomer. Developing biodegradable polymers from renewable resources appears to be the best scenario in the development of "green" materials and processing techniques. However, this can only be certain after carrying out a life cycle environmental impact analysis (mainly on energy consumption and CO_2 balance) on individual products. For example, to produce PLA using corn starch, the application of fertilizers, herbicides, and pesticides during the growth of corn may leave a deep environmental footprint. The chemical or biochemical processes such as extraction and purification of lactic acid require water, energy, and chemical or biological additives. The whole production process also produces various wastes which require energy and material-consuming treatment and disposal. Furthermore, CO_2 is released back to the environment during the degradation of PLA. Therefore, biodegradable polymers derived from renewable resources may not be as "green" as they appeared to be at the first sight. However, if significant part of the energy required to produce and process biodegradable polymers is from non-petroleum sources, e.g., solar power, wind energy, water/tide power, etc., biodegradable polymers based on renewable resources could still possess substantially better CO_2 balance than petroleum-based polymers.

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10 Polymeric Biomaterials

Wei He [1,2] and Roberto Benson [1]
[1] Department of Materials Science and Engineering, University of Tennessee, Knoxville, TN 37996, USA
[2] Department of Mechanical, Aerospace, and Biomedical Engineering, University of Tennessee, Knoxville, TN 37996, USA

10.1 Introduction

Biomaterials, an exciting and highly multidisciplinary field, have matured into an indispensable element in improving human health and quality of life in the modern era. Applications of biomaterials range from diagnostics such as gene arrays and biosensors, to medical supplies such as blood bags and surgical tools, to therapeutic treatments such as medical implants and devices, to emerging regenerative medicine such as tissue-engineered skin and cartilage, and more. A general classification divides biomaterials into three main categories: metals, ceramics, and polymers. Polymers, being organic in nature, offer a versatility that is unmatched by metals and ceramics. The wide spectrum of physical, mechanical, and chemical properties that polymers can provide has fueled the extensive research, development, and applications of polymeric biomaterials. Furthermore, the significance of polymers in the field of biomaterials is clearly reflected from the staggering market size of medical polymers, estimated to be roughly $1 billion business with yearly growth of 10–20% [1].

This chapter provides a brief overview of several medical applications that polymers have made seminal contributions to over the years. Many of the polymers discussed here are initially developed as plastics, elastomers, and fibers for nonmedical industrial applications. They were "borrowed" by the surgeons post-World War II to address medical problems. Since then, they have led to the development of biomedical-specific materials. Currently, with the rapid growth in modern biology and the collaborative effort, cross-disciplines such as materials science, engineering, chemistry, biology, and medicine, polymeric biomaterials are now being fashioned into bioactive, biomimetic, and most importantly, with excellent biocompatibility. Examples of this newer generation of polymeric biomaterials are also included in this chapter.

10.2 Polymeric Biomaterials in Ophthalmology

Ophthalmology focuses on the diseases of the eye, which is a complex and vital organ for daily life. Application of biomaterials in ophthalmology can be dated back to the mid-nineteenth century, when Adolf Fick successfully invented the glass contact lens. Since then, a wide variety of ophthalmological biomaterials have been developed and some are finding overwhelming success in clinical applications. Applications of biomaterials in ophthalmology include contact lenses [2], intraocular lenses (IOLs) [3], artificial orbital walls [4], artificial corneas [5], artificial lacrimal ducts [6], glaucoma filtration implants [7], viscoelastic replacements [8], drug delivery systems [9], scleral buckles [10], retinal tacks and adhesives [11], and ocular endotamponades [12]. Although ceramics and metals have also been used in ophthalmology, modern ophthalmic implants are mainly made of polymers. The focus of this section will be placed on polymers used for contact lens, IOL, and artificial corneas.

10.2.1 Polymeric Contact Lens

A contact lens is an optical device placed on the cornea of the eye for corrective, therapeutic, or cosmetic effects. It is estimated that there are approximately 125 million contact lens wearers worldwide. A myriad of principle properties have been sought in high performance contact lens materials, including: (1) good transmission of visible light; (2) high oxygen permeability; (3) tear-film wettability; (4) resistance to deposition of components from tear-film, such as lipid, protein, and mucus; (5) ion permeability; (6) chemical stability; (7) good thermal conductivity; and (8) amenability to manufacture [13]. A wide variety of polymers have been used in contact lenses, and their modulus of elasticity defines contact lenses to be either hard or soft. Structures of the various monomers commonly used in contact lenses are shown in Figure 10.1. The first generation of polymeric contact lenses was made of poly(methyl methacrylate) (PMMA), a polymer commercially known as Plexiglas® and is a classical example of hard or rigid lens material. PMMA can be prepared using bulk free-radical polymerization and lathed into lens shape. It has excellent optical properties such as index of refraction with greater clarity than glass, remarkable durability, and good resistant against deposition of components from the tear-film due to its hydrophobicity. However, major drawbacks such as lack of oxygen

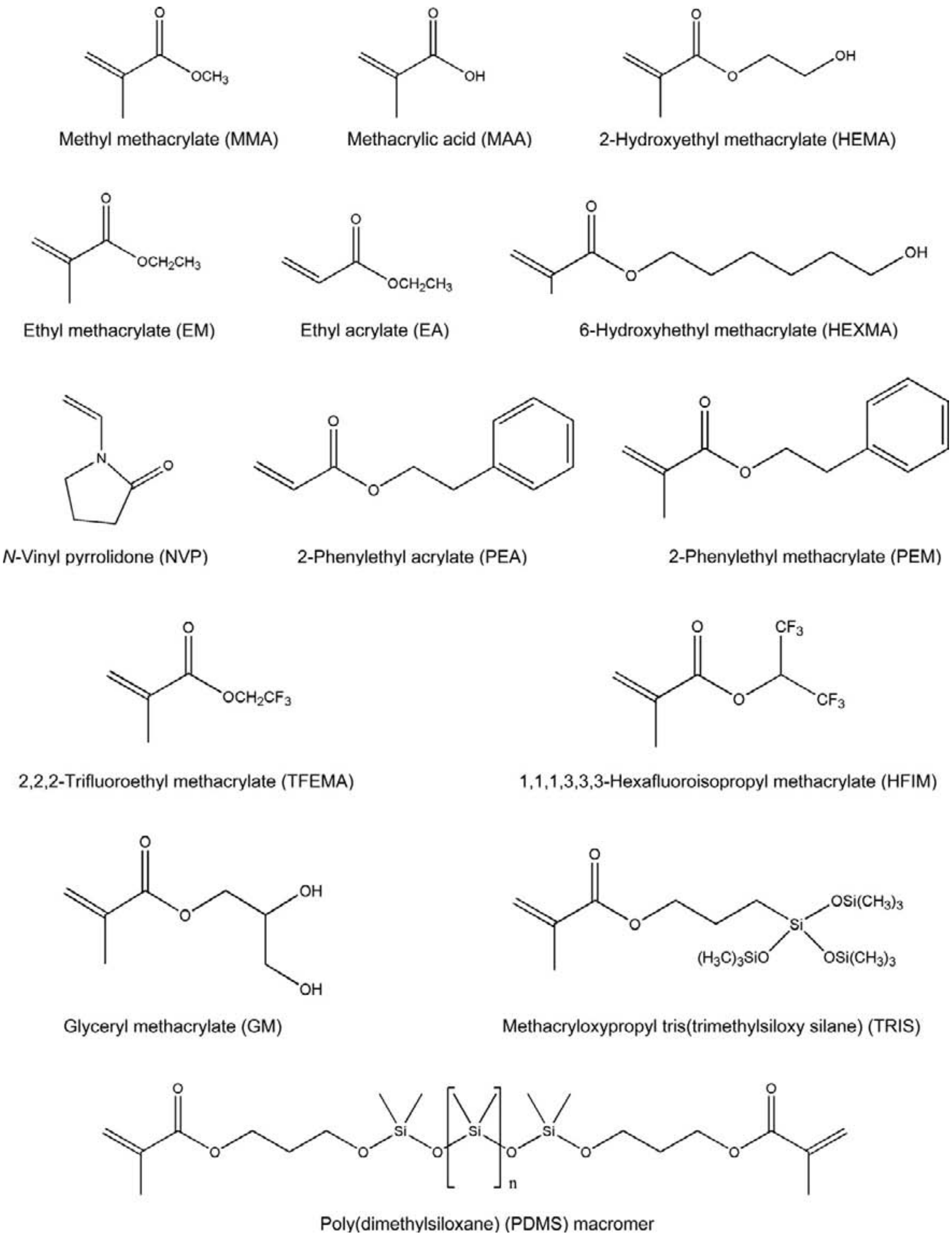

Figure 10.1 Chemical structures of common monomers used in contact lens and intraocular lens.

permeability and tendency to change the shape of the eye have limited the usage of PMMA contact lenses. In order to improve the permeability of oxygen, rigid gas-permeable (RGP) contact lenses were developed in the late 1970s. Materials used for RGP contact lenses are typically copolymers of methyl methacrylate (MMA) with a monomer that imparts high oxygen permeability, e.g., methacryloxypropyl tris(trimethylsiloxy silane) (TRIS), hexafluoroisopropyl methacrylate (HFIM), and 2,2,2-trifluoroethyl methacrylate (TFEMA). The incorporation of highly hydrophobic siloxane into the copolymer will reduce the lens wettability, which leads to undesired increase of lipid deposition. Therefore, hydrophilic monomers, such as methacrylic acid (MAA), 2-hydroxyethyl methacrylate (HEMA), or *N*-vinyl-2-pyrrolidone (NVP), are commonly used as wetting agents in RGP lens formulation to compensate for reduction in wettability.

Soft contact lenses emerged in the 1960s when Otto Wichterle developed poly(2-hydroxyethyl methacrylate) (PHEMA) [14] and forever changed the contact lens industry. Generally, soft contact lenses are made from hydrogel, a cross-linked network capable of retaining a significant amount of water. The first PHEMA soft lens contained 40% water of hydration. Despite its improvement in wearer comfort over rigid lens, the low oxygen permeability of PHEMA was interfering with the normal corneal metabolism. Since the extent of hydration directly affects the permeability of oxygen, hydrogels with high water content (>50%) have been developed by copolymerizing HEMA with highly hydrophilic monomers such as NVP, MAA, and glyceryl methacrylate (GMA). A drawback associated with increased hydrophilicity is the higher protein binding to the lens, which could cause discomfort and complications such as increased bacterial adhesion [15]. High water content hydrogels also tend to cause corneal desiccation. In the quest for high oxygen permeability, researchers have developed a new type of siloxane-containing hydrogels for soft contact lenses. It is well known that due to the bulkiness of the siloxane groups ($-Si(CH_3)_2-O-$) and the chain mobility, siloxane-containing materials typically have high diffusivity of oxygen. On the other hand, siloxane materials are highly hydrophobic, therefore, prone to lipid deposition and less comfortable with rubbery-like behavior. To offset these shortcomings, functionalized siloxane macromer (shown in Figure 10.1) was copolymerized with hydrophilic monomers (e.g., NVP and HEMA) into hydrogels that offer sufficiently high oxygen transmission required by the cornea as well as the softness for comfortable extended wear. Currently, commercialized siloxane hydrogel contact lenses include Focus® Night & Day™ (lotrafilcon A by CIBA Vision Corp.) and PureVision™ (balafilcon A by Bausch and Lomb). It is worth noting that the presence of siloxane moieties on the surface of these hydrogels demands further treatments in order for the lens to be tolerated on the eye. Examples of surface treatment for siloxane hydrogels include radio-frequency glow discharge (RFGD) [16] and graft polymerization of hydrophilic monomers (e.g., acrylamide [17]) on the lens surface to improve surface hydrophilicity.

10.2.2 Polymeric Intraocular Lens

IOLs are commonly used to replace natural lenses and provide clear optical imaging for patients undergoing cataract surgery. IOL is a major area in ocular biomaterials research for its critical role in treating cataract-induced blindness, which was predicted to reach 40 million cases by the year 2020 [18]. IOL also holds a special place in the biomaterials history, where its invention was originated from Sir Harold Ridley's accurate observations of biological reaction to accidentally implanted pieces of the canopy in World War II pilot's eyes. Since the canopy material, PMMA, was well tolerated by the eye, Ridley was inspired to use the material to invent the first biocompatible IOL and it is well recognized as a pioneering breakthrough in biomaterial science. The key material requirements for IOLs include the optical property, i.e., able to maintain a clear path for optical imaging and the long-term biocompatibility as the implant is intended to reside in the eye permanently. PMMA dominated the IOL market for 40 years before other materials emerged. Despite its excellent optical properties and relative tolerance by the eye, PMMA still induced damages to the tissues around the IOL implant. Of primary concerns are the injury of the corneal endothelium associated with the lens rigidity, and the accumulation of inflammatory cells to the IOL surface, which could lead to complications such as iris adhesion to the IOL, uveitis, and loss of vision [19]. Such issues have led to newer IOL designs and materials selection. In contrast to the original hard and bulky PMMA IOL, common IOLs nowadays are featured as soft and foldable.

The most widely used foldable IOL, AcrySof®, is fabricated from a copolymer of phenylethyl acrylate and phenylethyl methacrylate with a crosslinking reagent and a UV-absorbing chromophore. Its improved optical property, i.e., higher refractive index ($n = 1.55$) comparing to PMMA ($n = 1.49$), allows a thinner IOL configuration. The mechanical characteristic of the copolymer led to a slow and better controlled unfolding of the IOL, which contributed to the significant reduction in posterior capsular opacification (PCO). Other materials used in foldable IOL fabrication include silicone elastomers, hydrophilic acrylics (with water content higher than 18%), and collagen copolymers (Table 10.1). Although hydrophilic acrylic IOLs have shown good uveal biocompatibility due to the reduction in protein adsorption and macrophage adhesion, they tend to present

Table 10.1 Examples of biomaterials for IOLs (modified from Lloyd and Patel [20,21])

Manufacturer	Lens Type	Material	Refractive Index
Advanced Medical Optics	Rigid	PMMA	1.49
ALCON	ACRYSOF® foldable	PEA/ PEMA	1.55
Bausch & Lomb	Hydroview® foldable	HEMA/ HEXMA	1.47
Calhoun Vision	Multifocal foldable	PDMS	1.41
STAAR Surgical	Collamer® foldable	Collagen/ HEMA	1.45

higher rate of PCO and cause anterior capsular opacification, which reduced their application in the market [22−25].

10.2.3 Polymeric Artificial Cornea

Cornea is a transparent tissue situated at the front of the eye. It is the main element in the ocular optical system, and plays various roles from refracting light onto the retina to form an image, to acting as a protective barrier for the delicate internal eye tissue. Damages to the cornea can result in loss of vision, which accounts for the second most common cause of blindness worldwide behind cataract [26]. The most widely accepted treatment of corneal blindness is transplantation of human donor corneas. However, the limitations in the availability of donor cornea tissues have called for design and development of artificial cornea substitute. Artificial corneas, also known as keratoprostheses, come in a variety of forms, from fully synthetic to tissue-engineered. The focus of this discussion will be on polymer-based synthetic keratoprostheses. Several excellent comprehensive reviews on artificial corneas are available for further reading [27−29].

The cornea tissue is complex, avascular, highly innervated, and immune privileged. It is arranged in three major cellular layers: an outer stratified epithelium, an inner single-layered endothelium, and sandwiched in between a stromal compartment, which is responsible for the optical properties of the cornea. Although it is challenging to duplicate the complex structure of the natural cornea, it is possible to construct an artificial cornea, which can simulate the physical features of the natural cornea and to restore some functional level of vision. An ideal artificial cornea should meet the following specific requirements: (1) transparent with a smooth anterior surface of appropriate curvature; (2) suitable refractive index; (3) flexible and sufficient tensile strength for surgical handling; (4) ability to heal with the host cornea; (5) ability to promote and sustain the growth of epithelium over the anterior surface of the artificial cornea; (6) ability to avoid the formation of a retrocorneal fibroblastic membrane; and (7) biocompatibility [30]. Early generations of artificial cornea were made from a number of different hydrophobic polymers, such as PMMA, nylon, poly(tetrafluoroethylene) (PTFE), polyurethane (PU), and poly(ethylene terephthalate) (Dacron®) [20,31−33]. The design evolved from one material button-like full piece to the more widely used "core-and-skirt" configuration, where the core is made from transparent material with good optical properties and the skirt is made either from the same or different material to ensure host integration. Among these polymers, PMMA is arguably the most extensively used due to its remarkable optical properties as discussed in the above IOL section. Even though the application of PMMA in artificial cornea continues, the associated complications such as retroprosthetic membrane formation, glaucoma, extrusion, endophthalmitis, and rejection [34−36] have led to the development of soft, hydrogel-based artificial cornea. Majority of the research has been directed toward HEMA-based hydrogel. An interesting observation with HEMA is that when the monomer is polymerized with the presence of 40% or less of water, it forms a homogeneous transparent hydrogel; when the water content is higher, phase separation will occur during polymerization, and the resulting hydrogel is heterogeneous and opaque. Taking advantage of such characteristics, the first "core-and-skirt" hydrogel-based artificial cornea was created using HEMA, and the device is commercially known as AlphaCor [37]. The core is the transparent, lower water content PHEMA, and the skirt is the phase-separated, macroporous opaque PHEMA. Even though PHEMA is considered a hydrophilic polymer, its water content remains far below the water level found in the natural cornea (78%). Such high water content is essential for the stability and survival of the epithelium as it facilitates nutrient diffusion. In order to increase the water content of the artificial cornea, various strategies have been explored. Examples include copolymerization of HEMA with an ionic acrylate MAA [38], and hydrogels made from homopolymer of poly(vinyl alcohol) (PVA), which can contain over 80% water at equilibrium [39,40]. Several groups have also reported making biomimetic hydrogels for artificial cornea. As the extracellular matrix of the cornea is dominated by type I collagen, it has been used in preparation of a copolymeric hydrogel based on *N*-isopropylacrylamide (NIPAAm), acrylic acid, *N*-acryloxysuccinimide, and collagen [41]. The engineered hydrogel is essentially a network comprising of collagen crosslinked to the copolymers of acrylic acid and NIPAAm using the succinimide pendant groups. This material has demonstrated the biomechanical properties and the required optical clarity to be used for corneal transplantation. *In vivo* animal studies have shown successful regeneration of host corneal epithelium, stroma, and nerves [41]. Clinical trials are currently underway to evaluate this material for therapeutic use in humans.

Interpenetrating polymer networks (IPNs) have also been used for artificial cornea applications. IPN represents a mixture of polymer networks where one polymer is crosslinked in the presence of another polymer network to form a mesh of two different polymers. The major advantage with IPN is that it combines the beneficial properties of both polymers into the final material. Early application of IPNs in artificial cornea was at the connection between the optical core and the peripheral skirt, where an interdiffusion zone of IPN provides a permanent and reliable union of the PHEMA sponge skirt with the PHEMA core [42]. More recent efforts focus on incorporating IPNs in the entire artificial cornea construct. One design is based on IPNs of poly(dimethylsiloxane) (PDMS) and PNIPAAm [43], where the mechanical strength, transparency, and oxygen permeability of PDMS is combined with the hydrophilicity and nutrient permeability of PNIPAAm to form a functional artificial cornea. Another example is IPN of a neutral crosslinked poly(ethylene glycol) (PEG) and a charged, loosely crosslinked polyacrylic acid (PAA) [44,45]. Such IPN has displayed optical transparency with good mechanical properties and glucose diffusion coefficients comparable to that of the natural cornea [46]. Although majority of the artificial cornea have shown satisfying biocompatibility in animal models, it is critical to ensure that the materials are nontoxic, nonimmunogenic, nonmutagenic, and do not result in corneal opacification.

10.3 Polymeric Biomaterials in Orthopedics

Traditionally, orthopedic biomaterials are mainly metallic, largely due to the close property resemblance to that of bone tissue such as high strength, hardness, and fracture toughness. Polymers have also been used in orthopedics over the years, and they are receiving increasing interest for bone tissue engineering. Historically, the use of polymers in orthopedics for the most part is reserved to those capable of performing well for fixation of structural devices and under cyclic load-bearing conditions such as in knee and hip arthroplasty. Despite hundreds of orthopedics applications available in the market, they are dominated by only a few types of polymers, including ultrahigh-molecular-weight polyethylene (UHMWPE) and PMMA.

10.3.1 Polyethylene

UHMWPE is a linear polyethylene with molecular weight usually between 2 and 6 million. The fracture toughness, low friction coefficient, high impact strength, and low density of UHMWPE have made it a popular choice as the articulating surfaces of joint replacements, such as hip, knee, ankle, and shoulder. Although UHMWPE possesses numerous attractive bulk and surface properties, these properties can be compromised by the presence of long-term radicals in the bulk resulting from the ionizing radiation employed in the sterilization process [47]. These radicals can interact with oxygen, leading to the generation of oxygen containing functional groups and deterioration of the surface and bulk properties, particularly the rate of production of particles during the wear process. An overproduction of wear debris has been linked to the inflammatory reaction in the tissues adjacent to the implant. This adverse tissue response will lead to granulomatous lesions, osteolysis, bone resorption, and implant failure [48]. In an effort to overcome the oxidation, a number of additives, such as antioxidant α-tocoferol and vitamin C, are currently used to retard oxidation and enhance surface properties [49]. UHMWPE has been considered the weak link in any total joint replacement because of wear issue. To improve wear resistance, highly crosslinked UHMWPE has been produced and used in joint replacement. Crosslinking is achieved by irradiating UHMWPE with electron beam or gamma irradiation, followed by a melting step to eliminate the free radicals produced during irradiation. Currently, there is a debate on crosslinking and the clinical performance of UHMWPE. Those in favor have shown evidence of the efficacy of highly crosslinked UHMWPE in reducing the wear in total joint arthroplasties and the associated periprosthetic osteolysis [50]. The opposition states that improvement of wear resistance by crosslinking is at the expense of reduction in the static mechanical properties, such as tensile and yield strength as well as fatigue crack propagation resistance, which could affect the implant longevity especially in total knee arthroplasty [51]. Complete data regarding the ultimate long-term performance of highly crosslinked UHMWPE will help settle the scientific debate.

10.3.2 Polyacrylates

Application of PMMA as fixative for bone was first demonstrated by Charnley [52]. The PMMA bone cement is composed of the liquid monomer MMA, a partially polymerized PMMA powder, an initiator (commonly used dibenzoyl peroxide), an activator (*N*, *N*-dimethyl-*p*-toluidine), a radiopacifier (visible to X-rays) such as barium sulfate or zirconium oxide, and a copolymer to influence the mixing and handling of the cement [53]. In some cases, an antibiotic (e.g., gentamicin) is included in the formulation to minimize infection during implantation. The polymerization is initiated by the interaction between the activator and the initiator, yielding a free radical that reacts with the monomer. The solidified polymer is able to secure a firm fixation of the prosthesis in the bones. Although acrylic bone cements are widely used in orthopedics, several drawbacks are related with their use. The residual monomer could leak into the body and cause fat embolism [54]. The exothermic nature of the polymerization process can be a potential cause for necrosis of the surrounding tissue. The most critical drawback is aseptic loosening, i.e., loosening of the implant within the cement. The cause of aseptic loosening could be mechanical and/or biochemical. Mechanically, cyclic loading of the implant could lead to fatigue fracture of the cement [55]. Biochemically, wear debris of the polyethylene component could migrate to the bone–cement interface and trigger inflammatory response, leading to osteolysis and weakening the implant interface [56]. In order to improve upon PMMA fixation, a possible strategy is to avoid cement fracture by increasing the mechanical strength of the cement. Researchers have developed bone cement with higher bonding strength and compressive modulus than conventional PMMA, using a bisphenol-A-glycidyl dimethacrylate (Bis-GMA)-based resin impregnated with bioactive glass ceramics [57,58]. Another approach takes advantage of composites by reinforcing PMMA with hydroxyapatite (HA) [59] and bioactive glass [60], which combines strength and elasticity with bioactivity.

The other acrylate bone cement is based on polyethylmethacrylate (PEMA) and *n*-butylmethacrylate (*n*-BMA) monomer [61]. Comparing to PMMA cement, less heat is produced during polymerization of the PEMA-*n*-BMA cement, and the polymer has a relatively low modulus and high ductility to reduce the issue of fracture. The biocompatibility of the PEMA-*n*-BMA cement has been excellent [62]. But these bone cements have been found to be susceptible to creep. To improve creep resistance, bioactive HA particles were incorporated [63]. Although HA improved bioactivity and creep behavior of the cement, the cement failed at lower number of cycles.

10.3.3 Natural Polymers

Natural polymers are finding increasing applications in the area of bone replacement and hard tissue augmentation. Ideally, materials used for such purpose should be biocompatible, able to mimic the three-dimensional characteristics, physical, and mechanical nature of the bone and hard tissue, able to support appropriate cellular functions, and able to be replaced gradually by the regenerating new tissue. A variety of natural polymers have been used, including extracellular matrix proteins such as collagen [64], polysaccharides such as chitosan [65], alginate [66], starch [67], and cellulose [68], as well as glycosaminoglycans such as hyaluronic acid [69]. Some of the natural polymers can provide a template for biomimetic apatite formation, which is highly desirable to induce rapid bone colonization. Recent studies by Hutchens et al. [70] revealed the formation and characterization of bacterial cellulose/hydroxyapatite composites with potential for bone replacement. Both degradable and nondegradable bacterial cellulose were used to form the composite. The hydroxyapatite present in the composite has ordered nanometer needle-like particles with nonstoichiometric composition similar to that observed in human bone. The combined bioactivity and biocompatibility substantiates the potential of this composite for orthopedic application.

10.4 Polymeric Biomaterials in Cardiovascular

Biomaterials have played a vital role in the treatment of cardiovascular diseases, examples of applications including heart valve prostheses, vascular grafts, stents, indwelling catheters, ventricular assist devices, total implantable artificial heart, pacemakers, automatic internal cardioverter defibrillator, intra-aortic balloon pump, and more. A key requirement for materials in cardiovascular applications, particularly blood-contacting devices, is blood compatibility, i.e., nonthrombogenic. Additional requirements include mechanical and surface properties that are application specific. Surveying the field of polymers used in cardiovascular applications reveals that PUs, polyethylene terephthalate (PET), and expanded PTFE (ePTFE) are the most commonly used. This section will review each of the three polymers followed by a brief introduction of other emerging polymers for use in the cardiovascular area.

10.4.1 Polyurethanes

PUs are among the most commonly selected biomedical polymers for blood-contacting medical devices. They can be found in hemodialysis bloodline, catheters, stents, insulation for pacemaker leads, heart valves, vascular grafts and patches, left ventricular assist devices (LVADs), etc. PUs are characterized as segmented block copolymers with a wide range of mechanical and blood contact properties, simply by varying the type and/or molecular weight of the soft segment and coupling agents. The urethane linkage, $-NH-C(=O)-O-$, in biomedical PUs can be formed through a two-step process. The initial step is a reaction involving the end-capping of the macrodiol soft segments (e.g., polyether, polyester, polycarbonate, and polysiloxane) with diisocyanate to form a prepolymer. The second reaction is the coupling of the prepolymer with a low-molecular-weight chain extender, generally a diol or a diamine [71]. The hard segment usually refers to the combination of the chain extender and the diisocyanate components.

Due to the chemical incompatibility between the soft and hard segments, the morphology of PUs consists of hard segments aggregation to form domains that are dispersed in a matrix formed by the soft segments [72,73]. Such unique morphology is responsible for the exceptional mechanical properties and biocompatibility of the biomedical PUs. For example, depending on the relative molecular weights and amounts of the hard and soft segments, the obtained PU can be elastomeric or rigid. The mechanical properties of PU can also be tailored by changing the chemical nature of the chain extender. Generally, PUs prepared with aliphatic chain extender are softer than those with aromatic chain extender. Biocompatibility of PU is also closely related to the chemical nature of the chain extender and the soft segment. Early studies by Lyman et al. [74] showed that changes in the molecular weight of the polypropylene soft segments affected protein adsorption. Lysine diisocyanate and hexamethylene diisocyanate are preferred over aromatic diisocyanates in the synthesis of biodegradable PUs, partly because of the putative carcinogenic nature of aromatic diisocyanates [75]. Recent studies have reported using natural polymers, such as chitin [76] and chitosan [77], as chain extender to improve the biocompatibility of PUs.

Biostability has been and continues to be a main research focus of PUs. Depending on the intended medical applications, the desired biostability of PUs varies. For example, PUs used as pacemaker lead covering should have superior long-term stability, whereas PUs used as a scaffold to build engineered tissue construct for replacement of diseased cardiovascular tissues should be biodegradable. The challenge to maintain long-term *in vivo* biostability of PUs lies in the fact that biodegradation of PUs is a complicated and multifactor-mediated process. Mechanisms responsible for PU biodegradation include: (1) hydrolysis; (2) oxidative degradation, metal or cell catalyzed; (3) enzymatic degradation; (4) surface cracking; (5) environmental stress cracking; and (6) calcification [75]. It is well known that PUs containing polyester soft segments have poor hydrolytic stability, and PUs with polyether soft segments are prone to oxidative degradation. Guided with valuable information collected from extensive investigation of molecular pathways leading to the biodegradation of PUs, more bioresistant PUs have been designed over the years. These strategies include using polycarbonate macrodiols [78,79], polyether macrodiols with larger hydrocarbon segments between ether groups [80], and siloxane-based macrodiols [81−83]. On the other end of the spectrum, bioresorbable PUs are attracting growing attentions as elastomeric tissue engineering scaffolds. For this class of PUs, soft segments such as polylactide or polyglycolide, polycaprolactone, and polyethylene oxide are most commonly used [84]. Furthermore, degradation is engineered into the hard segments. Enzyme-sensitive linkages have been incorporated into the hard segment, leading to specific enzymatic degradation in contrast to nonspecific hydrolytic degradation [85−87]. Another interesting addition to the hard segments is bioactive molecule such as antimicrobial drug [88]. Polymer degradation will thus lead to free drug release, making this class of PUs very attractive for biomedical applications.

10.4.2 Polyethylene Terephthalate

PET is a member of the engineering polyester family. It is a semicrystalline polymer with industrial applications of synthetic fibers and beverage and food containers. In the medical field, PET is widely used as prosthetic vascular grafts, suture, and wound dressing in either fiber or fabric form (commercially known as Dacron®). Despite the presence of hydrolytically cleavable ester linkage, PET is relatively stable *in vivo* largely due to the high crystallinity and hydrophobicity. It is one of the two standard biomaterials of prosthetic vascular grafts used clinically. It is widely used for larger vessel (diameter > 6 mm) applications. PET for vascular applications can be prepared either as woven or knitted, which will determine the porosity and mechanical property of the graft. Generally, woven finish has less porosity than a knitted graft, therefore, reducing the chance of transmural blood extravasation. Dacron® vascular graft is strong and stiff, much less compliant than natural arteries [89]. Such compliance mismatch has been considered the cause of patency loss of the graft over a long time frame (>6 months) [90]. The other major complication related to PET graft is its thrombogenicity. When the graft comes in contact with blood, plasma protein will adsorb to the luminal and capsular surfaces, leading to thrombus formation and inflammatory response. Various strategies have been explored to make the graft surface thrombo-resistant, including passivating the surface with albumin [91], coating with fluoropolymer [92], coating with hydrophilic polymer [93], covalent or ionic binding of the anticoagulant heparin albumin [94−96], covalent linkage of antithrombotic agent thrombomodulin [97], and more. Although some improvement has been reported in terms of acute thrombosis, there is still a long way to go to achieve satisfying long-term functionality of PET-based vascular grafts.

10.4.3 Expanded PTFE

ePTFE, commercially also known as Gore-Tex®, is the other one of the two standard biomaterials of prosthetic vascular grafts used clinically. Besides vascular, ePTFE is also used as patches for soft tissue regeneration, such as hernia repair, and surgical sutures. It is produced by a series of extrusion, stretching, and heating process to create a microporous material with pore size ranging from 30 to about 100 μm. Similar to PET, ePTFE is highly crystalline, hydrophobic, and highly stable. It has an extremely low coefficient of friction, making it easy for handling. Its tensile strength and tensile modulus are lower than those of PET. Even though the compliance of ePTFE grafts is relatively lower than that of PET grafts, it is still too high comparing to the natural arteries. Generally, ePTFE is the choice over PET to bypass smaller vessels. However, it still faces patency issue. Femoropopliteal reconstruction using ePTFE has a 5-year patency rate of 40−50%, comparing to the 70−80% achieved by using autogenous vein grafts [98]. Similar to PET, the cause of low patency is the thrombogenicity of the material. It has been reported that the graft failed to develop a full coverage of endothelial cells on the lumen side of the graft [99,100]. To address this issue, one approach is to increase the porosity to promote tissue ingrowth. But it requires a careful balance to prevent leakage of blood elements as mentioned above. Other approaches focus on reducing surface thrombogenicity, including carbon coating to increase surface electronegativity [101], attachment of anticoagulant or antithrombotic agents [102,103], and impregnation with fibrin glue to deliver growth factors that can promote endothelialization [104,105]. The actual benefits of these treatments are yet to be determined through longer-term *in vivo* investigations.

The challenge posed by small diameter vascular repair has spurred research for alternative biomaterials that would match or surpass the autograft. A notable effort is to build a tissue-engineered graft *ex vivo* using a synthetic biodegradable scaffold. Conceptually, such graft will have mechanical properties closely mimicking those of the native tissues without the concern of chronic inflammatory responses commonly induced by the presence of synthetic material. Up to now a wide variety of biodegradable polymers have been used to build such construct, including the poly(α-hydroxyesters): poly(glycolic acid) (PGA), poly(-lactic acid) (PLA), and their copolymers poly(lactic-*co*-glycolic acid) (PLGA); polycaprolactone; polyanhydride; polyhydroxyalkanoate; and polypeptide. Several excellent reviews are available discussing the current status of materials as scaffolding for vascular tissue engineering [106—108].

The other cardiovascular application in which polymers are poised to make a significant impact is biodegradable stents. Current stents are mainly made of metallic materials, such as stainless steel, cobalt—chromium, or Nitinol. However, long-term complications associated with metal stents have prompted research of fully degradable replacement. Several key requirements have to be satisfied by the polymeric stent, with the top two being mechanical properties and degradation characteristics. In terms of degradation, the products of degradation should be biocompatible, and the degradation process should not compromise the structural integrity of the device up to 6 months [90]. As for mechanical properties, the polymer should withstand the deployment and the blood vessel contractions. Both requirements are challenging, but with a good appreciation of the underlying biology and the versatility of polymer structure—property relationship, newer materials are likely to emerge in the near future. For example, researchers are imparting degradation and shape-memory capabilities into polymers that can self-expand and degrade over time [109,110].

10.5 Polymeric Biomaterials for Wound Closure

Surgical wounds can be closed by various means, including sutures [111], adhesives [111], tapes [111], staples [111], and laser tissue welding [112]. Among these methods, sutures are the most frequently used. The sutures are sterile filaments used to approximate and maintain tissue until the healing has provided the wound with appropriate strength to withstand mechanical stresses. Sutures can be classified based on the origin of the materials: natural or synthetic; performance of the materials: absorbable or nonabsorbable; and physical configurations: monofilament, multifilament, braided, or twisted. In general, polymers selected for sutures should elicit minimal adverse biological response in addition to having fiber forming rheological properties. The sutures must have minimum tissue drag, good strength retention, and knot security. To improve the lubricity and reduce tissue drag, coatings such as tetrafluoroethylene and silicones are normally applied to the suture. The following sections will discuss some of the common nonabsorbable polymeric sutures and currently commercially available.

In general, nonabsorbable sutures can retain their tensile strength longer than 2 months [113]. The synthetic polymers used to make nondegradable sutures include polypropylene (PP), polyamides, polyesters such PET and polybutylene terephthalate (PBT), and polyether—ester based on poly(-tetramethylene glycol), 1,4-butanediol, and dimethyl terephthalic acid [114]. The base polymer and filament configuration for common nonabsorbable sutures are summarized in Table 10.2.

The PP monofilament sutures are made from isotactic polypropylene [115]. During preparation, the PP monofilament is subjected to a series of post-spinning operations including annealing, designed to increase crystallinity [116]. Although PP sutures are highly resistant to hydrolytic degradation, it can undergo thermo-oxidative degradation [117]. PP sutures are usually sterilized by ethylene oxide or autoclave due to their susceptibility to ionizing radiation such as γ-radiation from cobalt-60 source that is normally used for radiation sterilization. In terms of performance, PP suture causes one of the lowest tissue responses.

Polyamide sutures are commonly made out of nylon-6 and nylon-6,6. Nylon-6 is synthesized by ring-opening polymerization of caprolactam, while nylon-6,6 is prepared by condensation polymerization of adipic acid and hexamethylene diamine. These polyamide sutures are processed into monofilament, braided multifilament, and core—sheath

Table 10.2 A list of commercially available nonabsorbable suture materials

Generic Name	Polymer	Configuration	Trade Name
Polyamide	Nylon-6, -6,6	Monofilament	Dermalon
		Multifilament, braided	Nurolon
		Multifilament, braided and silicone coating	
Polypropylene	PP	Monofilament	Prolene
		Monofilament	Surgipro
Polyethylene	Polyethylene	Monofilament	Dermalene
Polyester	PET	Braided	Dacron
		Braided with silicone coating	Ti-Cron
		Braided with polybutylate coating	Ethibond
		Braided with PTFE coating	Polydek

configurations. The braided multifilament nylon sutures are often coated (e.g., silicone coating) to reduce tissue drag. The observed decrease in strength retention over time is associated with the susceptibility of the amide bond to hydrolytic degradation in the nylon structure. The tensile strength of nylon sutures decreases at a yearly rate of approximately 15−25% [118]. The tissue reaction to nylon sutures appears to be independent of configuration, with both braided and monofilament eliciting low reactivity.

The need to suture very delicate and complicated tissues have led to the development and use of sutures based on fluoropolymers such as PTFE, polyvinylidene fluoride (PVDF), and copolymers of PVDF and hexafluoropropylene (HFP) [119]. PTFE is a stable ($T_m = 327$ °C) semicrystalline linear polymer. ePTFE sutures are highly crystalline microporous fibers prepared by wet spinning an aqueous mixture of PTFE powder and cellulose xanthate. The morphology of ePTFE fibers consists of nodules connected by thin crystalline fibers that control tensile strength. The mechanical properties, biological response, and handling can be directly correlated with the porosity of the PTFE fibers [120]. The bending stiffness of ePTFE suture is low due to the microporous structure [121], but the porous structure also contributes to the decrease in strength. PVDF is also highly crystalline ($T_m = 175$ °C). Sutures prepared from PVDF exhibit good creep resistance and tensile strength retention. Morphological studies have demonstrated high surface stability, i.e., no visible signs of bulk or surface fracture [122]. PVDF sutures are susceptible to thermo-oxidative degradation, but can be readily sterilized with γ-radiation. PVDF elicits moderate tissue and cell response, a behavior similar to PP sutures. Sutures derived from copolymers of PVDF and HFP were originally designed to combine the beneficial handling properties and biological response of PVDF and PP into one material. In addition, PVDF/HFP sutures were also designed to emulate the durability of polyester sutures. The tensile strength, size, biological response, and handling of the PVDF/HFP sutures can be tailored by manipulating the copolymer compositions. The major target areas for usage of PVDF/HFP sutures are wound closure during cardiovascular, neurological, and ophthalmic surgeries [119]. These PVDF/HFP sutures are normally used as uncoated monofilaments.

Among the most commonly used polyester-based nonabsorbable sutures are PET and PBT. In addition, there are polyester-based sutures made from copolymers of poly(tetramethylene ether terephthalate) and poly(tetramethylene terephthalate) called polyetheresters. PET is synthesized by condensation polymerization of ethylene glycol and terephthalic acid. PET is a polymer with a melting temperature of approximately 265 °C. The thermal stability of PET enables melt spinning to form monofilament fibers with variable profiles. During processing, the fibers are subjected to hot drawing that enhances molecular orientation, crystallinity, and tensile strength. The PET sutures are commercially available as coated or uncoated monofilament or braided multifilament configurations. The surface treatments of PET sutures include coatings of PTFE and silicone. PET sutures are very stable in the biological environment with no evidence of hydrolytic degradation. The strength retention of PET sutures remains for extended period of time. The tissue response to PET sutures is dependent on the configuration with braided multifilament and monofilament having moderate and low tissue reactivity, respectively. Comparing to PET, PBT sutures are generally less brittle and stiff, due to the longer aliphatic segment in the polymer structure. Polybutester sutures are obtained from block copolymers of PBT and poly(tetramethylene ether) glycol terephthalate (PTMG). In the copolymer, the PBT is the hard segment and PTMG is the flexible segment. Chemical incompatibility between the hard PBT and soft PTMG blocks renders these copolymers elastomeric properties. Such unique mechanical behavior makes the polybutester sutures ideal for wounds prone to edema formation.

The synthetic absorbable sutures are made from polymers capable of degradation in the biological environment without adverse effects. One overall advantage of absorbable sutures is the elimination of clinical visits for their removal. These sutures are either homopolymers or copolymers based on degradable polymeric units such as polyglycolic acid, polylactic acid, or poly-*p*-dioxanone.

Polyglycolic acid (PGA) can be synthesized by condensation or ring-opening polymerization. Sutures based on PGA were the first absorbable sutures made [123]. PGA sutures are commercially available coated or uncoated in a braided configuration. Glycolide have been copolymerized with lactic acid, trimethylene carbonate, and ε-caprolactone [119]. Glycolic acid was copolymerized with L- or DL-lactic acid to form random copolymer. The performance of the glycolide-L-lactide sutures is dependent on composition. The initial tensile strength and retention through the healing process of the glycolide-L-lactide sutured wound is directly dependent on the concentration of the crystallizable glycolide monomers [124]. Copolymers based on the DL-lactide do not exhibit the same properties dependence as observed for the L-lactide copolymers [119]. Glycolide has been copolymerized with trimethylene carbonate to form a triblock copolymer where the middle block is a random copolymer of glycolide and trimethylene carbonate and the terminal blocks based on glycolide. These sutures are available as uncoated monofilaments. The copolymerization of glycolide and ε-caprolactone leads to formation of segmented copolymers. In these copolymers the glycolide and ε-caprolactone form the soft and hard segments, respectively.

Poly-*p*-dioxanone (PDS) is synthesized by ring-opening polymerization of 1,4-dioxanone-2,5-dione. The monofilament sutures are produced by melt spinning. The fibers are subjected to a drawing process to improve tensile strength and performance. Recently, attempts have been made to copolymerize PDS with PGA and PLLA to produce sutures with different properties [125].

Current research focus in wound closure suture is to incorporate extra functionality to the suture besides closing the wound. These efforts include to control wound infection by developing antimicrobial sutures, and to accelerate wound healing process by using bioactive material such as chitin, or to deliver therapeutics that can impact wound healing response.

10.6 Polymeric Biomaterials in Extracorporeal Artificial Organs

Extracorporeal artificial organs provide mass-transfer operations to support failing or impaired organ systems [126]. Common examples include kidney substitute, hemodialysis, cardiopulmonary bypass (CPB), apheresis therapy, peritoneal dialysis, lung substitute and assist, and plasma separation. A critical component involved in the extracorporeal artificial organ is the membrane, which serves to separate the undesired substance from the blood or plasma. Ideally, materials used as the membrane in these particular applications should have appropriate cellular and molecular permeability, as well as blood compatibility (i.e., hemocompatibility). Over the years, both natural and synthetic polymers have been used as membrane materials.

The most widely used natural membrane is cellulosic. Taking hemodialysis as an example, early applications of cellulose membrane in the dialyzer used regenerated cellulose, i.e., unsubstituted with rich hydroxyl groups along the repeating saccharide units. Studies have found that regenerated cellulose has poor hemocompatibility. It activates the complement system, which leads to inflammation and other serious immune response. The complement activation has been attributed to high concentration of hydroxyl groups on the membrane rendering it nucleophilic and susceptible to protein deposition, particularly C3b. Such observation spurred later research of using substituted cellulose for dialysis membrane, examples including cellulose acetate and cellulose triacetate, where in both cases a fraction of the hydroxyl groups are replaced with acetate functionality. These modified cellulose materials greatly limited complement activation by eliminating the active surface sites for complement protein interaction. Besides chemically blocking complement interaction, approaches using steric hindrance effect have also been explored. A bulky chemical group such as benzyl substitution group or tertiary amine group has been used to replace the hydroxyl group to sterically minimize the complement protein interaction with the membrane [127,128].

Current dialysis membranes are mostly made from synthetic polymers, including polysulfone, polyethersulfone, polyacrylonitrile, PMMA, polyamide, and polypropylene hollow fibers. Comparing with natural cellulosic membrane, synthetic membranes are less prone to complement activation. The reason behind the improved complement compatibility is the diminished level of surface nucleophiles for C3b deposition. Furthermore, some of the synthetic membranes are rich in negative charges on the surface, which can absorb the activated cationic complement peptide (e.g., C5a) and minimize the subsequent cascade of inflammation. Synthetic membranes generally have significantly larger pore size and higher hydraulic permeability than cellulosic membranes [129]. Therefore, synthetic membranes are the choice for high-flux applications. The larger pore size also allows for removal of middle molecule with molecular weight between 500 and 2000 Da, which have been deemed bioactive and may have a potential biological impact [130]. The hydrophobic nature of most synthetic membranes contributes to the adsorptive capacity toward noxious compounds such as interleukin-1, tumor necrosis factor, interleukin-6, and β_2-microglobulin [131]. PMMA and polyacrylonitrile usually exhibit the most pronounced adsorption capacity. Regardless of their origin, the membranes have been used either in hollow-fiber design, which is most common, or as sheet films in parallel-plate design.

10.7 Polymeric Biomaterials for Nerve Regeneration

Repair of the damaged nerves presents enormous challenge due to the physiology complexity of the nervous system. Even though progress has been made over the past decades, it is still elusive to fully repair the damage so that lost functions of the nervous systems could be restored. The nervous system is generally classified into the central nervous system (CNS) and the peripheral nervous system (PNS). Various strategies have been explored for nerve repair in both the CNS and the PNS, including guidance conduit, scaffolds with cell transplantation, and delivery of therapeutics. This section will mainly focus on polymers used in the nerve guidance conduit approach.

It has been widely accepted that physical guidance of axons, the long processes extending from the neuron cell body and conducting electrical signals, plays a critical role in nerve repair. The nerve guidance conduit is designed to: (1) direct the outgrowth of axons from the proximal nerve end bridging across the lesion; (2) provide a channel for the diffusion of biomolecules secreted by the injured nerve ends; and (3) reduce the scar tissue invasion to the regeneration zone [132]. To fulfill these functions, an ideal nerve guidance conduit should be semipermeable with oriented topographical features inside the conduit, supportive of electrical activity, able to deliver bioactive factors, and able to support cell adhesion and migration. The versatility of polymers makes them the top choice in engineering of nerve guidance conduit. Early research has used nondegradable synthetic polymers including silicone [133] and ePTFE [134].

Although silicone nerve guidance conduit has shown success in bridging gaps up to 10 mm, it failed to support regeneration across larger defects. Therefore, later effort has been shifted to develop biodegradable guidance conduit. The advantage of using a degradable material lies in the fact that long-term complications such as fibrotic reaction and nerve compression can be minimized. The degradation characteristics of the material should meet the following requirements: (1) the degradation profile should match with the axonal outgrowth profile, so that the guidance conduit will maintain sufficient mechanical support during the regeneration process; and (2) the degradation product(s) should induce minimum to zero tissue reaction. A series of degradable polymers have been used, including biodegradable poly(-esters) such as PGA [135], PLA [136], PLGA [137], and poly(caprolactones) [138]; polyphosphazenes [139]; polyurethanes [140]; and poly(3-hydroxybutyrate) [141].

Since the emergence of studies showing electrical charge affects neurite extension *in vitro* [142,143] and improves nerve regeneration *in vivo* [144], polymers that can provide electrical stimulus have been included in guidance conduit development. These polymers include piezoelectric polymers such as PVDF and its copolymer [144], and conducting polymers like polypyrrole and its biologically modified derivatives [143,145]. Other electroactive polymers, such as polyaniline, may also provide support for nerve growth, as studies have shown encouraging results with cardiac myoblast cells [146].

Nerve guidance conduit can be hollow or filled with matrix to support axonal elongation. A popular filler choice is natural polymeric gel. Ideally, the gel should be soft with mechanical properties matching those of the nervous tissue; porous to allow axonal ingrowth; biodegradable; and biocompatible. A number of natural polymers have been investigated, including agarose [147], chitosan [148], methylcellulose [149], hyaluronic acid [150], alginate [151], fibrin gels [152], collagen [153], keratin [154], and self-assembling peptide scaffolds [155]. Agarose is a thermally reversible polysaccharide hydrogel. Its gelling temperature can be modified by changing the functional groups attached to the sugar residues. It can also be functionalized with various biological motifs, such as laminin-derived peptide sequences RGD, YIGSR, and IKVAV, to enhance neurite extension [156]. Fibrin is a natural wound-healing matrix that can be found in the early stages of regeneration. It is formed from the blood coagulation cascade to restore hemostasis and initiate tissue repair. Using fibrin gels as the filler can closely mimic the natural matrix formed in the guidance conduit bridging short nerve gaps, where a fibrin cable is usually formed from the exuding serum by the damaged blood vessels in the nerve ends [157]. Peptide sequences have also been crosslinked into the filling fibrin matrix to further induce neurite extension [158]. In addition to gel filler, longitudinal filaments, either synthetic or natural, have been used in the conduit to align the growing axons in the direction of regeneration. Materials used in filament preparation include polyamide, catgut, polydioxanone, polyglactin, poly(acrylonitrile-*co*-methyl-acrylate), collagen, PLA, PGA, and more [159−162].

Recently, materials research on nerve guidance conduit has been taken to a new level where old paradigm of passive material has been shifted to new bioactive material design. Chemical messengers such as neurotransmitters have been polymerized into the polymer backbone to impart neuroactivity for the resulting biomaterial [163]. The first example of this new class of polymer is dopamine polymerized with a diglycidyl ester to form a biodegradable material that has shown vigorous neurite outgrowth *in vitro* and good tissue compatibility *in vivo*. Another example of new bioactive polymer is polysialic acid and its hydrogel. Polysialic acid is a dynamically regulated posttranslational modification of the neural cell adhesion molecule [164]. It has been shown to significantly improve cell adhesion and viability *in vitro*. With the increasing understanding of the biology behind nerve regeneration, it is expected that more bioactive materials will be developed in the future to achieve timely functional recovery from nerve damage.

10.8 Conclusions and Future Outlook

Polymers have made significant impact on biomedical research and medical practice, and will continue to be the major workforce for biomaterials in the twenty-first century. The polymeric biomaterials and their applications presented here are only the tip of an iceberg. With the growing understanding of the biological response to existing biomaterials and a better grasp of human organ composition, function, biomechanics, and disease etiology, chemists and polymer scientists should continue working collaboratively with biologists, physicians, and engineers to develop tailor-made polymers for biomedical applications. In contrast to the old inert synthetic polymers, bioactive, biomimetic, and smart polymers will be at the center stage. Furthermore, as the interactions of the biological system with polymers occur at the interface, surface-related research will continue to thrive, especially surface characterization and surface modification. One can be hopeful to foresee a better management of diseases with the help of a new generation of biomaterials, and a seamless integration of the biomaterials into the body.

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11 Recycling of Plastics

Dr Adrian Merrington
Michigan Molecular Institute, 1910 W. St. Andrews Road, Midland, MI 48640, USA

11.1 Introduction

The United States Environmental Protection Agency (USEPA) defines municipal solid waste (MSW) as any garbage or refuse; sludge from a wastewater treatment plant, water supply treatment plant, or an air pollution control facility; and other discarded material, including solid, liquid, semisolid, or contained gaseous material resulting from industrial, commercial, mining, and agricultural operations, and from community activities [1]. The plastics component of MSW has risen from 390,000 tons in 1960 to 30.7 million tons in 2007. Perhaps more significantly, the percentage of plastic waste in MSW increased from <1% in 1960 to 12.1% in 2007. It is perhaps this increase in the quantity discarded that has made plastics an obvious target for environmentalists [2–4] and plastic recycling a publicly desired alternative to disposal in landfills [5].

And yet, the plastic recycling rate in the USA remains stagnant and some reports indicate an actual drop in recent years [6]. The recycling rate of one of the more sought-after plastics, polyethylene terephthalate (PET), has dropped in the last decade. The National Association for PET Container Resources (NAPCOR) reports that the gross recycling rate for PET has dropped from 31.7% in 1995 to 24.6% in 2007. The Energy Information Administration (EIA) who provides official US government energy statistics suggests an even lower recycling rate for most of the plastics on which they focused their analysis and sets PET recycling as low as 20.6% (see Table 11.1).

The quantity of plastics recycled annually has increased steadily since records have been kept. Nevertheless, the rate of recycling is not keeping up with the rate at which virgin plastics are being produced. USEPA [1] tracks the generation and recovery of plastics in the USA and reports that a higher proportion of plastics are being disposed of in landfills than ever before (see Figure 11.1).

The amounts of plastics produced and the quantities that are discarded in landfills have meant that plastic recycling continues to be an ever-increasing political issue. Organizations and their respective web sites vie to sway public opinion. Consolidating their efforts behind a single organization, the American Chemistry Council (ACC) has become the voice of many chemical industries, including the plastics industry [7]. In fact, ACC membership is limited to companies as they *represent the leading companies engaged in the business of chemistry, including significant business groups such as the Plastics Division and the Chlorine Chemistry Division* [8]. The ACC promotes the benefits of using plastics, highlights recycling success stories, and identifies the plastics industry as a large player in the reduction in the amounts of plastics disposed of in landfills.

There are many organizations presenting opposing views to those represented by the ACC, some more actively than others. Greenpeace [9] had in the past been reported to suggest banning the use of plastics as a viable solution to the amount of plastic waste being generated [10]. The unambiguously named *Campaign Against the Plastic Plague* has the long-term goal of seeing zero-waste attained [11]. There is also an ongoing petition to ban the use of plastics [12]. These organizations argue against the use of some or all plastics and some argue against the efficacy of recycling though most acknowledge recycling as a better option to disposal in landfills.

Some organizations focus on the technical aspects of recycling plastics and leave political opinion out of their mandate. One such organization is the Society of Plastics Engineers (SPE) Environmental Division that was established to disseminate information on plastic recycling [13]. The organization runs an annual conference as well as online technical presentations on the subject of recycling that focuses on the technological and business aspects of recycling to help educate the public [14].

11.1.1 Definitions of Plastic and Recycling to the Plastics Recycler

American Society for Testing and Materials (ASTM) defines a plastic as a material that contains as an essential ingredient an organic substance of large molecular weight, is solid in its finished state, and, at some stage in its manufacture or processing into finished articles, can be shaped by flow [15]. That definition fails to include the multitude of additives, coatings, or treatments that are incorporated into the majority of parts made from plastics. It is this combination of resin, additives, and coatings that the recycler encounters when recovering plastics for reuse.

Plastic recycling has been described as the process of recovering scrap or waste plastics and reprocessing the

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Table 11.1 Types of plastic, amounts recycled in 2007 and common recycle uses [1]

SPI Number	Plastic	SPI Symbol	Amount Recycled (%, 2007)	Recycle Uses
1	PET	♳ PETE	20.6	Clothing, carpet, film, food and beverage containers.
2	HDPE	♴ HDPE	9.6	Nonfood containers (laundry detergent, shampoo, conditioner, and motor oil bottles) plastic lumber, pipe, buckets, crates, flowerpots, film, recycling bins, and floor tiles.
3	PVC	♵ V	0.0	Packaging, loose-leaf binders, decking, paneling, gutters, mud flaps, film, floor tiles and mats, traffic cones, electrical equipment, garden hoses, and mobile home skirting.
4	LDPE	♶ LDPE	2.2	Shipping envelopes, garbage can liners, floor tile, plastic lumber, film, compost bins, and trashcans.
5	PP	♷ PP	5.0	Automobile battery cases, signal lights, brooms, oil funnels, brushes, ice scrapers, bicycle racks, and rakes.
6	PS	♸ PS	1.5	Thermometers, light switch plates, thermal insulation, egg cartons, vents, rulers, license plate frames, foam packing, and dishware.
7	Other	♹ OTHER	1.0	Bottles and plastic lumber.

material into useful products, sometimes completely different in form from their original state [16]. Classifying by the final product of any given recovery process has further differentiated between alternative plastic recycling methodologies [17]. For example:

- *Primary recycling*: The recovered plastic is used in products with performance characteristics that are equivalent to those made using virgin plastics. Ideally, closed-loop recycling takes the recovered material and uses it back in the original application. An example of primary recycling is where PET recovered from postconsumer bottles is used in the production of new bottles.
- *Secondary recycling*: The recovered plastic is used in products that have less demanding performance requirements than the original application. An example of secondary recycling is in the production of flooring tiles from mixed polyolefins.
- *Tertiary recycling*: Waste plastic is used as the feedstock in a process that generates chemicals and fuels. An example of tertiary recycling is the glycolysis of PET into diols and dimethyl terephthalate that can then be used to make virgin PET.

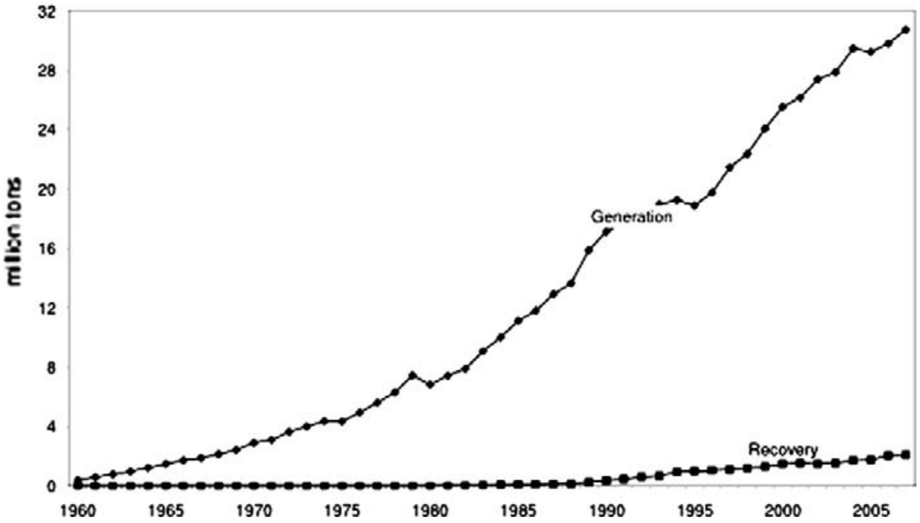

Figure 11.1 Rates of plastics produced and recycled in the US.

- *Quaternary recycling*: Energy is recovered from waste plastic by incineration. Tire-derived fuel (TDF) is an example of quaternary recycling.

This chapter will focus on *primary* and *secondary* recycling where the plastic is reused rather than converted into chemicals or fuel to meet energy needs. Although tertiary and quaternary recycling routes are valid alternatives to the disposal of plastics in landfills, the plastic, *per se*, no longer exists.

There are terms used within the recycling industry that differentiate the source material. *Postindustrial* plastics are recovered from the parts or resin manufacturer before being sold to the public. This stream is typically cleaner, newer, more homogeneous and more valuable than the alternative postconsumer plastic. *Postconsumer* plastic is collected after the consumer has used it so it may be separated by resin family by the user (such as pop bottles in *Bottle Bill States* [18]) or, more typically, recovered from comingled waste streams. Postconsumer plastic may be many decades old before it is received at the recyclers' facilities.

11.1.2 Why Is It Hard to Recycle Plastics?

Plastic may require greater processing to be recycled than glass and metal materials. Mixed plastics typically have poor mechanical properties resulting from the poor interfacial adhesion. Low entropy of mixing is typically established when bringing two or more different plastics together, so resins must often be of nearly identical composition in order to mix efficiently. When different types of plastics are melted together they tend to phase-separate and set up in these phases. The interfaces at the phase boundaries are weak and cause structural weakness in the resulting compound. As such, mixed, untreated polymer blends are useful only in limited applications [19].

The plastic recycling industry initially focused on the primary recycling of single types of plastics that, in turn, generate the greatest financial returns. To that end, postindustrial streams have been the focus of many recycling businesses as the material from these sources is known, newer, essentially the same from part to part and relatively clean when compared with postconsumer plastics. Successful recycling of postconsumer plastics has been mostly limited to easily identified parts that use a single, high-value resin type and that are available in large quantities. There are examples where mixed postconsumer plastics have been utilized in secondary recycling applications such as plastic lumber and floor tiles.

Recycling single resin plastics from postindustrial or postconsumer sources utilizes standard processing equipment for the most part. Plastics are melted, extruded, pelletized, and then formed into a final product. Additives may be added that compensate for prior use, additional processing caused thermal histories or new product needs, but the use of these additives is minimized to control the overall cost of the recycled plastic and thereby increase the overall profitability of the process. The next section addresses some of the issues associated with recycling-specific individual plastic streams.

11.2 Technology to Recycle Plastics

11.2.1 Single Resins

Single resins are obtained most typically from postindustrial scrap (a known plastic type, grade, and source) or limited postconsumer scrap where the item is known to be made from a single type of plastic, is easily identified, can be separated from the mix inexpensively, and is available in quantity. The type of resin might be identified by:

- using Manufacturers' data logs
- using Society of the Plastics Industry (SPI) identification codes
- using knowledge of the product (e.g., high-density polyethylene (HDPE) is recovered from postconsumer milk bottles)
- determining some property of the plastic (e.g., Raman spectrophotometers are used to identify the resin used to make plastic parts).

Most single resins undergo a similar basic recycling process. They are collected through some infrastructure mechanism, transported to a recycling facility, separated by resin type, washed and dried to remove debris, ground into flake, possibly pelletized, and may have some additive package added to meet application needs or rejuvenate properties diminished by use or the recycling process. Each step introduces barriers to the technologies developed in the laboratory being economically viable in the real world. Price fluctuation of the virgin resin may also pose a significant barrier to commercialization and this variable is one that is beyond the control of the recycler; price fluctuation alone caused the virtual collapse of many of the small-scale, *mom-and-pop* PET recyclers in the late 1990s.

11.2.1.1 Polyethylene terephthalate

Amount produced: 1700 thousand tons

Amount recycled: 350 thousand tons [20]

The demand for recycled PET, as with most recycled plastics, closely follows that of the virgin resin. The opportunity to lower costs is the factor that typically drives the manufacturer to look at the recycle market but virgin PET can cost less than recycled PET in some cases. Where PET recycling has been particularly successful is where its reclamation has been subsidized or in vertically integrated operations. Transparent PET has the highest value and the widest variety of end-use applications. Translucent and opaque PET may be less desirable due to the presence of additives such as titanium dioxide. This additive is very detrimental to PET recycling for bottle-to-bottle and engineered resin uses [21]. Products including polyester carpet, thermoformed sheet, T-shirts, and car parts are all made by companies that manufacture products using recycle PET [22].

Some states, termed *Bottle Bill States*, demand a deposit be paid on each drink container [18]. The consumer and retail outlet serve as unpaid aggregation and separation facilities for the PET recycling industry providing relatively homogeneous postconsumer recycling streams. PET from these streams can be used in the manufacture of new bottles but is equally as likely to be found in the manufacture of fibers used in the clothing and carpet industries. In fact, some of the largest PET recyclers in the USA are manufacturers integrated into the fiber industry and they use the entire PET that they recover.

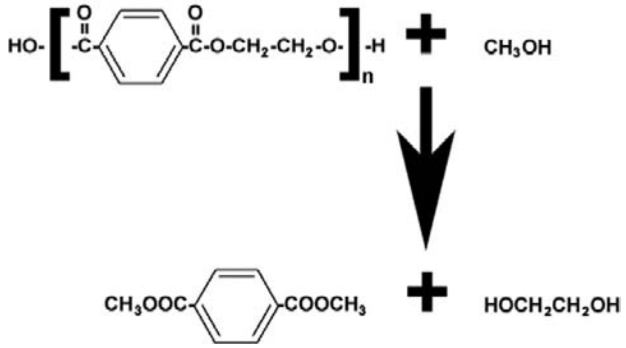

Figure 11.2 Depolymerization of polyethylene terephthalate.

Contaminants that can catalyze the hydrolysis of PET into lower-molecular-weight entities with carboxylic acid end groups are a significant issue. The contaminants may be acid, base, or even water; wet PET may show significant property degradation when processed. These lower-molecular-weight entities themselves may further catalyze the hydrolysis of PET so that the degradation becomes autocatalytic. Contamination by other plastics, particularly polyvinyl chloride (PVC), can be a substantial issue. PVC will degrade at PET-processing temperatures and release hydrochloric acid that will also catalyze the hydrolysis of PET.

Reprocessing PET may subject the resin to additional heat histories that may reduce the molecular weight. Some producers propose that the legislated inclusion of PET recycle into pop bottle manufacturing would lead to significant degradation in the product over a relatively short period of time [23]. However, the potential for degradation of the PET feedstock has not deterred many manufacturers from using recycled PET [24].

In addition to recycling PET, technologies to depolymerize PET to its monomers have been established by major PET producers. Glycolysis and methanolysis (using glycols and methanol, respectively, at elevated temperatures) have been shown to depolymerize PET into low-molecular-weight diols and dimethyl terephthalate (see Figure 11.2). Goodyear, for example, produced REPETE resin with 20% recycle material recovered by this technique [25]. Pepsi used REPETE in the manufacture of its pop bottles [26].

11.2.1.2 Polyethylene

Amount produced: 4120 thousand tons (HDPE) and 5010 thousand tons low-density polyethylene (LDPE)

Amount recycled: 410 thousand tons (HDPE) and 110 thousand tons (LDPE) [20]

There are many different grades of PE available in today's marketplace. Application needs typically dictate using low ($<0.925\ \mathrm{g\,cm^{-3}}$) or high ($>0.940\ \mathrm{g\,cm^{-3}}$) density varieties but may also demand specific rheological characteristics in their manufacturing processes. Density, beyond defining the type of PE (and its uses), may also indicate the presence of filler. However, mechanical properties, processing characteristics, photochemical resistance, and surface and opacity properties may also be used to classify the characteristics of the recycled PE [27]. Recovered HDPE and LDPE have sufficient value that they are usually processed into separate recycle streams.

Although many users of recycled PE have a robust stream available, some manufacturers using recycled PE in place of virgin materials may experience lower manufacturing efficiency resulting in an increased scrap rate from lower product quality. A manufacturer may have a specific property and processing window within which the purchased resin must fall. The use of a recycled PE resin may not ensure that all of the narrow specifications can be met. Outside of recovering PE from a single postindustrial source, simply describing the melt flow index (MFI) and the density may not adequately describe the characteristics of the resin. Further, it may be difficult to find sufficient quantities of recycled materials that meet the exact specifications required by the process, especially given the hundreds of grades of PE available. Advanced Blending Technologies [28] has developed software that compounds low-cost optimized blends from wide spec, off spec, or recycled PE streams by providing blend formulations based on selectable material properties. The resulting alternative blends can be prioritized by factors such as lowest cost— usually the main parameter in the manufacturer choosing to use recycle resins over virgin materials.

Polypropylene (PP) contamination of PE will decrease the mechanical properties of the resin due to the difference in the melting point. Clumps of PP may act as stress concentrators in the PE matrix at high concentrations though some have reported that low amounts of PP can be tolerated [29]. Other contaminants that have been reported to have a detrimental effect on PE include adhesives, paper, metal, and PET [23].

11.2.1.3 Polyvinyl chloride

Amount produced: 1230 thousand tons
Amount recycled: 0 thousand tons [20]

Vinyl 2010 [30] is a European industry-based organization establishing recycling goals for PVC users. Each industry that uses PVC (windows, pipes, wiring, etc.) has established goals for recycling within that organization. This activity is a countermeasure to some of the activities of environmental activist organizations that highlight the problems of recycling PVC [31,32]. However, most of the problems on which those that oppose the use of PVC focus are not actually problems with recycling rigid PVC. Rather, the problems are associated with recycling other materials that are contaminated with PVC scrap or they deal with the debated health issues associated with PVC additives, especially those used in flexible PVC skins.

PVC contamination in other plastics is a major concern. PVC labels have been used in the past on PET pop bottles. The presence of PVC bottles can also contaminate the PET recycle stream. Very low quantities of PVC have been shown to significantly diminish the mechanical properties of PET. PVC can break down to form hydrochloric acid when mixed with PET during processing. This acid diminishes the physical and chemical structure of PET, causing it to turn yellow and brittle in addition to the potential out-gassing of chlorine gas during reprocessing [33]. The potential for out-gassing of chlorine gas when recycling PVC, however, is a debated issue [34]. Conversely, small amounts of PET contamination in PVC bottle streams can similarly render that stream useless [35].

Phthalates, for example, di-2-ethyl-hexyl phthalate, are common plasticizers used in the PVC industry. These additives make the hard PVC flexible. The USEPA classifies this additive as a probable human carcinogen and there is also evidence of other health issues [36].

Despite that the USEPA records the recycling rate of PVC as negligible [20], postindustrial rigid PVC regrind has been reportedly used in the manufacture of extruded parts such as pipes [37] and in the manufacture of windows [38]. Postindustrial flexible PVC has been ground up and reintroduced into the production stream for vinyl flooring and carpet backing [39]. Some feasibility studies have investigated recycling vinyl recovered from wiring applications [40].

11.2.1.4 Polypropylene

Amount produced: 2580 thousand tons
Amount recycled: 130 thousand tons [20]

The economic viability of PP recycling is hindered by the low cost of the virgin polymer and the type of applications that use the resin. The costly transportation of relatively large parts that contain little polymer is also a hindrance to commercially viable recyclability given the extensive use of PP in packaging applications. The economic constraints do not allow the recycler much opportunity to perform costly recycling processes such as any extended separation protocol or property rejuvenation using expensive additives. The Preserve Group [41] recently announced a program to try to address the low recycle rate of PP, called *Gimme 5* [42]. It is unlikely that a program that suggests activities such as *the unpaid and unregulated consumer transporting the waste to collection sites* or *paying to mail the scrap plastic to a recycler* can be viewed as having long-term viability.

Carpeting and battery industries have long been active in developing recycling uses for PP waste. The Carpet America Recovery Effort (CARE) reports that its partners have recycled materials used in the manufacture of carpeting. However, even within their activities, the amount of PP in their recycle streams has dropped from 22% in 2006 to 8% in 2007 and 2008 [43]. Battery Council International (BCI) [44], a similar organization for the battery industry, describes how 97% of batteries sold in the USA are recycled, but the driving force is the recovery and reuse of the lead. The PP cases comprise only a small percentage of the total weight but this PP is recycled back into new plastic cases.

11.2.1.5 Polystyrene

Amount produced: 1990 thousand tons
Amount recycled: 30 thousand tons [20]

Polystyrene (PS) is principally used in solid, foam, and expanded PS (EPS) forms. Many of the applications for PS are single use and disposable. Hurdles to PS recycling are similar to those for PP. Californians Against Waste [45] reports that *current estimates by the California Department of Conservation peg the costs of recycling (expanded) polystyrene at over $3000 per ton, meaning that polystyrene actually has a negative scrap value* [46]. The National Polystyrene Recycling Company was a coventure between a number of PS-producing chemical companies intended to increase PS recycling but success was limited. Some PS is recycled (audio and video cassettes, jewel cases, etc.), but comparatively little from food packaging usage.

Routes to recycle solid PS include the basic wash, dry, and pelletize route described earlier but EPS typically requires a densification process to be applied. Densification eliminates the air in the foam beads by mechanical grinding or solvent attack. The recycled plastic is used in low-cost applications such as horticultural trays, wastebaskets, wood substitutes, packaging foam, and desk trays.

11.2.1.6 Other thermoplastics

Amount produced: 3130 thousand tons
Amount recycled: 30 thousand tons [20]

There are recycling opportunities for other plastics beyond the few recognized by SPI resin identification codes. The automobile industry, for instance, utilizes a series of engineering thermoplastics that have a built-in market if they can be recovered and reprocessed. These high-value plastics include polyamides (nylon 6, nylon 6,6, etc.), polycarbonates (PC), acrylics (polymethyl methacrylate – PMMA), styrenics (acrylonitrile butadiene styrene – ABS), and blends (thermoplastic polyolefin – TPO, PC/ABS, etc.). Their higher value and demand give recyclers the opportunity to practice more exotic recovery schemes and still have an economically viable product.

There are many examples in industry where niche-recycling processes are successfully meeting business needs. CARE [47] recycles nylon from carpets and reuses the material to make new carpets by blending it in with the virgin resin. PC is recovered for reuse in automotive parts [48] despite the media attention on the potential for producing bisphenol A by-products [49]. PMMA has been depolymerized to the monomer through pyrolysis for reuse [50]. Fujitsu is recovering ABS from computer housing and reusing it in the manufacture of new computers [51].

Schiers [23] reviewed a number of techniques to remove paints and plating from engineering thermoplastics that include hydrolysis, chemical stripping, liquid cyclone, compressed vibration, melt filtration, mechanical abrasion, cryogenic grinding, dry crushing, and roller crushing. Although some of these techniques are not inherently economic, they may be when developed by the recycler to recover a particular resin. American Commodities, Inc. has commercialized a process to remove paint from TPO bumpers. The TPO recovered can be recycled back into products requiring a grade A surface finish. That company also uses a process to separate the styrene maleic anhydride (SMA) substrate from shredded automotive instrument panels [52].

These few examples should indicate the level of activity within the recycling community in recovering engineering thermoplastics. These high-value plastics are being utilized in a variety of applications where they compete favorably with virgin resins on properties and, most importantly, price. However, the reduction in need and falling commodity pricing of virgin resins experienced in late 2008 have seen many recyclers facing tough times, even where they have patented good technologies [53].

11.2.1.7 Thermosets

The majority of this chapter has dealt with thermoplastic recycling where the recycled plastic can be heated and remolded into a new desired shape. Another type of plastic, thermosets, where the plastic cannot be remolded upon heating, is recovered for reuse but to a lesser extent. Thermoset recycling is typically limited to grinding and incorporation of the regrind into an uncured monomer as a filler (polyurethanes, epoxies, phenolic resins, etc.) or, less commonly, compression molding (e.g., with some polyurethanes) [54]. There is also some level of fuel or energy recovery being practiced, for example, *tire-derived fuel* (TDF), that consumes up to half of the discarded tires [55].

11.2.2 Mixed Plastics

Mixed plastics, as described earlier, cannot usually be combined into a single part that has good mechanical properties. Either the commingled stream needs to be separated by resin type or the resins made compatible with each other by the addition of surface-active agents, termed *compatibilizers*. The following section describes those two alternative routes in some detail.

11.2.2.1 Separation of plastic resins

Manual

Perhaps the most basic separation technique and still the most commonly employed around the world is to utilize manpower to separate the plastics. An activity not limited to operations in developing countries, manual separation is employed in many US materials recovery facilities (MRFs) and other operations [56]. This *low-tech* option sees individuals sorting parts using predefined characteristics. For instance, milk and pop bottles may be extracted from household waste by hand as they are easily and quickly identified.

Density

Float—sink segregation uses density to separate different plastics. Parts are ground into small pieces and placed into a container containing a liquid. Those plastics with a density lower than that of the liquid will float whereas those with a density higher than the liquid will sink. Simple liquids such as water can be used in some situations but a saline solution, where the density can be more tightly controlled, is typically required to optimize resin separation [57]. Table 11.2 displays the density of the base resins of those plastics classified by SPI resin identification codes.

Density separation is complicated in many cases as the density ranges of given plastics may cross. Separation is further complicated by the incorporation of fillers, foams, adhesives, or other additives into some plastics as they can substantially change the density. For example, 15% talc-filled PP has a density similar to that of ABS (1.02—1.20 g cm^{-3}) and may be used in similar applications resulting in a difficult mixture to separate. An alternative to simple density separation would be required in such a case [67].

Air classification also uses density as the characteristic by which different plastics may be separated. A blast of air is blown through a steady stream of falling ground, mixed plastics. The dense plastics continue to fall while expanded foams and other lighter materials are blown into a separate collector. This technique is used to separate plastics with significantly different densities whereas liquid-based density separations may be tuned more tightly.

Optical

Optical sensors can be used to separate plastics based on either color or transparency. This technique is used to separate bottles by color. Developed from the coffee bean separators that are used to eliminate unripe green beans from the mix, these computer-controlled systems can rapidly differentiate between the various hues of the plastic regrind. The color of each piece of plastic is quickly established using a type of charge coupled device (CCD) camera and is either allowed to flow downward or ejected with a puff of air into the reject or collection pile. Satake, for example, produces equipment that is specifically designed to separate plastics by color but their main business is still from the agricultural industry. Satake's ScanMaster IE & DE Optical Sorters are used to differentiate the colors of HDPE and PET materials in recycling applications [59].

Table 11.2 Density of plastics by SPI resin identification code

SPI Number	Plastic	Density g cm^{-3}
1	PET	1.35—1.38
2	HDPE	0.94—0.96
3	PVC	1.32—1.42
4	LDPE	0.91—0.93
5	PP	0.90—0.92
6	PS	1.03—1.06
7	Other	Very broad

Spectroscopic

Plastics identification by spectroscopic techniques has increasingly focused on the use of near infrared (NIR) and Raman spectroscopic techniques.

LLA instruments, in conjunction with DaimlerChrysler [60] have developed a super-fast NIR sensor system that has been used to separate mixed plastics by type from shredded automotive parts. NIR spectroscopy uses the NIR region of the electromagnetic spectrum (from about 800 to 2500 nm). Their two-phase process initially separates bright and colored polymers and black PP from the mix. A second long-wavelength NIR sensor is employed to then separate the black plastics such as PC, PMMA, ABS, PC/ABS blends, and others.

Raman spectroscopy relies on inelastic (Raman) scattering of monochromatic light from a laser in the visible, NIR, or near ultraviolet range. Raman spectroscopic techniques have historically failed to separate different black resins. SpectraCode [61] was originally developed at Purdue University [62] and they are a manufacturer of Raman-based instruments used for materials identification. The RP-1 handheld unit is well known within the recycling community and has somewhat overcome the limitation that other Raman spectrometers suffer when separating black plastics. Although not a fast process, taking perhaps 30 seconds to identify the resin type of a black plastic, this technique may still have utility in identifying large parts. It should be noted that failure to correctly identify the type of resin used to make black parts is of significance because most mixed recycle streams end up being black in color.

There are other spectroscopic techniques that could find utility in the recycling industry. Laser acoustic, laser-induced emission spectral analysis, plasma emission spectroscopy, polarized light, phase contrast illumination, UV light, and fluorescent tagging have all been reported [23].

Electrostatic

Electrostatic separators were developed for the metallurgical industry but have been used to separate plastics for many decades. The technique is employed typically to separate two different plastics rather than separate one plastic from a commingled waste source but it has also found utility in the latter [63]. The plastics are charged by ion bombardment. A slight positive or negative static charge is imparted to the flakes of different resins as they collide with each other and with the walls of the charging chamber. An electrostatic field is applied across a falling stream of regrind to separate the plastics by resin type. This technique has been used to separate HDPE from LDPE to greater than 90% purity [64].

Other techniques

Froth flotation is a relatively expensive process that has been privilege to significant US government funding to define its efficacy to the recycling industry. The process is used to selectively separate hydrophobic from hydrophilic materials [65]. The recycled plastic is ground and treated with a reagent that imparts specific charges to the surface of the different resins within the mix. A stream of air or nitrogen is then bubbled into the separator and froth is produced on the surface where different plastics are then separated by charge. The technology's uptake within the recycling industry is negligible and unlikely to change without some outside intervention given the high up-front investment the equipment demands despite being able to produce recovered streams of 95% purity from *automotive shredder residue* (ASR).

11.2.3 Compatibilization of Plastic Resins

Parts are often manufactured using many plastics (e.g., PP housing and nylon gears) or else plastic blends (e.g., polycarbonate/ABS blends). Recycling parts made from mixed plastics remain chemically complex because of the general lack of compatibility. An overview article [66] highlighted how new materials advance parts production and that the majority of the new materials identified were blends.

The cost to separate parts made from many plastics is often the main restriction to any recovery technology being commercially successful. The problem is such that virgin plastics may cost less than their postconsumer recycled counterparts. Further, consumers refuse to pay a premium for recycled parts or accept recycle parts with properties or qualities inferior to those made from virgin resins.

One method to improve the economics of plastic recycling is by reducing the need to separate plastics and directly produce plastic blends [67]. These blends must be of sufficient quality to be used as direct replacements for virgin plastics. Also, blends with enhanced properties can be formulated by combining more than one plastic. Current activities employed within the recycling industry to handle mixed plastics or blends are effectively limited to the following:

- Use of complex and costly processing techniques such as coinjection molding or coextrusion and laminating.
- Identifying compatible plastics from compatibility charts [68].

Few existing plastic blends are recycled with the notable exceptions of TPO, SMA, and some ABS streams. More complex recycle blends have not yet made a significant impact on the recycle market. The use of recycle materials from complex mixtures is currently limited to low-cost applications such as floor tiles and plastic lumber. A search of the patent literature shows that there are many proposed solutions to the problem of recycling blends. Where they fail in commercialization is that they:

- are too expensive to pursue
- result in materials with inconsistent properties
- use feed streams that are too low in quantity or too inconsistent in their composition
- exhibit poor mechanical properties and/or
- are used only in low-cost applications and can therefore only demand a low price for the mixed recycled plastics

Knowledge of the compatibility of materials is useful in making informed materials choices related to recyclability. Other significant factors, such as additive packages, resin history, contamination, range of variability within the family, thermal and environmental history, as well as any chemical changes in the recycled materials, will also affect the ability to melt mix materials. The compatibility of pairs of virgin materials may, in fact, be vastly different than the compatibility of the same pair of materials after each has been fabricated, modified, subjected to use, recycled, and remelted.

Within a given resin family, different grades must be identified to correctly define compatibility. The inclusion of additives and the use of specific formulations or grades of material will affect the compatibility. An example of a plastic blend that is sold commercially is PC/ABS. This material is used extensively in the computer, communications, and office equipment industries, as well as in the automotive industry. For optimal physical and mechanical performance, formulations with very specific grades of ABS must be used. Obtaining generic recycled ABS for use in these applications leads to inferior parts. Further, the additives used in the production and property modification of certain ABS grades can also greatly reduce efficacy in blends with PC [69].

The compatibility of two commonly used plastics in a blend is reported in Table 11.3. The compatibility chart should be considered as only one of several pieces of information required to determine if plastics can be mixed. Materials, even within the same family, may not readily mix if the density is substantially different. High- and low-density polyethylene represent such a relationship.

Table 11.3 Compatibility of commonly used thermoplastics

	Minor Component							
Major Component	**PMMA**	**Nylon 66**	**PC**	**PET**	**HDPE**	**PP**	**PVC**	**PS**
Acrylic (PMMA)	3	0	2	1	0	1	0	2
Polyamide (Nylon 66)	0	3	1	1	1	2	0	1
Polycarbonate (PC)	2	1	3	2	1	1	0	2
Polyester (PET)	1	1	2	3	1	1	0	1
Polyolefin (HDPE)	0	1	1	1	3	2	0	0
Polyolefin (PP)	1	2	1	1	2	3	0	0
Vinyl (PVC)	1	0	0	0	0	0	3	0
Styrenic (PS)	2	1	2	1	0	0	0	3

3—Compatible in many concentrations; have properties that are useful. 2—May need to add a simple additive to get a useful product; technology exists. 1—May be a useful product but requires significant modification; avoid unless necessary; technology exists. 0—Not compatible; technology unknown; avoid.

It is unusual to find different plastics that mix at the molecular level. A blend of two plastics rarely produces a system with single homogeneous phase and that is thermodynamically stable. A compatible system is considered to be a useful multicomponent plastic blend that has desirable properties. Some incompatible plastic blends may be made useful by the presence of an additive, frequently termed a *compatibilizer* or *compatibilizing agent*.

Compatibilizers are frequently materials such as block or graft copolymers. A specific example would be a copolymer comprising two blocks where each is compatible with one component of the blend (in a blend of two plastics) and incompatible with the other. An A—x—B block copolymer, where A and B are long sequences of monomer that are identical to the corresponding A and B polymers forming the blend, and x is a bond between the blocks, is one of the simplest forms of compatibilizer. A functionalized polymer where the main polymer is compatible in one phase and the functionality is compatible in the other phase would be an alternative agent. One example of such a material would be maleic anhydride functionalized polypropylene (PP-MA) used to compatibilize blends of PP and nylon 66. Recent advances in the production of PP-MA have seen an increase in the impact resistance of polyolefin-based blends by up to 25% over the less pure alternatives [70].

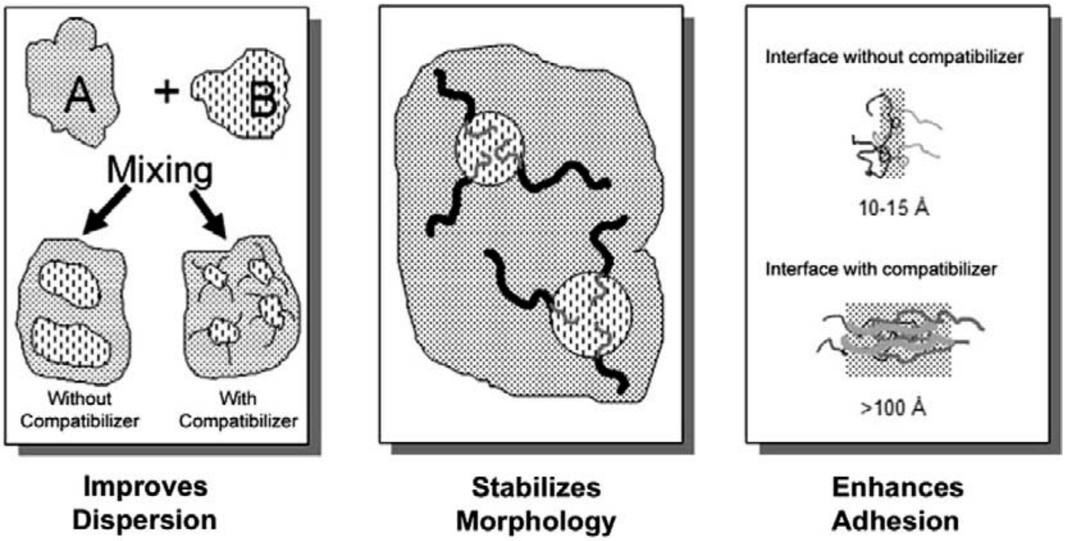

Figure 11.3 Schematic representation of the effects of compatibilizers on multi-component plastic blends.

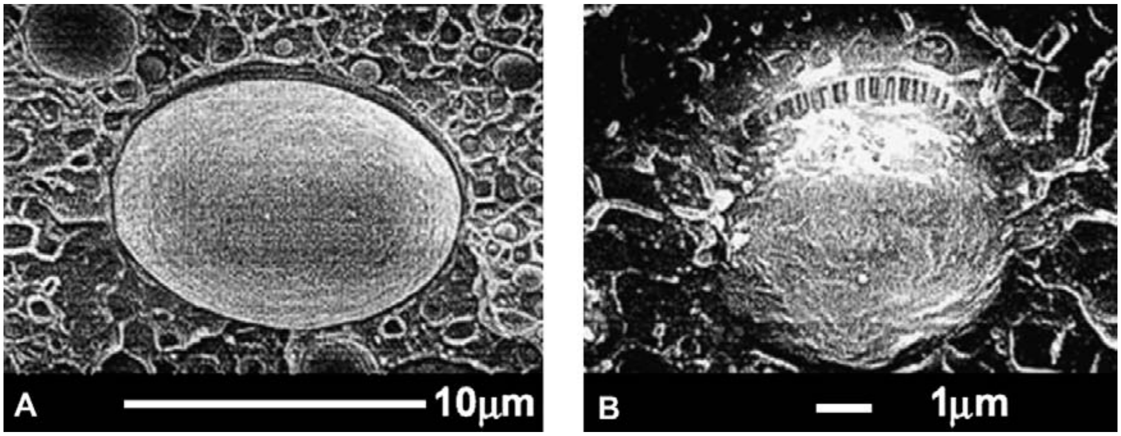

Figure 11.4 Micrographic evidence of the effects of multi-component plastic blends.

A compatibilizer may be used to modify the morphology [71,72] and the interfacial adhesion of a blend by the following:

- Reducing the interfacial tension between two phases, which leads to a finer dispersion of one phase in the other. For example, the incorporation of 1% poly(styrene-*b*-ethylene) diblock copolymer in a blend of polystyrene and polyethylene results in a reduction in interfacial tension from 4.5 to 1.0 dyne cm^{-1}.
- Enhancing the adhesion between the phases by residing at the interface and providing a mechanism by which the two phases chemically knit together.
- Stabilizing the dispersed phase against coalescence.

These actions combine to drastically improve blend mechanical properties and are shown schematically in Figure 11.3.

The photomicrograph in Figure 11.4 shows a blend of PS, LDPE, and PMMA, and dramatically demonstrates the effects of compatibilization on the morphology.

- The addition of the compatibilizer to this system has reduced the nominal average phase size diameter of the minor phase from 10 to 3 μm. The reduction in the size of the minor phase increases the impact resistance as large, incompatible phase particles can act as stress concentrators.
- The addition of compatibilizers reduces the surface smoothness that can be used to visualize how the surface tension has been affected. The strength of the attraction between the two phases has been increased as the degree of incompatibility has been decreased.
- Another effect is the introduction of the binding fibrils such as those seen at the top of Figure 11.4B. These fibrils bind the phase in place and eliminate the possibility of phase coalescence. Both the binding action and the barrier to coalescence increase the strength of the interface.

This example demonstrates how a single compatibilizer can be used to improve the properties of a multicomponent blend through numerous mechanisms [73].

Some preformed compatibilizers, such as Kraton [74] and Vector [75], are commercially available and ready for use. Other postformed compatibilizers require a reaction or chemical or physical change during the mixing or processing step before they show efficacy. Materials used as postformed compatibilizers are generally not compatibilizers themselves but, because of an *in situ* reaction, result in compatibilization.

An example of where compatibilization can be used to help recover value from parts made using different resins is presented in Figure 11.5 where the schematic to recycle the plastics contained within an automotive part is discussed. More than 99% of the plastics used in the manufacture of a minivan door were recovered in this pilot scheme [58].

11.3 Challenges

11.3.1 Technical Issues

11.3.1.1 Additives

Manufactured plastic parts contain the polymer resin and additives. The additives used may impart a specific property to the plastic or else serve as a processing aid. A nonexclusive list of additives that are commonly used in plastics would include antiblocking agents, antifogging agents, antioxidants, antistatic agents, blowing agents, colorants, coupling agents, crosslinking agents, curing agents, fillers, flame retardants, heat stabilizers, hydrolytic stabilizers, impact modifiers, lubricants, pigments, plasticizers, preservatives, release agents, thermal stabilizers, UV stabilizers, and viscosity depressants [14]. There are numerous examples in the literature and in the field where additives can cause the recycler issues. A short list used to demonstrate the complexity additives pose to the recycler would include, for example:

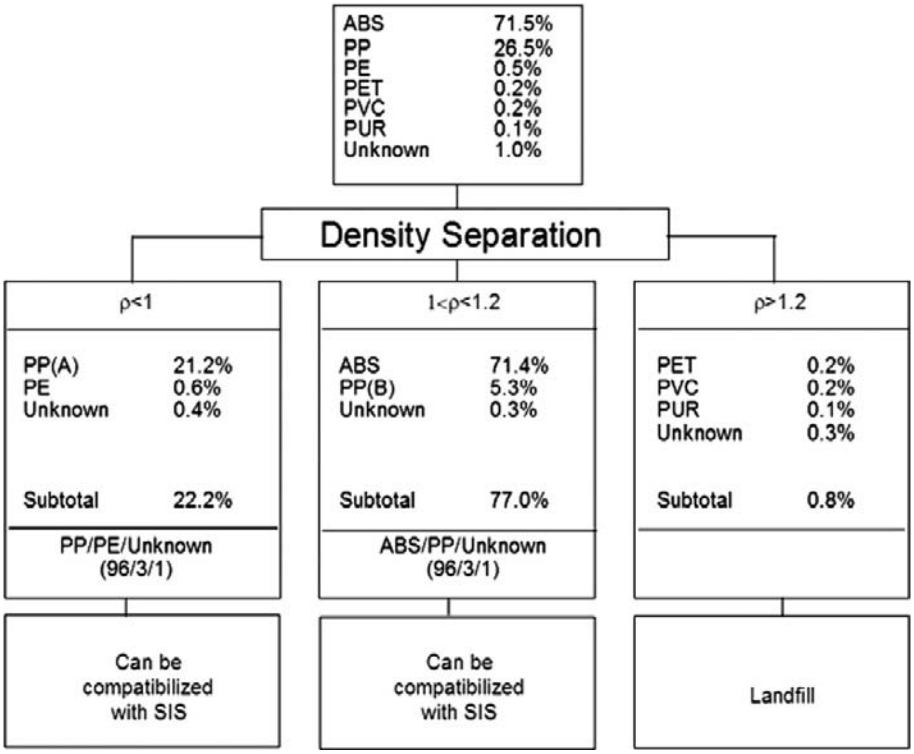

Figure 11.5 Using density separation to facilitate recycling of plastics recovered from a minivan door.

- Some additives such as UV stabilizers may have been used up during the initial lifetime of the plastic [76]. These additives would need to be rejuvenated before reuse. Companies such as Ciba sell Recyclossorb and Recyclostab additive packages for the recycler, which produce rejuvenated plastics [77].
- Some additives such as long glass fillers may degrade (break) during the recycling process. These additives may demand that the recycling process be modified to limit the effect on the properties of the recycled plastics or else that more filler be compounded into the resin to enable the plastic to meet the demands of the application [78].
- Some additives used in one plastic may degrade another plastic if used in a blend. For example, compounding certain grades of recycled ABS with virgin or recycled PC or PC/ABS will cause the PC to degrade [69]. Such combinations should be avoided.

The list above is obviously not exhaustive but highlights how the recycler must consider what is incorporated into the resin to make it a useful plastic for a particular part.

11.3.1.2 Chain scission

Some plastics such as PET may suffer degradation through processing, as discussed earlier in this chapter. The hydrolysis of PET into lower-molecular-weight entities with carboxylic acid end groups is a significant issue. Epoxy-functional, styrene-acrylic polymers with low molecular weight, high functionality, and tailored polydispersity are sold as chain extenders or recycling aids for PET and other polyesters. The inclusion of these additives leads to an increase in molecular weight, mechanical and rheological properties where used, be it in virgin, reprocessed, or postconsumer recycled polyesters [79].

11.3.1.3 Coatings or adhesives

Many coatings or adhesives are thermoset materials. Thermosets do not blend well with thermoplastics. Even when they can be made to blend [80], they do not provide for a homogeneous surface. The surface inhomogeneities that such a mix introduces prevent the recycled plastic from being used in parts requiring a high visual quality. A number of commercial processes have been developed to reduce problems associated with recycling painted plastics or plastics with adhesives. Paint removal has been commercialized using solvent and mechanical separation techniques [52]. Occasionally, melt filtration is sufficient to remove some of the inhomogeneities but this is the exception rather than the rule [81].

11.3.1.4 Discoloring

A discolored plastic may be an issue if a white or uncoated part is the end product. Often the answer that the parts producer employs is to avoid using discolored plastics. Some common examples of discoloring of which the recycler must be aware include:

- Polystyrene that has undergone degradation is subject to an increase in the amount of free monomer content, a decrease in molecular weight, changes in morphology, and a tendency to yellow [82].
- Additives can also cause yellowing. Computer gamers who still have old gaming systems will notice that the flame-resistant chemical used in an ABS case may have caused the part to discolor through exposure to heat, air, or light [83].
- Some batches of titanium dioxide, an additive used to impart brightness, whiteness, or high opacity, have been known to cause pinking in PVC windows and seals [84].

11.3.1.5 Contamination

Any number of materials may cause contamination in recovered plastics depending upon the source of the recycle stream, including foodstuff, dirt, fuel, oils, adhesives, and secondary resins. A plastics stream with significant contamination issues is ASR. The valuable parts of an automobile are typically removed by hand and the remaining material is shredded using a hammer mill. The resulting mixture of metals, plastics, glass, fuels, and so on is ASR. Ferrous and nonferrous metals are separated from the mix as they have value. There has been some research [65] into mining the different plastics from the residue but none that have made any significant impact on the problem have been successfully commercialized. There has also been effort at incorporating ASR into asphalt [85] but there is often resistance to that kind of application from the asphalt manufacturers.

11.3.2 Political Issues

Plastic recycling is often the subject of government legislation due to concerns for the environment and pressure from the media, the public and special interest groups. Legislation may dictate minimum recycled content amounts, procurement directives, producer responsibility, bottle-bill deposits, disposal fees and design legislation, and so on.

11.3.2.1 United States

The USEPA oversees a variety of waste regulatory issues including setting recycling goals. However, mandatory recycling is legislated through state and local governments, as a national law for recycling does not exist in the USA. California is often seen as the state leading the recycling effort in the USA by developing laws that other states or the USEPA later adopt. However, all states are essentially free to set their own limits and some examples of how states' laws differ include:

- *Who pays for the recycling?* Texas passed legislation that producers of computers and monitors pay for the collection, transportation, and recycling of their products. California legislation assesses a fee on the consumer at the point of purchase for these items.
- *How to increase recycling rates?* Michigan assesses a deposit of 10¢ for each beverage container purchased while Ohio does not. Michigan's bottle recovery rate is 97% of those sold, whereas the national average is around 22%.

11.3.2.2 Europe

As California is seen as the leader in the US, Germany has a similar reputation in Europe. A number of laws that the EU dictates [86] through legislation have been focused on specific industries and anecdotal evidence, whether reality or not, points to many of these laws deriving from the German legislature.

The *Packaging and Packaging Waste Directive* and the *Producer Responsibility Regulations* are directed at the European packaging industry and include:

- Minimization of packaging volume and weight to a level that meets standards of safety, hygiene, and acceptance by the consumer.
- Design and use of packaging in a manner that permits its reuse and recovery.

The *End-of-Life Vehicles (ELV) Directive* was established to prevent waste from ELVs being disposed of in landfills and promote the collection, reuse, and recycling of the components. The law establishes recycling targets for producers, dismantlers, and shredders and directs that:

- Vehicles must be accepted at collection systems without charge to the owner.
- Vehicle manufacturers or importers must pay the costs associated with take back and treatment.

The *Waste Electrical and Electronic Equipment (WEEE) Directive* aims to reduce the amount of electrical waste, increase recovery and recycling, and improve the environmental performance of all operators involved in the life cycle of electrical and electronic equipment.

11.3.2.3 China

China has become a significant consumer of the world's plastic waste in the last decade. Cheap labor and infrastructure costs ensure that the economics allow many plastics to be recycled in China that cannot be recovered in the western world. China's legislature passed a law that came into force in 2009 that was aimed at boosting *sustainable development through energy saving and reduction of pollutant discharges*. The *Recycling Economy Promotion Law* will have impact on various enterprises, including *those featuring packaging design or production, construction, and agriculture* [87]. How this will affect China's voracious appetite for plastics and the quality of the factories in which they are recycled remains to be seen once the economy recovers from the current recession.

11.3.3 Economic Issues

The cost to recycle plastics is typically in the 15–40¢/lb range, depending on resin, process, and degree and type of contamination. That money covers the cost to collect, transport, process, clean, compound, rejuvenate, and pelletize. Many of these costs are fixed with the price of the source plastic being one of the few variables. Recycled plastics usually demand 60–70% of the price of the corresponding virgin resin. There needs to be some finite difference between the cost to recover and the price the product can demand for recycling a particular resin by a given process to be economically viable.

The economics of plastic recycling becomes less favorable as the commodity pricing of virgin resins falls. This variability in virgin resin pricing is beyond the control of the recycler but something of which he must be aware. Good resources to follow plastic pricing, for both virgin and recycle, include:

- Plastics News at plasticsnews.com/resin-pricing/all-resins.html. This publication is also available as a weekly subscription newspaper.
- IDES: The Plastics Web at www.ides.com/resinprice/resinpricingreport.asp.

11.4 Industries and Industry Organizations

Industries that use recycled plastics are as varied as those that use virgin plastics. Companies may have initially focused on the use of recycled plastics to lower environmental impacts but the continued use is usually driven by economic concerns. Companies typically continue to use recycled plastic only when it makes good economic sense. There is a smaller subset of industries that have taken a more focused approach to promote the use of recycled materials in the manufacturing of their products. The automotive industry uses significant volumes of recycled plastics in the manufacture of automotive parts. The Vehicle Recycling Partnership (VRP), part of United States Council for Automotive Research (USCAR) [88], is a precompetitive coalition of the US automakers and was established to conduct collaborative research to develop the technical and economic feasibility of vehicle recycling in North America. The Automotive Recyclers Association (ARA) represents the recyclers that serve the automotive industry [89]. The automotive industry has, in the past, specified minimum recycle content requirements to their suppliers. Although recent bankruptcy proceedings ensure that the use of recycled plastics is not as prevalent in discussions with the media now, recycled plastics are used to help control costs and maximize profits. NAPCOR [90] is the trade association for the PET plastic industry in the USA and Canada. Their activities, along with those of the Association of Postconsumer Plastic Recyclers (APR) [91], promote recycling ideals in the packaging and bottle industries. The National Center for Electronics Recycling (NCER) [92] is a nonprofit organization that is dedicated to the development and enhancement of a national infrastructure for the recycling of used electronics in the US. CARE [47] is a joint industry–government effort to increase the recycling rate and the volumes of postconsumer carpet that are reused and to reduce the amount of waste carpet going to landfills. These organizations do not control their respective industries. Rather, they are a combined voice when representation is needed for the plastics manufacturers, users, or the many small to large recyclers that drive those industries. In reality, most recyclers are not tied to one industry and many act as plastics brokers selling to wherever the plastic is needed and where the most profit is generated.

Recycled plastics are typically sold through independent brokers and dealers [93]. Their number is too large to do anything but mention a few of the better-known companies. Some of these companies are buyers and sellers of recycled plastics but many are also recyclers and innovators as they continue to develop new processes to recover value from waste plastic. MBA Polymers [94] is an acknowledged leader at developing technology that recovers high-value engineering plastics from durable goods. American Commodities, Inc. [95] has concentrated activity on becoming a recycler focused on helping the automotive industry recycle their plastic waste. They have developed technologies that separate automotive parts made from mixed plastics and that recover painted or coated plastics. Butler MacDonald [96] has a long history in recycling engineering thermoplastics. They, like others, recover plastics for resale on the open market as well as offering recovery services for hire.

11.5 Products

There are numerous applications for recycled plastics. From reuse in the same application as initially used, whether at 100% or more commonly compounded at some lower quantity, to being used in less demanding applications, recycled plastics utilization has made dramatic in-roads in many industries. The manufacture of plastic lumber, however, exists almost solely because of recycling. Plastic lumber does not age or splinter as does real wood but its cost to manufacture is significantly higher when using virgin resins than the cost to cut and transport traditional lumber materials. The use of recycled alternatives to virgin plastic ensures that the product is more commercially competitive. Plastic lumber is typically made from recycled PE that may contain other plastics and/or fillers. Commingled plastics used with PE may include PVC, PS, PP, PET, and other materials. Fillers used in these systems may include glass fibers, PS fibers, or cellulosic fillers such as wood fibers. The principal use of plastic lumber is to replace wood in areas where weathering is an issue such as in decking, road barriers, or railroad ties.

11.6 Conclusions

There is an increasing need to recycle plastic scrap as a vocal segment of the public demands that less plastic waste is disposed of in landfills and the political climate mandates that demand. There are many opportunities to use recycled plastics but utilization must be financially viable, technically feasible, and environmentally safe to be anything but a temporary measure. Recyclers in the US and around the world are businesses first and they will only stay in business and continue to divert plastics from disposal in landfills *if* they make a profit recycling what others discard. To that end, most of the technology used today has been focused initially on recovering value from homogenous high-value, low-contamination streams. That *low hanging fruit* has been or is becoming successfully recovered. Some manufacturers use other recycled plastics in less demanding applications. Yet there still remain a number of plastics that cannot be economically recovered and that number changes daily with the price of oil. As the price of oil dropped significantly in late 2008 and early 2009, the cost to produce virgin plastics also decreased and that makes many recycling processes less economically attractive. As always, some plastics can be recycled, some can be recycled economically, and some can be recycled economically in quantity but not all and those that can be, change with outside drivers beyond the control of plastics recyclers.

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Part III: Plastic Processing

12 Plastics Processing

Kirk M. Cantor[1] **and Patrick Watts**[2]
[1] Plastics and Polymer Engineering Technology, Pennsylvania College of Technology, Williamsport, PA 17701, USA
[2] Medcomp Inc., Harleysville, PA 19438, USA

12.1 Overview of Rheology

Rheology is simply defined as the study of flow. It is important to understand how polymers will flow so that the structural integrity and flow characteristics of a part are able to be established.

Flow is the permanent deformation of a liquid with an applied force. This can also be interpreted as a strain (deformation) occurring as a result of a stress (force). In the case of polymers, flow occurs when the chains are caused to slide past one another freely.

12.2 Plastics in Flow

Flow occurs in at least one of four ways. These four types of flow are pressure flow, drag flow, shear flow, and elongation flow. A liquid may experience one or more of these types of flow at the same time. The first two types are driving mechanisms for flow to occur. The last two types describe how the fluid deforms during flow. Stress accompanies the driving forces and deformation is quantified by strain.

There are two driving mechanisms that can cause flow to occur. These two mechanisms are known as pressure flow and drag flow. If neither of these is present in a system, there will be no flow present either.

There are also two flow fields in which polymer deformation occurs. These fields are shear flow and elongational flow.

12.3 Types of Flow

Pressure flow is experienced when the flow front is moving due to pressure differences. Fluids flow from a high pressure toward a lower pressure in a system. A common example of this is found in the water faucet. Within the plastics industry, pressure flow is found in injection-molding applications. The polymer is forced into the mold using pressure flow.

Drag flow is induced by a surface dragging over a fluid. This is similar to a boat causing water to flow as it travels. In the extrusion industry, the screw rotating causes the polymer to flow by dragging the polymer along the barrel.

Shear flow is defined as a flow field in which adjacent fluid elements are moving at different velocities. Polymers experience friction as they flow along a stationary object, whether it is the barrel or part of a mold. The polymer next to the stationary object is moving at a much slower rate than the polymer in the center of the channel or far from the wall.

Elongational flow occurs when a fluid is being stretched in the direction of flow. This action takes place through the acceleration of the fluid elements along a streamline. The most common occurrence of this in the plastics industry is found as polymer is stretched by a puller as it exits an extrusion die.

12.4 Orientation

Orientation of the polymer chains is found when the molecules are forced to line up in a common direction. Shear and elongation cause chains to align in the direction of flow. Figure 12.1 shows how a molecule becomes oriented with the direction of flow over time.

12.5 Shear

Shear can be calculated for a flow field. The shear stress of a system can be represented by the Greek lower case letter tau (τ) and can be calculated with the equation: $\tau = F/A$. The equation is read, “Shear stress is equal to force divided by area.” The units given for shear stress are: psi or Pa (Figure 12.2).

Figure 12.1 Molecular orientation.

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- Shear Stress ≡ $\tau = F / A$ [psi]
- Shear Rate ≡ $\dot{\gamma} = V / y$ [1/sec]

Figure 12.2 Shear equations.

Likewise, the shear rate of a system can be represented by the Greek lower case letter gamma dot (γ). Shear rate can be calculated by using the equation: $\gamma = \Delta V/\Delta y$. The equation is read, "Shear rate is equal to velocity difference at two points divided by the separation distance." The units assigned to shear rate are 1/second.

It is fairly simple to realize that different fluids flow at different rates and with different amounts of force. The inherent property of the fluid that causes these differences is known as viscosity. Viscosity is simply defined as the resistance to flow. Viscosity is represented by the Greek lower case letter eta (η). It can be calculated by using the equation: $\eta = \tau/\gamma$. This equation is read, "Viscosity is equal to shear stress divided by shear rate." The units for viscosity are: psi·sec or Pa·sec.

12.6 Viscosity

The viscosity of a liquid will vary depending on any of four conditions. These conditions include temperature, shear rate, molecular weight, and fillers or reinforcements. Each of these factors will have a different effect on the viscosity of the material.

Temperature has a negative correlation with viscosity (Figure 12.3). This means that as the temperature of the polymer rises, the viscosity will decrease. As the polymer heats up, there is more free volume created. Free volume is the term used to describe the void space between the molecules. The molecules are able to flow past one another more easily when more free volume is present.

As shear rate increases, viscosity decreases as shown in Figure 12.4. Therefore, shear rate also has a negative correlation with viscosity. The viscosity will decrease due to an effect known as shear thinning. Molecular orientation occurs due to the shear, causing the polymer to flow easier.

Molecular weight has a positive correlation with viscosity. As the molecular weight of a polymer increases, so too will the viscosity. Molecular weight is determined as a result of the overall length of the molecular chains. As the weight increases, so too will the length. Longer chains will promote the presence of more chain entanglements. Thus, with many entanglements, there is less ability for the polymer to flow (Figure 12.5).

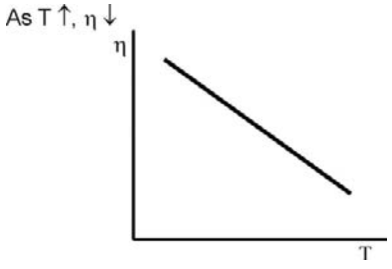


Figure 12.3 Viscosity dependence on temperature.

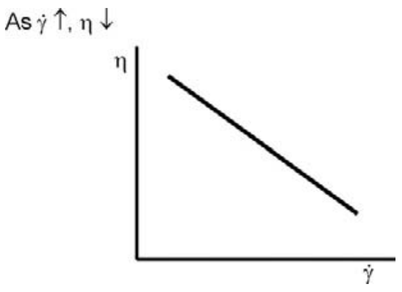


Figure 12.4 Viscosity dependence on shear rate.

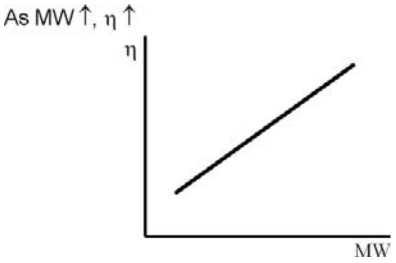


Figure 12.5 Viscosity dependence on molecular weight.

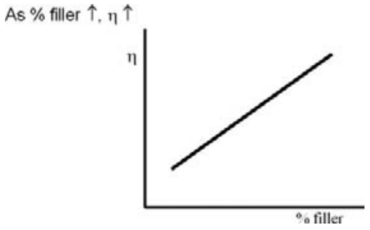


Figure 12.6 Viscosity dependence on percentage of filler.

Fillers and reinforcements also have a positive correlation with the viscosity of the polymer. As the percentage of fillers and reinforcements increases, the viscosity will generally increase. Usually when fillers are added to a polymer, a denser and stiffer fluid is created. This is displayed in Figure 12.6.

12.7 Measuring Viscosity

There are two main ways used in industry today to measure the viscosity of a polymer. Both measuring instruments use a force to push the molten polymer through a die opening known as an orifice.

The first device is the Melt Indexer. It uses a weight to provide the force to move the molten polymer. Different weights are used for different polymer types as determined by industry standards. The result is recorded in grams/10 minutes. A higher melt index would equate to a lower viscosity. In other words, the plastic was able to flow easier through the orifice.

The second device is the Capillary Rheometer. With this instrument, the piston is driven by a variable-speed motor as opposed to a weight. The true viscosity of the polymer is thus determined over a range of shear rates.

12.7.1 Polymer Processing

It is easy to see that polymer processing plays an extremely large role in the plastics industry. Although there are many different methods of polymer processing, they all use various ways to accomplish the same three tasks: flow, forming, and solidification.

Flow must occur by either heating the polymer or through the use of pressure. Flow allows the molecular chains to slide past one another to form a new shape. The flowing polymer then is formed by using molds, dies, and other forms that have been machined to the correct tolerances. The parts must then be solidified in one of two ways. Thermoplastics are cooled to a temperature below which they flow, while thermosetting polymers are solidified by crosslinking the molecular chains.

There are six main groups of polymer-processing techniques—molding, extrusion, blow molding, thermoforming, rotational molding, and composites fabrication. All of these use different methods to accomplish the three steps previously discussed.

12.8 Molding

Molding is the process of shaping a pliable material by using a common pattern to create identical parts. A mold is used to facilitate the formation of parts within this process. The mold consists of a solid block containing one or multiple cavities, which are filled with plastic to form a part containing the shape of the mold.

Within the plastics industry, molding plays a significant role. Molding was not only the first available process for shaping plastic, but arguably is still the leader among the plastics processes. There are many subprocesses within the molding process, but injection molding is by far the most widely used molding process within the plastics industry. Others include, but are not limited to, compression molding, transfer molding, sintering, reaction injection molding (RIM), and resin transfer molding (RTM).

12.8.1 Injection Molding

A large portion of the products produced by injection molding are used within the automotive industry. This fact makes it easy to see why International Automotive Components Group North America LLC is the top injection molder in North America according to PlasticsNews.com. The industry leader is located in the Detroit suburb of Dearborn, MI, conveniently close to the automotive capital of the world.

In injection molding, the polymer is plasticized outside of a mold and then forced into a closed mold via a ramming mechanism. Injection molding is typically used with thermoplastics and is capable of producing high volumes quicker than the other molding processes.

An injection-molding machine consists of an injection end, where the polymer is stored and the ramming mechanism is located, and the clamping end, where the mold and the clamping mechanism are positioned. Over 99% of industry uses a reciprocating screw as the ramming mechanism. There are very few companies today that continue to use a ram as the driving mechanism. For clamping, both mechanical, also called toggle, and hydraulic machines are used relatively equally. However, all-electric machines are a third option and are becoming more widely used.

Machines are rated by either clamp tonnage or shot size. Required clamp tonnage is determined by calculating the projected area of a part. As the projected area of the part increases, the clamp tonnage needed increases as well. Clamp tonnage is referenced more often than shot size. The shot size is the total volume of plastic needed to fill the part. This includes the plastic needed in the part, runners, and sprue.

There are four phases to the injection-molding process. First, the filling phase fills the closed mold with the polymer shot. Then, the packing phase holds pressure on the part to ensure that the part is filled and to prevent backflow of polymer. The cooling and plasticating phase occurs after the cavity gate is frozen and allows the screw to recover while the part cools. Lastly, the ejection phase removes the solid part from the mold and the cycle repeats.

Gas-assisted injection molding (GAIN), co-injection molding, and insert molding are all variations of injection molding that provide various advantages to the original process. GAIN allows the part to be hollowed out by injecting an inert gas, usually nitrogen, after a mold has been short shot, or partially filled with plastic. GAIN allows for lighter parts and less consumption of material. Co-injection uses multiple colors or polymers in order to allow for different appearances or properties within the final product. Insert molding begins by planting a metal insert within the mold. The polymer is then ejected around it to form a plastic outer layer for a metal part.

12.8.2 Compression Molding

Another molding process is compression molding. It is the oldest mass production process for plastics. This process is typically used with thermosets that are crosslinked with heat. The material for compression molding is placed directly into the cavity of the mold. The cavity is then filled through the use of heat and pressure. Compression molding machines are positioned with the mold opening and closing vertically so that the charge of material will not fall out prior to closing the mold.

The charge is the term used that refers to the plastic material placed within the cavity to be molded. The charge can consist of either a preform or pellets. In both instances, however, the size of the charge is calculated according to the cavity volume so as to minimize waste. A bulk molding compound (BMC) is usually used in industry as the charge for compression molding applications. BMCs consist of resins, fillers/reinforcements, catalysts, accelerators, and colorants, which have previously been compounded into either the preform or the pellets that are to be used.

The low material waste is just one of the benefits of compression molding. The tooling cost is generally low since the molds are not very complex. Low shear flow is present, which will not cause much wear on the tools. This also causes low molecular orientation, which prevents warpage.

12.8.3 Transfer Molding

Transfer molding is similar to compression molding; however, the material is first placed in a transfer chamber prior to entering the mold. As in compression molding, thermosets that are cross-linked with heat are used for transfer-molding applications. Multiple cavities can be used within transfer molding since the material is entering the mold after the mold is closed. Since runners and sprues are present, shear is created. This facilitates heat needed for crosslinking and flow to the cavities. Transfer-molding machines are also generally positioned with the molds opening vertically.

Since the mold is closed and clamped prior to the material entering the mold, there is no presence of flash with transfer molded parts. The dimensions of the final parts are very accurate due to the flow of the polymer being gated. Another advantage is that the cure time is faster since there is the presence of shear flow, which creates heat. Inserts can also be used to create more complex parts than can be created by compression molding.

12.8.4 Sintering

Sintering is also similar to compression molding, but a powder material is used instead of pellets or a preform. The powdered material fuses at the interface without fully melting. This allows for intractable, or non-melting, polymers to be molded. Porosity can also be provided in the final part by controlling the fuse time. Sintering is mostly used in applications involving polytetrafluoroethylene (PTFE) or ultra-high-molecular-weight polyethylene (UHMWPE).

12.8.5 Reaction Injection Molding

RIM is a two-component, thermoset molding system. The thermoset is created by mixing two or more materials just prior to injection into the mold. A typical example of this is when isocyanate and alcohol are mixed in order to form polyurethane.

The thermoset product of this method is strong and dimensionally stable. This method can be accomplished by using lower clamping pressures, which makes the process safer for operators. Another advantage of RIM is that it is easy to create a foamed product out of the resins formed.

12.8.6 Resin Transfer Molding

RTM uses a low viscosity thermosetting resin. The resin encapsulates a preform, usually a foam core or glass mat, that is positioned in the mold prior to the resin entering the mold. This method is sometimes referred to as liquid composite molding (LCM).

A main advantage to using RTM deals directly with the preform insert. The parts produced are lightweight, yet have excellent strength characteristics. The mold allows for a good surface finish as well, which is not present in many other composite molding methods.

Injection molding has long been known as the primary industry leader for the plastics industry. Although many extrusion companies have greater sales output than injection molders, injection molders outnumber extruders. Extrusion continues to gain ground on injection molding, but it has not yet passed the premier plastics process in total sales.

12.9 Extrusion

Extrusion is generally considered the second leading plastics industry in the world, even though this process uses about the same volume of plastic as the injection-molding industry. Extrusion is the process by which a material is extruded in a constant profile shape through a die. Within the plastics industry, there are primarily two differing processes used, single screw extrusion and twin screw extrusion.

12.9.1 Single Screw Extrusion

Single screw extrusion uses one screw within a cylindrical barrel to continuously push plastic through a constant profile die (Figure 12.7). Production rate is typically measured in mass per hour (lb/hour or kg/hour) and is controlled by the screw speed of the machine.

Most extruded products are produced using single screw extrusion. Parts such as window frames, house siding, and weather stripping, which have a constant profile, are generally produced by means of single screw extrusion. Due to such factors as the melt swelling as it exits the die, the die design for an extruder is critical. Great complexity is sometimes needed with an extrusion die in order to gain the correct profile.

The two largest industries for extrusion are pipe and tubing extrusion and film and sheet extrusion. There are many other industries that use extrusion to create their

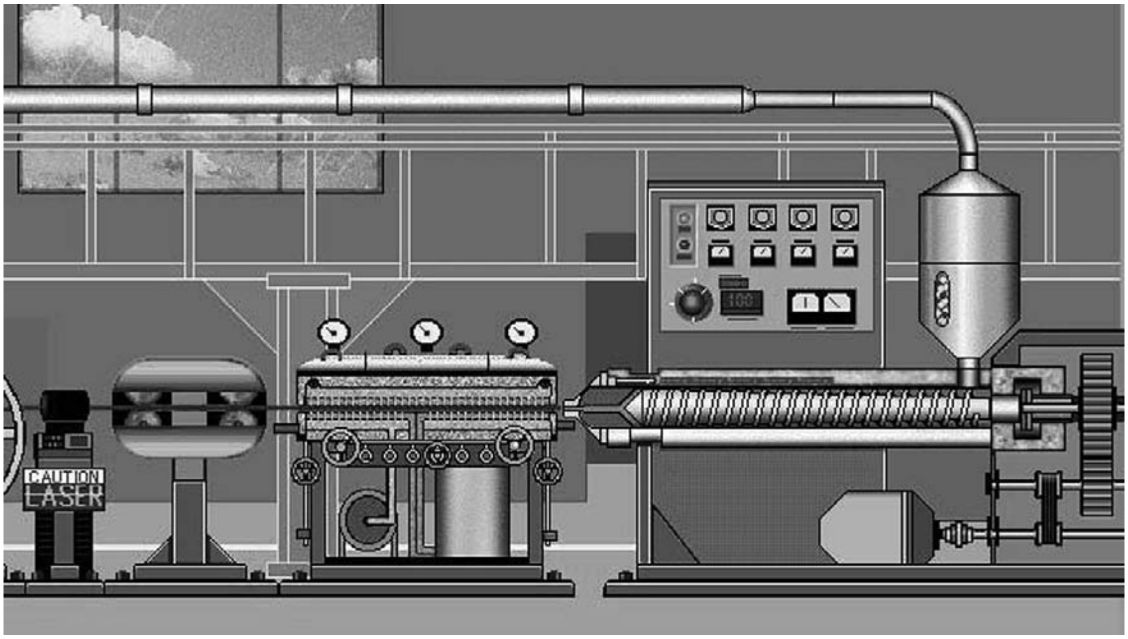


Figure 12.7 Tubing extrusion line (Pennsylvania College of Technology).

products though. Fiber extrusion, for clothing, coating extrusion, and blown film extrusion are just a few of the others.

There are seven North American film and sheet extruders who recorded over a billion dollars in sales for 2008 as recorded by PlasticsNews.com. However, Bemis Co. Inc., of Neenah, WI, was the leader of the industry as the only company having over two billion dollars in sales. Only two North American pipe and tubing extrusion companies surpassed the billion dollar mark in 2007. JM Eagle, of Los Angeles, CA, easily led the way. They nearly reached two billion dollars in sales.

12.9.2 Twin Screw Extrusion

Twin screw extrusion is used in order to generate a superior mixture compared to single screw extrusion (Figure 12.8). Two screws are used within a figure-eight-shaped barrel. Twin screw is used to compound or blend two or more different materials. It is also used to facilitate

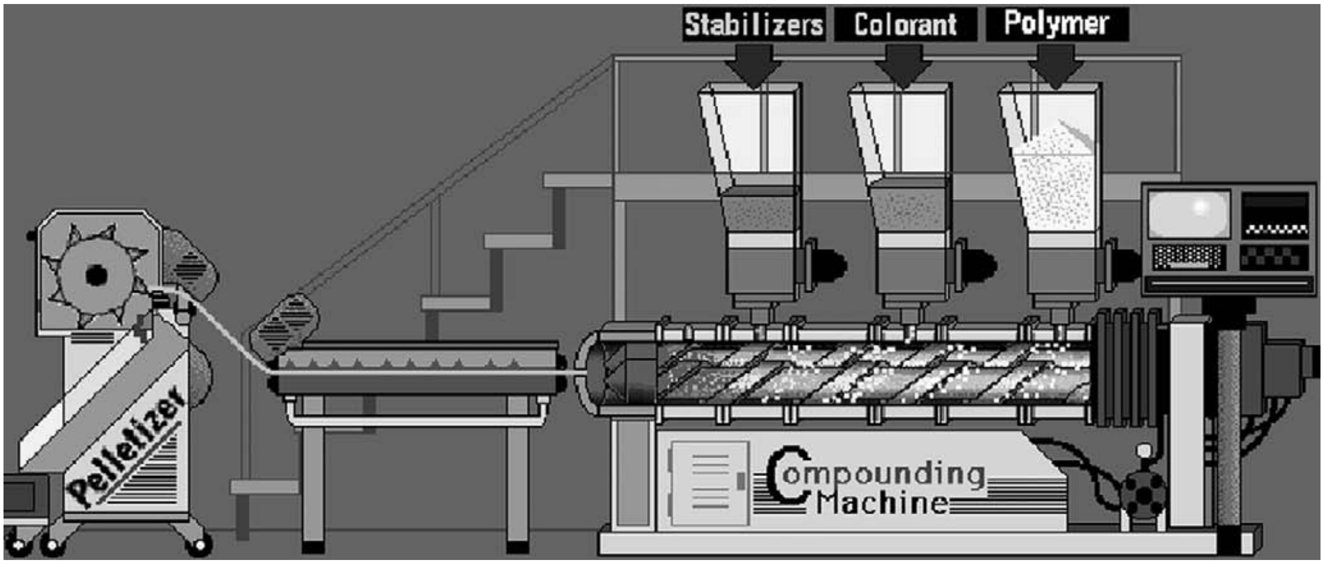


Figure 12.8 Twin screw extrusion line (Pennsylvania College of Technology).

devolatilization of gases from the melt or even the polymerization process. In some cases, the forming of finished parts is done with twin screw extrusion.

Twin screw extrusion can be executed using many types of materials, including thermoplastics, thermosets, elastomers (rubbers), fillers and reinforcements, and other additives. This process is used largely in order to gain a thorough mix of the additives and the polymer. Often the product of a twin screw extruder will be pellets used for another process.

The screws of a twin screw extruder are different from those used in single screw extrusion. They are sectioned along with the barrels so that the screw can be built to facilitate the proper mixing for each system.

The pressure buildup can be much higher for a twin screw extruder. In order to combat this and run the machinery safely, twin screw extruders use metered, or starve, feeding, meaning the barrel is only permitted to fill to a partial level. The throughput of the system is also controlled by the feeding mechanism as opposed to the screw speed.

Twin screw extrusion also is used to produce products from such polymers as polyvinyl chloride (PVC), which may degrade and release harmful gases when processed. It is still potentially harmful to process using twin screw extrusion, but many of the dangers are reduced or minimized to a safer operating level.

Extrusion continues to provide a vital processing technique to the plastics industry. Constant profile parts are able to be produced at a rapid speed that would be unfathomable for other processing methods.

12.10 Blow Molding

Another main polymer-processing technique is blow molding. Blow molding is a process that produces hollow parts by forcing the plastic against the mold walls through the use of air pressure. This process is primarily used to create containers such as soda bottles and milk jugs, but blow molding is not limited to the formation of only containers.

There are two main subprocesses within blow molding. These are extrusion blow molding and injection blow molding. Each process has its own advantages and disadvantages. There are also limitations to each.

12.10.1 Extrusion Blow Molding

Extrusion blow molding is recognizable by the hollow tube that is extruded from the machine to create the parts. This tube is referred to as a parison. A hollow mold then closes around the parison and cycles to the blow station. When at the blow station, the parison within the mold is molded through utilizing air pressure while another parison is being extruded from the machine. This allows for a quicker cycle time (Figure 12.9).

Since the parison is required to hang freely during extrusion, a higher-molecular-weight polymer is required.

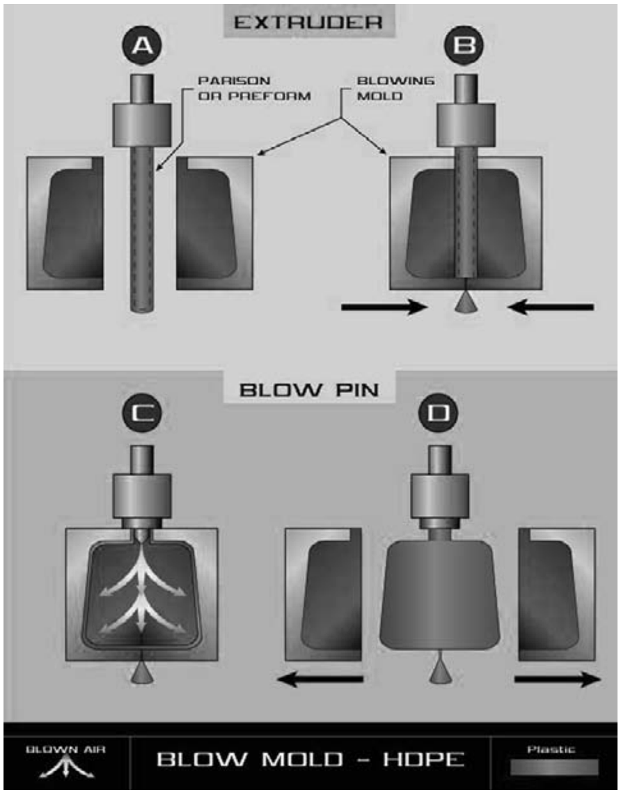


Figure 12.9 Extrusion blow molding (Pennsylvania College of Technology).

High-density polyethylene (HDPE) is most often used within extrusion blow molding applications. Multiple heads can be used on an extrusion blow molding machine in order to create a greater output (Figure 12.10).

The two types of extrusion blow molding machines are the two-station machine and the continuous machine. A two-station, or "shuttle," machine transfers a common mold back and forth between the extruding parison and the blow station. A continuous, or "wheel," machine uses multiple, identical molds to continuously produce parts.

Extrusion blow molding can produce larger parts than injection blow molding. It is also less expensive, and there are no internal stresses within the part. However, more scrap is produced when using extrusion blow molding, and there is less control over the accuracy of the critical dimensions.

12.10.2 Injection Blow Molding

Injection blow molding utilizes an injection molded preform as opposed to a parison to create the final part. After the preform is molded, it is transferred to a second mold where the preform is blown into its final shape.

12.10.3 One-Stage

A part can either be molded by using one-stage or two-stage injection blow molding. One-stage occurs when the preform is cycled to a blow station on the same machine on

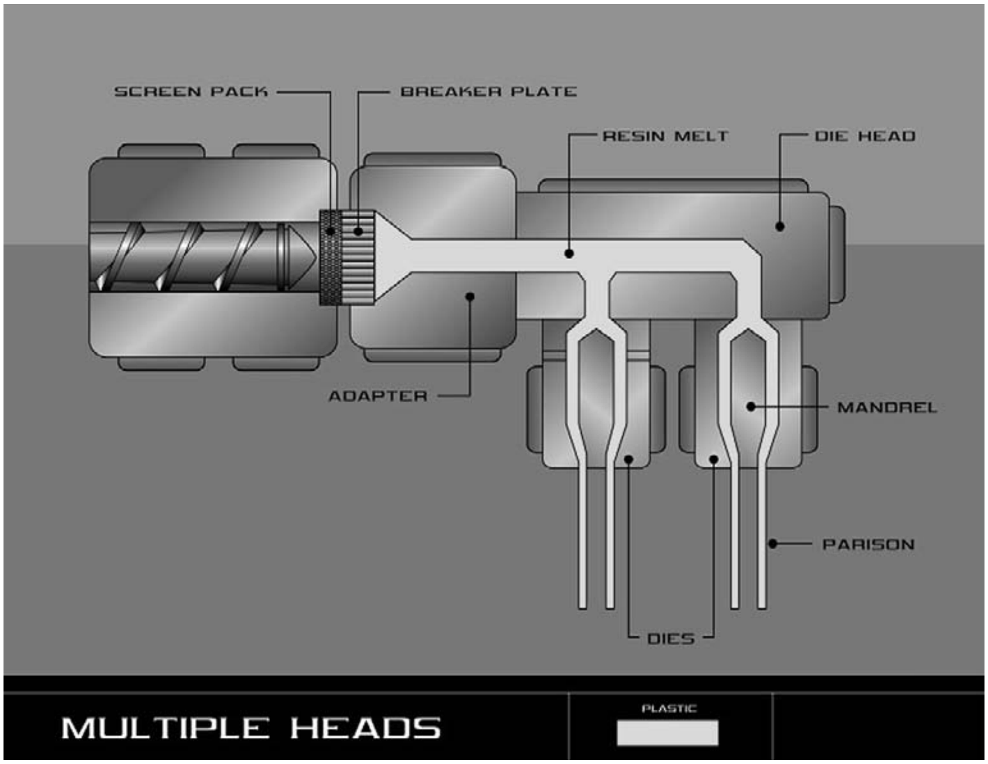


Figure 12.10 Dual-head blow molder (Pennsylvania College of Technology).

which it was injection molded. This allows for the process to be done in one continuous step and only one machine is needed. Also, the polymer only has to be exposed to one heat history since the preform is not completely cooled.

12.10.4 Two-Stage

During two-stage injection blow molding, the preform is completely cooled and then transferred to another machine to be blown into the final shape. The preforms must be reheated and are then blown. By using two-stage, shipping costs can be lowered by shipping preforms as opposed to shipping empty bottles to a bottling plant. The bottles are then blown at the bottling plant prior to filling.

Injection-stretch blow molding is a significant variation of this process. It is used to provide optimum optical and barrier properties, which are obtained through biaxial orientation of the polymer chains. This process is used primarily with polyethylene terephthalate (PET). Biaxial orientation is gained through the supplemental use of a stretching rod just prior to the bottle being blown. The rod allows the preform to be stretched in the vertical direction more uniformly than the blowing air allows.

Along with a reduced shipping cost, injection blow molding offers many other advantages. A higher volume of output is able to be attained. A better control of dimensions is available and there is no bottom weld, which is created when an extruded parison is pinched shut by a mold.

There are disadvantages though with injection blow molding applications. There is a higher capital cost associated with this process than with extrusion blow molding. Also, the process is more complex and subsequently requires more skill.

The top three North American blow molders in 2007 each reached one billion dollars in sales. Graham Packaging Co. LP of York, PA led the way with over two billion. Not far behind were two companies located within 30 minutes of one another. Amcor PET Packaging of Ann Arbor, MI and Plastipak Packaging Inc. of Plymouth, MI were the second and third ranked companies, respectively, in sales during 2007 stated on PlasticsNews.com.

Blow molding is the primary plastic bottle producing method available. The production rate of plastic bottles is significantly higher than that of bottles using different materials. There are also many other benefits to using a plastic bottle, such as the barrier properties of plastic and the flexible yet rigid characteristic of plastic.

12.11 Thermoforming

Thermoforming is a unique plastics process that utilizes a heated thermoplastic sheet to create the final products. The sheet used is first heated to soften it, but the polymer is not heated high enough to reach its molten state. The part is then formed around a mold by using one of six main subprocesses.

These processes are straight vacuum forming, drape forming, plug-assist forming, pressure-bubble plug-assist vacuum forming, vacuum snap-back forming, and mechanical forming.

Since the molecules are forced to stretch instead of being allowed to flow, there are residual stresses left behind within the created parts. These stresses could create difficulties in the application of the product if the stress is located in a critical part of the product.

12.11.1 Straight Vacuum Forming

Straight vacuum forming is one of the two basic types of thermoforming. It is accomplished by drawing a heated sheet into a cavity using vacuum pressure. Straight vacuum forming works well for shallow parts that do not require a high draw ratio.

The draw ratio of a thermoformed part is calculated by dividing the draw, or depth of the cavity, by the width of the cavity (Figure 12.11). A draft angle, shown as α in the figure, is included to aid in part removal from the mold. A draw ratio less than one is ideal for straight vacuum formed parts.

12.11.2 Drape Forming

Drape forming is similar to straight vacuum forming except that a core is used to create the part as opposed to a cavity. This process would be used when the convex side of the part needs to be aesthetically pure. This is due to the rough mold surface contacting the concave portion of the part. Higher draw ratios are possible with drape forming as long as the draft angle is suitable for part removal.

12.11.3 Plug-Assist Forming

Plug-assist forming is the same as straight vacuum forming only with an added step. A disadvantage of straight vacuum forming is that the sheet becomes stretched extremely thin in the corners of the parts. This is why high draw ratio parts cannot be straight vacuum formed.

With plug-assist vacuum forming, a form, usually a wooden plug, is used to stretch the heated sheet part way into a high draw ratio cavity. By using the action of a plug, the thinning that occurs in the corners of the part is reduced.

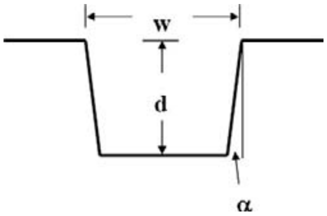


Figure 12.11 Draw ratio (d/w) and draft angle (α).

12.11.4 Pressure-Bubble Plug-Assist Vacuum Forming

Pressure-bubble plug-assist vacuum forming takes straight vacuum forming one step further than plug-assist forming. By using air pressure, this molding technique creates a bubble to prevent large sheets from sagging into the mold under their own weight. Since large sheets are used within large applications, a plug is often used coincidently with the pressure bubble.

12.11.5 Vacuum Snap-Back Forming

Vacuum snap-back forming is a unique process that allows for shapes with a higher complexity to be molded. As the polymer sheet is heated, it is allowed to sag until it reaches a trigger mechanism that is located below. When the sheet contacts the trigger, the mold core closes on the sheet from above and begins the vacuuming action. The trigger is used so that each part is allowed to sag to a similar span as the rest of the parts.

12.11.6 Mechanical Forming

Mechanical forming is unique from the other thermoforming techniques in that it uses jigs or hand-forming techniques to form the softened polymer sheets, rods, etc. Many complex shapes that are unable to be formed using traditional thermoforming techniques can be produced using mechanical forming.

The top two North American thermoforming companies, Pactiv Corp. and Solo Cup Co. are located within a 15-minute drive of each other and less than 45 minutes from the windy city of Chicago, IL. Pactiv Corp. is by far the thermoforming industry leader generating over twice as much as their next closest competitor, Solo Cup Co. according to PlasticsNews.com.

Like all other plastics processing methods, thermoforming allows for more products to be produced from plastic than can be produced using another method. Thermoforming is also very widely used within the packaging industry to assure that parts are tightly secured as they are shipped and stocked in stores.

12.12 Rotational Molding

Rotational molding, also called rotomolding or rotational casting, is a unique process that allows for the creation of a fully encapsulated hollow part. Also, very large parts can be formed by using this process. The part is created by rotating the fully enclosed mold on two axes. A polymer in a powder form is usually used within this process.

The mold begins to heat up in the oven portion of a rotational molding machine. The powder polymer begins to melt and flows on the bottom of the mold. The polymer is able to coat the entire surface of the mold since the mold is rotated on both axes.

It is critical that the mold is in the oven for the correct amount of time. Too little time will not allow the entire amount of polymer to melt. Too much time in the oven will allow degradation to occur within the polymer chains. The process of finding the correct oven times used to be determined by using the trial and error method. Recently the guess work of the process is becoming more scientific and technologically calculated through advancements in reading the temperature of the air inside the mold.

When the mold is removed from the oven, it continues to spin on both axes until the part is solidified. A cooling mechanism, usually a fan, is used to lower the cooling time. Once the part is cooled, one half of the mold is removed, and the finished part is taken from the mold.

Toter Inc. of Statesville, NC and Step 2 Co. LLC of Streetsboro, OH were the top two North American rotational molders during 2007 as recorded by PlasticsNews.com. A slim margin separated the two with Toter Inc. having only two million dollars more in sales.

The large majority of rotational molded parts are produced from polyethylene (PE). Crosslinked PE, linear low-density PE (LLDPE), and high-density PE (HDPE) are the leading classifications of polyethylene used in rotational molding.

Rotational molding is not a large portion of the plastics industry, but is still very important. Many applications that are produced by means of rotational molding cannot or are very difficult to mold with another process.

12.13 Composites Fabrication

Composites fabrication is the process by which composite materials are made. A composite is a material system that comprises two or more material types. In the context of the plastics industry, one of the materials used would be a polymer resin. Laminar composites and reinforced composites are the two primary methods for fabricating composites with plastic.

12.13.1 Laminar Composites

Laminar composites comprise layers of different materials. Each layer is bonded to the next to create a composite structure. Examples would range from plastic—metal to plastic—paper or even plastic—plastic. The layers are combined so that the finished product contains an array of the properties present within the individual layers.

Each layer contributes different properties. The layers could allow for printability on the outer layer. A layer of regrind would reduce the cost of the product without using as much virgin resin. Barrier layers to protect against oxygen or water are present in many food-packaging applications. In many cases, a separate adhesion layer is needed to tie two other layers together. A more rigid layer may be added to provide strength to a weaker part.

Laminar composites are usually either batch processed or continuously processed. A batch process consists of laminated stacks being loaded into a press and then either heated or compressed in order to fuse the layers together. This process is slower than the continuous process since the stacks must be reloaded.

The continuous process is much faster and can be achieved by using squeeze rollers to combine the separate layers of sheet into one multilayered composite sheet. The middle step of producing individual sheets can be skipped by using co-extrusion. This process uses separate extruders but only one die. The layers are created in the separate extruders and are combined into a composite just prior to exiting the die.

12.13.2 Reinforced Composites

Reinforced composites comprise a high-strength additive included with the virgin resin. The additive is usually glass, carbon, or Kevlar fiber. These fibers may be random, oriented, or in a mat format. In some cases, fine metal shavings are used.

A common means of achieving this process is through spray up. A catalyst, resin, and chopped rovings are all sprayed onto a mold. In the case of spas, the tub is thermoformed and then spray up is done to strengthen the part.

Filament winding is another reinforced composite method. In this process, a continuous fiber is wrapped repeatedly onto a mold to produce directional strength. A large portion of the filament winding done in industry is custom manufacturing.

Pultrusion is a third process by which reinforced composites are produced. This process allows for a composite of a constant profile to be continuously produced. The rovings or fibers are pulled through a resin, which impregnates the material. The part strengthens as the resin is allowed to cure.

Composites fabrication is a largely specialized field. Thus, there are very few large companies that focus on composites fabrication to make the bulk of their income. These companies are usually self-managed as opposed to having a corporate office that oversees many smaller plants spread throughout the United States or the world.

13 Injection Molding Technology

William G. Frizelle
Consultant, 15707 Old Jamestown Road, St Louis, MO 63034, USA

The injection molding process in its simplest form has been in use for nearly 150 years (the Society of Plastics Engineers, SPE, celebrated the 100th anniversary of the J.W. Hiatt injection molded billiard ball in 1968.) Compared with the injection molding machines of today, the early machines were, of course, primitive. Most advances have been made since the 1960s with the introduction of the reciprocating screw injection molding machine (IMM). These are the machines that are in use today.

The IMM can be considered to have two halves: the injection unit, where the material is prepared for injection into the mold, and the clamping unit, where the injected plastic is captured in the mold under conditions of temperature and pressure to form the finished product. Figure 13.1 shows the arrangement.

In the early machines, the injection unit was simply a piston traveling in a heated cylinder. The raw material was fed into the cylinder by volume or by weight, and the material came to process temperature by thermal conduction. This approach had two severe limitations:

1. Since the plastic was heated by thermal conduction from the cylinder, the heating must be from the outside of the plastic cross-section to the inside. Plastic is a very poor thermal conductor. Thus, thermal homogeneity came at the expense of long residence times, and productivity suffered.
2. Since the plastic temperature, and, hence its viscosity, is a function of residence time in the cylinder, the material closest to the injection piston will be relatively cold. When injection occurs, a significant portion of the force available will be lost trying to push through the cold material. This "granular zone pressure loss" is typically half of the pressure available, making it difficult to fill out mold cavities that are not well-designed or with materials that do not flow well.

Variations on these machines include installing a heated "torpedo" or "spreader" within the cylinder to provide two-side heat transfer and minimize the thickness through which the heat must be transferred. This in turn improves the temperature uniformity in a shorter period of time (Figure 13.2).

Another variation is to install an accumulator or second injection unit (a piggy-back machine) so that the final injection step is from the second unit. This maximizes injection pressure in the mold cavities (the granular zone pressure loss still exists but does not affect injection pressure from the accumulator cylinder).

These kinds of injection units have mostly been replaced by reciprocating screws, but they are occasionally found in applications such as multi-colored parts where a mottled appearance is desired. They excel here because there is very little mixing in the process.

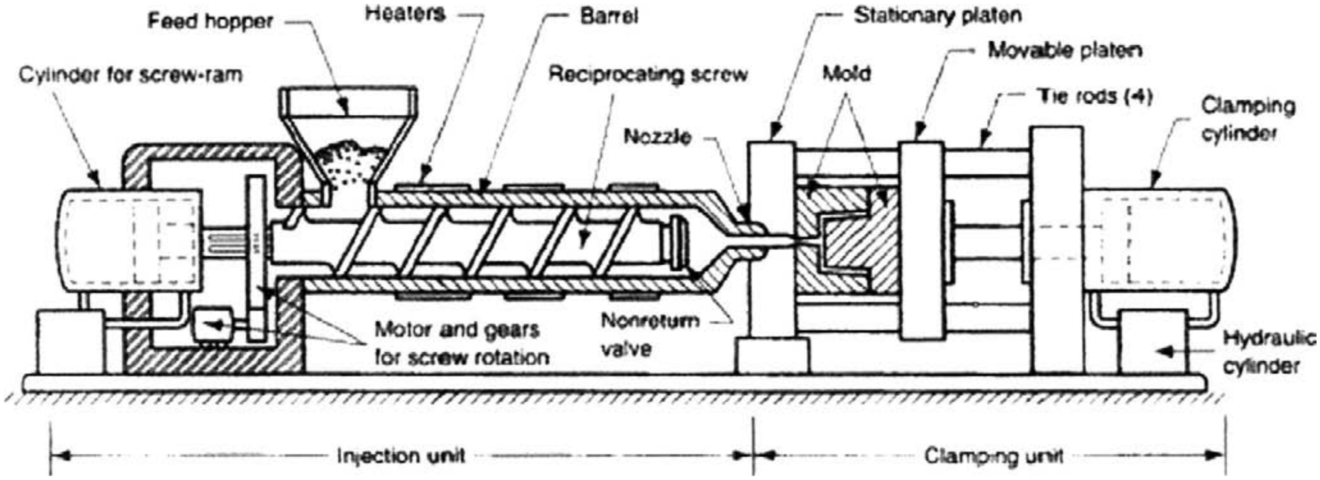


Figure 13.1 Injection and clamping units.

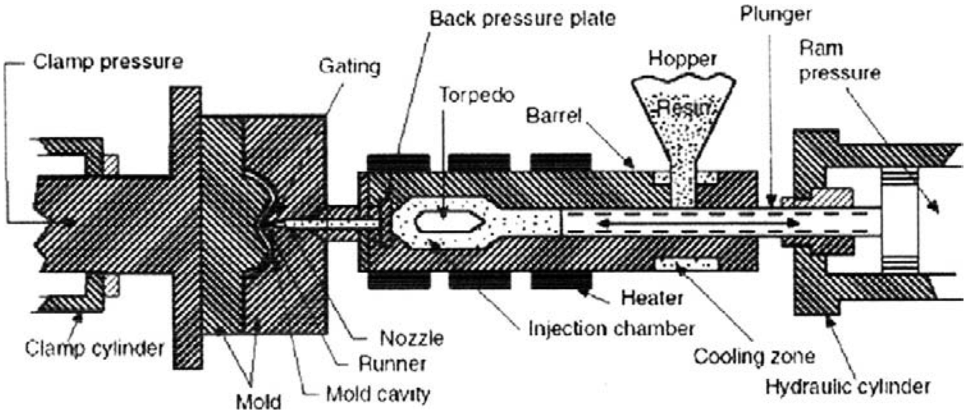


Figure 13.2 Plunger machine with torpedo.

The modernization of the injection molding process began in the 1950s with attempts to introduce extrusion technology to the molding process. The beauty of the extruder is that it does not rely on thermal conduction to get energy into the plastic. Rather, the screw uses geometry and drive motor power to do work on the material, generating frictional heat. The combination provides rapid and effective heating as well as mixing the material. Unlike extrusion, injection molding is an intermittent or batch process. Thus, the screw does not rotate continuously, and the plastic has residence time in the cylinder that does not occur in the continuous extrusion process. This residence time must be managed carefully. It is a temperature variable because heat transfer is likely to occur, and this can lead to shot to shot variation that will be considered as this discussion progresses.

The hardware associated with the injection unit in the reciprocating screw IMM consists of:

- Feed hopper
- Barrel (cylinder)
- Reciprocating screw
- Means for screw rotation (hydraulic or electric)
- Cooling system
- Hydraulic pumps (or electric motors)

These are shown schematically in Figure 13.1, along with the components for a typical clamping section:

- Fixed platen
- Moving platen
- Tie bars
- Clamping mechanism (hydraulic, mechanical, or some combination)
- Mold

The physical actions occurring in the process are shown in the timeline below. This would be representative of a typical older production unit, but it does not change much as the machines are upgraded to the most recent technology. The effect of the actions is established by monitoring the pressure vs. time curve in the mold cavity measured in fair proximity to the gate into the cavity.

A. The injection unit has prepared the shot
   1. Mold closes, and a signal is sent to the injection unit
   2. Screw moves forward acting as a plunger (piston) causing plastic to flow through the delivery system (nozzle, sprue, runner, and gate) into the mold cavity (ies). This is reflected by increasing pressure in the cavity as the mold fills. If plastic is not in the cavity then air is, and provision must be made to allow the air to be pushed out as the cavity fills (called venting). Note that at the point where the cavity is full the process is not complete. This is hot plastic: after cooling, it will not yield an acceptable part. There must be enough hot molecules before cooling to provide the appropriate number of molecules after cooling (mold shrinkage will be considered later.) This step is called “packing” the cavity.
      2a. During this time, the mold is closed and cooling is taking place.
      2b. At this point the cavity has filled, and the actual time to fill can be measured. While not routinely done, this data can be used to calculate the shear rate seen by the plastic. In turn, this can be used to help characterize the flow behavior of the material.
   3. The screw, acting as a plunger, capitalizes on the fact that hot plastic is somewhat compressible, 1/2% or so for every 1000 psi of pressure in the cavity. An excess of hot molecules are packed into the mold cavity in order to have the correct number in the part after cooling has taken place. In the very early screw machines (1960s), the filling and packing functions were performed with a single hydraulic pump. However, it

soon became evident that there are two separate actions involved.

The first is getting the material into the mold and filling out the cavity(ies). This is done as quickly as possible to minimize thermal loss from the plastic and to capitalize on the relatively low viscosity associated with high shear rates in most plastics. Thus, later machines (1970s to the 1980s) usually used two pumps: one for filling the mold (high volume at relatively low pressure) and one for packing molecules in the cavity(ies) (a low volume, high pressure pump). While they are often referred to as first stage and second stage pumps, there is no standard terminology. Thus the terms "inject" and "hold," or "boost" and "hold," or some other combination of words was used. The modern computer-controlled hydraulic machine may have as many as a dozen different stages programmed to provide an appropriate "fill and pack" profile. The modern electric reciprocating screw molding machine provides the same functions with electric motors rather than hydraulic pumps. These machines are much more efficient in their use of energy (which can justify their higher initial cost.)

4. The gate has solidified and isolated the cavity from the rest of the process. Second stage pressure is held until just after this point to assure time for complete solidification. If the second stage pressure is relieved before the gate has frozen, the greater pressure inside the cavity will allow plastic to "discharge" back into the runner, resulting in a loss of control in the cavity, decreasing the part weight, and opening the door for a number of quality issues (note that in thin-wall, short-cycle parts, it is sometimes desirable to allow a slight discharge in order to relieve stresses built in at the gate, thus minimizing a tendency to warp after ejection from the process).
   - 4a. Second stage pressure is dropped, and screw rotation begins in order to prepare the next shot for injection.
   - 4b. In the time interval between 4a and 4b, the screw is rotating, preparing the material for the next shot. The screw rotational speed should be such that the shot is accumulated just before the mold opens.

The screw does work on the material and generates frictional heat. At the present level of technology there is no good way to measure the temperature of the accumulated shot. It is either the same temperature as the barrel or it is not. And, if it is not, then it must be either hotter or colder than the barrel. The same statements hold true with respect to the screw. If there is significant residence time in the barrel after the shot is accumulated, any temperature difference between the plastic and the surrounding metal will be the driving force for heat transfer. This in turn will lead to non-uniform temperature within each shot. For highest quality product, it is preferable to have the most uniform temperature possible.

5. The interval from 4b to 5 is short as explained above. At 5, the mold opens and the part ejects.
6. The mold closes and the process repeats itself. The time interval from 1–6 is the "cycle time" and is a measure of the productivity of the process (specific to the mold and material).

The machines themselves are sized by several methods, most commonly as follows:

1. *Shot capacity*: the amount of plastic that can be injected into a mold cavity with one stroke of the screw acting as a plunger. (Note that there are screws that can make multiple stokes.) This is reported in ounces of polystyrene (in the early days, polystyrene was the material a molder was most likely processing). What really is happening is a piston stroking through a bore, much like a piston in an automobile engine. Thus the true sizing is volumetric displacement, but this is of limited value. It is a volume of hot plastic and would require volumetric thermal coefficient of expansion values for each material, because part dimensions are usually given as room temperature values.

However, there is a relationship between mass and volume that we call density, or, more often, specific gravity. By definition, specific gravity is the ratio of the density of a material compared with the density of water.

The density of water is considered to be one gram per cubic centimeter.

Polystyrene has a specific gravity of 1.05 (note that there are no units, for the number is a ratio). For a given screw and barrel, the machine will have the same shot size for all materials with a specific gravity of 1.05. If a higher specific gravity material is used, the machine will have a larger shot size. Thus a machine having a 10-ounce shot capacity in polystyrene will have a capacity slightly greater than 14 ounces when molding an acetal with a specific gravity of 1.42. The arithmetic says:

$$\begin{aligned}\text{New shot capacity} &= (\text{rated capacity in P/S}) \\ &\quad \times (\text{Sp.Gr. New mat}'\text{l/Sp.Gr.P/S})\end{aligned}$$

If polypropylene (Sp.Gr. = 0.9) is to be used, the new capacity is (10oz)(.9/1.05) or approximately 9 ounces in P/P.

Very small machines have shot sizes less than an ounce, while very large machines are upward of 1400 ounces.

2. *Clamp tonnage*: The amount of force available to hold the mold halves together under injection pressure, is measured in tons. The rule of thumb in general use in the industry is 2–5 tons of clamp capacity (clamping force) for every square inch of part projected surface area. The word "projected" provides for the three dimensions of most parts. If a flat plate is to be molded, the molding area is simply the length times the width, and the actual clamp tonnage required is a function of the material being processed as well as the injection temperature and pressure.

As a processor, you hope that you will never be asked to mold a part with parallel sides (such as a cylinder). Figure 13.4 shows that cavity pressure decreases as the mold cools the plastic. The outer dimension of the part is established by the cavity, and the inner dimension is determined by the core.

The cavity pressure decreases as the material cools and shrinks away from the cavity, but the core pressure increases as the plastic shrinks on to it.

This makes part removal from the core difficult, and can lead to part damage.

To avoid this problem, "draft" or "draft angle" is provided in the part design.

Figure 13.5 shows a cross-section of a tumbler-shaped part designed without and with draft. There is no draft provided in Part A. Core pressure will be high after cooling, and removal of the part with depth "d" will be burdensome if even possible regardless of the ejection mechanism used. The probability of damage to the part at the ejection surface is high. This is not so in Part B. Even if the core pressure is high, if the part can be moved at all, it is free.

Draft is required for the molding process to proceed smoothly and economically.

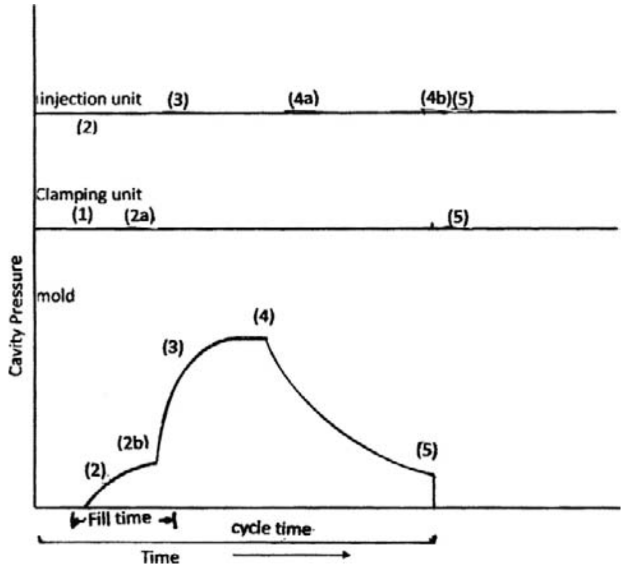


Figure 13.4 Injection molding event time line.

From the designers' point of view, it is almost always considered a necessary evil. One of the problems is that a recommended draft angle of one degree causes a dimensional variation of 0.0175 inches per inch of draft depth. And the designer must specify the direction of the draft, or the toolmaker will surely get it messed up.

Consider an open cylinder one inch in diameter and 6 inches long as shown in Figure 13.6. (This is a simplification of a real part that was to be molded.) The designer specified "no draft allowed." The molder cannot accept this, and responds "One degree of draft per side." But wait! One degree of draft over 6 inches is 6(0.0175) = 0.105 inches dimensional change per side. This part will be 0.210 inches wider at the base than it is at the top if it is cored from the base and drafted to the top; and that has not addressed the question of which end will have the target one inch dimension.

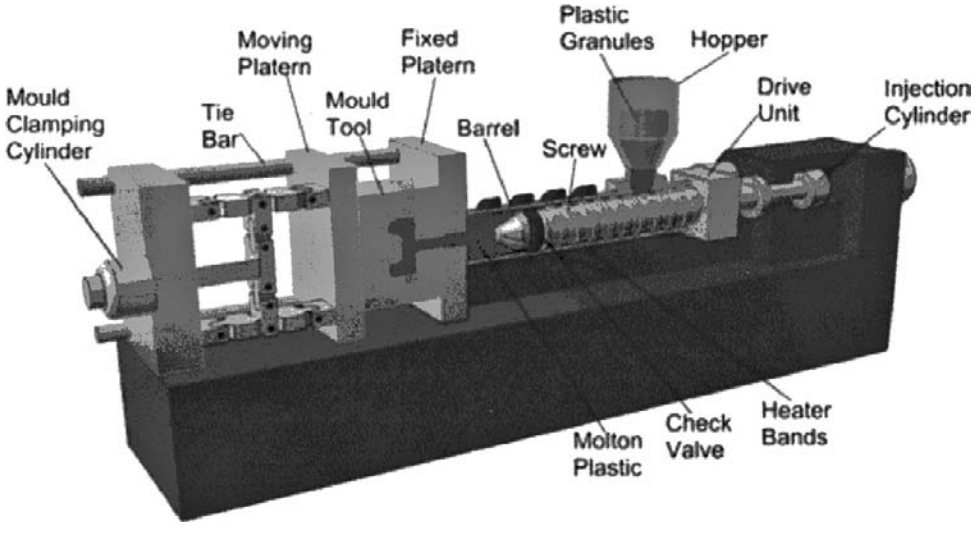


Figure 13.3 Typical injection molding machine.

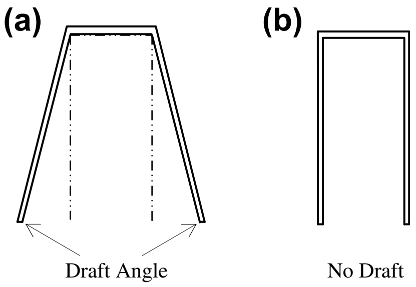


Figure 13.5 Tumbler with (a) draft and (b) no draft.

The dimensional variation could be halved if the part was cored from both ends.

However, the tool (mold) is more expensive, and the part is now shaped like an hour glass (Figure 13.6). The ultimate solution was found when the designer acknowledged that what he really needed was an internal area where the part diameter was fixed.

Thus four opposing internal flats 2 inches long and one quarter inch wide were provided with no draft. The rest of the part was designed with 0.1 degrees of draft, and a material with very low mold shrinkage was specified.

Acceptable parts were successfully molded.

An aside here on mold shrinkage. Some segments of the industry carelessly use the words “shrink rate” in place of “mold shrinkage.” Mold shrinkage literally is the difference between a cavity dimension and the corresponding dimension of the part that came from that cavity, reported in percentage, or inches per inch, or millimeters per millimeter. This dimensional difference exists because of the thermal coefficient of expansion (actually contraction as the material cools) combined with any dimensional change due to phase changes in the material over the temperature range involved in the processing of that material (this subject is examined in more detail in the section “specifying a screw for an injection-molding machine”). Since “rate” is a time-dependent phenomenon (think miles per hour, feet per second, etc.), it is clear that mold shrinkage is not a shrink rate. There is a rate of shrinkage, but it probably is of more interest in post mold shrinkage than in the process itself.

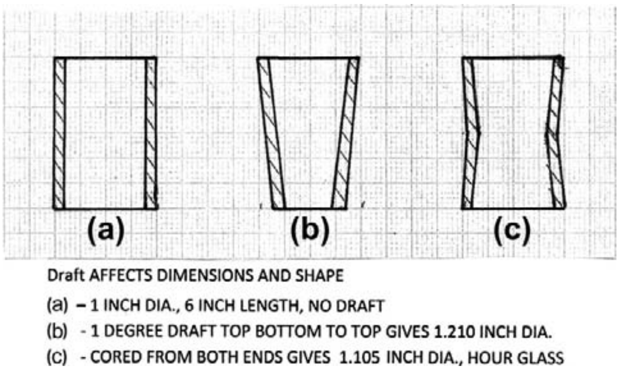


Figure 13.6 Draft affects dimensions and shape.

In checking back to Figure 13.6, it is evident that Part B will be easier to eject than Part A. The price paid for easier ejection is a higher clamp tonnage requirement. The plastic entering the mold cavity acts much like a hydraulic fluid, exerting pressure at right angles to the face of the cavity as filling is completed. A vector component of this pressure is acting to push the two mold halves apart. Our rule of thumb says:

$$\text{Clamp tonnage required} = 2\text{–}5 \text{ tons clamp per square inch of part projected surface area}$$

and accounts for that vector force by projecting the area at the base of the part rather than using the smaller area at the top of the part.

Small machines will have a clamp capacity of a few tons, while very large machines may run up into the range of 9000 tons.

A third method for sizing molding machines is in terms of injection pressure capability measured in pounds per square inch. This has become increasingly important as materials (and the process) become more sophisticated. As a material flows, it loses pressure, pounds per square inch of pressure loss per inch of flow distance. There must be sufficient pressure available to fill and pack the cavity to an appropriate level. That pressure is material dependent, process dependent and tooling dependent (a function of gate location).

In a hydraulic machine, the injection pressure is obtained by amplifying a relatively low hydraulic pressure generated by a hydraulic pump. While there is no standard pressure, a typical pumping system will generate in the order of 2000 psi.

The pump pressure is applied to a piston that is functionally the backside of the screw. By Pascal’s Law, pressure times area at point one must be equal to pressure times area at point two. This is illustrated in Figure 13.7.

The arithmetic is:

$$P_1 A_1 = P_2 A_2$$

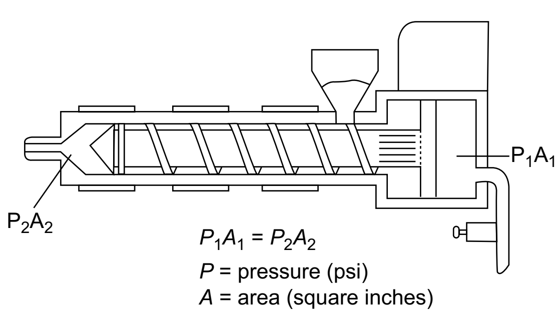


Figure 13.7 Pressure amplification.

In a typical machine, the area at one (the backside) is about 10 times the area at two (the face of the screw). So, if the pressure at one is 2000 psi, then the pressure available at two is 20 000 psi (2000)(10 A_2) = P_2A_2. This is a typical injection pressure capability for a molding machine and will accommodate the processing of many materials. Note that the material loses pressure as it flows through the nozzle, sprue, runner, gate, and into the cavity. In a typical mold, one can anticipate that about half of the available pressure will be lost in delivering the material to the cavity, and there must be sufficient pressure left to be able to pack out the cavity. If there is not enough pressure available, the result will be a short shot.

If there is not enough pressure to pack the cavity, the result will almost always be a part with unacceptable characteristics. The viscosity of the material (the resistance to flow) is often shear rate sensitive (see Figure 13.8). For now, it means keeping the flow passages as small as possible without getting so small that significant cooling takes place. In other words, shear rate increases as the flow passage size decreases, but so does cooling. The objective is to find the optimum point. This means having access to viscosity—shear rate curves as well as viscosity—temperature curves. Some material vendors have done a much better job in this respect than others.

The viscosity of some materials is not very sensitive to shear rate—polycarbonate and polysulfone are two common examples. Processing of these materials is accomplished at relatively high temperatures and pressures compared with other materials. The high temperatures and pressures are required to compensate for the poor shear rate sensitivity.

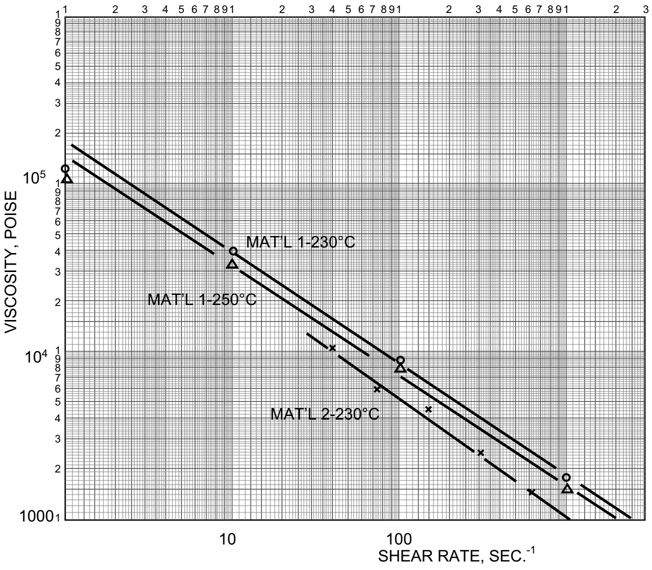


Figure 13.8 Viscosity changes with shear rate. Note that the affect of temperature is much less than that of shear rate.

It is important to note here that the control panel on most older equipment is only able to provide a hydraulic pressure measurement. This is the pressure before amplification. The plastic being processed only knows about the amplified pressure, which we can consider to be plastic pressure. Two machines providing the same hydraulic pressure do not necessarily provide the same plastic pressure. That depends on the ratio of A_1 to A_2 as we considered above. It also partly explains why a given job running well on one machine will not run under what appear to be the same process conditions on another machine. We must work with plastic conditions rather machine conditions, and this will require that we know about the inside of our machines.

Most machine manufacturers today offer several screw—barrel configurations to fit a given hydraulic system. For example, a "standard" machine may be sized to provide 2000 psi hydraulic pressure (20 000 psi plastic pressure) with a 10-ounce (arbitrarily) shot capacity. This may be referred to as a "B" barrel configuration. If the machine is used primarily to make larger shots in easy processing materials (say ABS, PE, etc.), it may make economic sense to install a larger diameter screw and barrel. This might be called a "C" barrel configuration. It will have a larger shot capacity at the expense of injection pressure capability (the A_1/A_2 ratio has decreased). Conversely, an "A" barrel configuration would have a smaller diameter than a "B" barrel. It would have a smaller shot size capability with the highest injection pressure capability. Many manufacturers also offer a "D" barrel configuration for processing thermosets.

In all cases, the barrel length and the hydraulic system remain the same. The details of a screw suited for thermoset processing are considered in the section on screw design.

It should be noted here that the vast majority of molding machines in service in 2010 are hydraulic machines. In the long term, they are doomed because they are not electrically efficient. All-electric molding machines are more expensive than their hydraulic counterparts, but the incremental cost is recovered with higher efficiency and lower operating costs (servo motors are turned on and off at will while hydraulic pumps run continuously). The approach to processing is not changed because of a difference in machinery. Machines do not make plastic parts. Plastic molecules make plastic parts.

There are some general characteristics that plastics have that become very important in the design and processing of plastic parts. First, while there are many references to dealing with polymer processing, we must recognize that commercial plastics are material systems, that is, they contain not only polymer molecules but also an additive package. These additives are typically present in quantities measured in parts per million and are intended to provide specific characteristics to the material during processing and/or in the final application. These additives can influence what is actually done during the molding process.

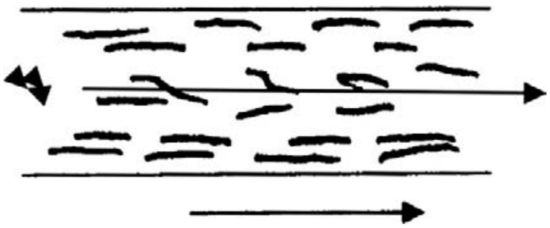


Figure 13.9 Molecular orientation as a result of flow.

Second, molecules can be characterized by their length-to-diameter ratio, called their aspect ratio. While there will be a range of aspect ratios in the system, molecules with the highest ratios have a tendency to "string out" as they flow, particularly in the area of highest shear rate. This is illustrated in Figure 13.9. If these molecules are cooled rapidly, they will be captured in this state, which will be a state of stress. (These molecules need time and energy to relax to their preferred random coil configuration, and with rapid cooling they do not have enough of either.) All injection molded parts will have a residual stress level unless steps are taken to reduce it. Note that this is not to say that residual stress is bad. It is there, and whether it is bad is a function of what the molded part has to do. It affects mechanical, chemical, thermal, and electrical properties that may lead to unexpected failure. This is a processing problem as much as it is a material problem. The stress is generated under high shear rates (which will translate to rapid injection rates through small flow passages) and is retained with rapid cooling.

Third, contrary to what many processors believe, most plastics do not "melt" in the true sense of the word. Melting rigorously means that energy can be added to a material in order to change its state (solid to fluid) without changing its temperature. This behavior is limited to a few thermoplastic materials, including polyethylenes, poly-propylenes, some nylons, the acetals, and thermoplastic polyesters. (There are others, such as polyetherether ketone (PEEK) and polymethylpentene, but these are relatively uncommon materials.)

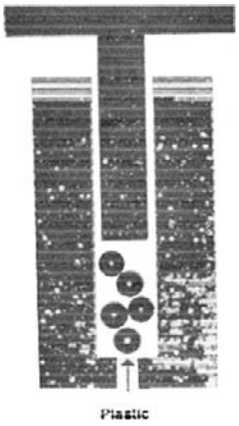


Figure 13.10 Schematic melt flow indexer.

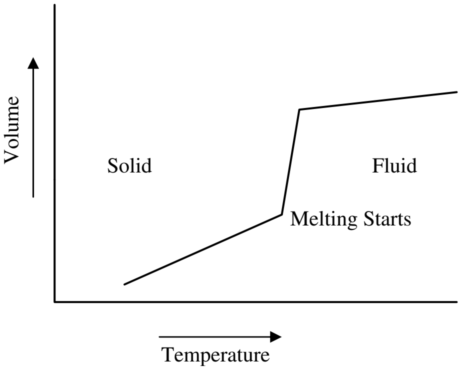


Figure 13.11 Volume-temperature curve for a crystalline material.

These materials are referred to as "crystalline" plastics. Since no plastic is 100% crystalline, technically these are semi-crystalline materials. The implication of crystallinity is some form of internal order which is lost with the addition of sufficient energy. The alternative to internal order is disorder, and the material is considered to be "amorphous." Most of the common plastics are amorphous and do not melt. Their behavior is like taffy—heat it and it gets soft, cool it and it gets hard.

There are implications from a processing standpoint. A qualitative plot of relative volume versus temperature is shown in Figures 13.11 and 13.12. In the first, the behavior of the crystalline material is characterized by a sharp increase in the volume at the melting temperature. This volume change does not happen in the amorphous material.

Instead we see only a change in the slope of the volume—temperature curve at a specific temperature. Note that these curves would still be comparable if "relative volume" were replaced with "enthalpy." The injection molding process can be presented in terms of fluid flow and heat transfer:

add energy remove energy
Raw Material ------------> fluid behavior -----------> Finished product
by work In the mold

Now we run an experiment where the only process variable is the rate at which the energy is removed from the material—the final step in the process. The alternatives are (1) to remove energy rapidly (rapid cooling) with a large temperature difference between the plastic and the mold surface (cold mold), or (2) remove energy slowly (slow cooling) using a relatively small temperature difference between the plastic and the mold surface (hot mold surface). We use a crystalline material for the experiment.

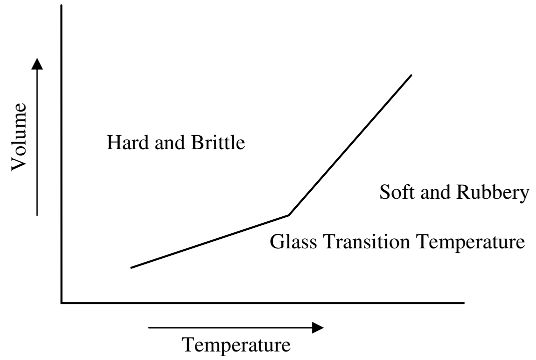


Figure 13.12 Volume-temperature curve for an amorphous material.

Comparing the properties of slow cooled parts versus parts made with rapid cooling:

Slow Cooled Parts Fast Cooled Parts

- Better mechanical properties
- Better thermal properties
- Better chemical resistance
- Higher density
- Greater mold shrinkage
- Longer cycle time

If the application for these parts requires the best properties attainable, it is clear that slow cooling is required. The higher density suggests that slow cooling develops more crystalline content (an ordered system can have more molecules in a given volume. Disorder requires more space than order. If we question this, we must take a look at our own desk!) Inspection of Figure 13.11 gives us some insight into what is happening. When crystalline materials are below their melting point, they will show order in 30 to 90 percent of their structure (the actual amount of order that can be developed is polymer dependent, with low density polyethylene at the low end and thermoplasticpolyester at the high end). When they are heated above their melting point, all order disappears (because of the relatively high energy level in the system). When these disordered systems are cooled, the molecular order can reform, if the molecules have enough time and enough energy. So, if the mold is hot enough and the part thickness is relatively large, all of the crystalline content can develop, and the original heating curve can be traced back as a cooling curve. If the mold is cold and the part is thin, some molecules will be cooled before they can get into an ordered form. This leaves them with a larger volume—the original volume–temperature curve is no longer being followed, and the mold shrinkage has been reduced.

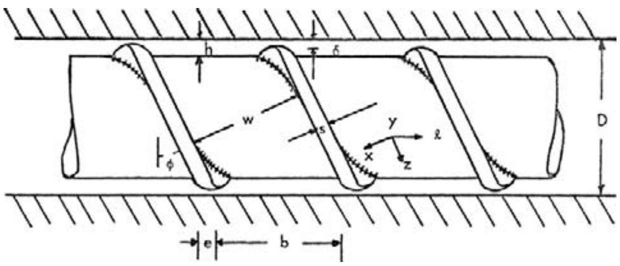


Figure 13.13 Schematic symbology for a screw.

It seems obvious then that if the mold surface is cold the material that contacts that surface will not be able to develop full crystalline content (even if it can only develop 50% content at best). Further, this means a differential in properties through the thickness of the part (the inside must cool more slowly than the outside. And the difference is significant because of the poor thermal conductivity of the plastic).

Thus mold shrinkage is a composite of the shrinkage values dependent on the crystalline content developed. Worse, we end up with a part that can change both in dimensions and properties with time in service if the service conditions are such that additional crystalline content can develop.

Thus there is mold shrinkage (occurring during processing) and post mold shrinkage (occurring after processing.) Higher mold shrinkage values lead to lower post mold shrinkage values (more crystalline content is developed during the process) and vice versa.

This also suggests that mold shrinkage values can serve as an indication of the presence of crystalline content. The components contributing to mold shrinkage are thermal coefficient of expansion and the presence of crystallinity. In general, amorphous materials (no crystalline content) will show shrinkage values in the range of 0.003–0.007 inches per inch, while crystalline materials can be expected to be in the range of 0.015–0.030 inches per inch. However, we must be careful! These values are typical for unfilled, unreinforced materials. The use of fillers and reinforcements can substantially reduce the shrinkage values.

Consideration of the presence of crystalline content will also be important in the screw design for injection molding. In regrind considerations, the use of regrind material is still a much misunderstood area in injection molding. The primary interest here is in thermoplastic materials (many thermosets are highly filled, and the addition of regrind is akin to adding more filler content). Thermoplastic regrinds are often considered "degraded materials." In abusive processes, (excesses of temperature and pressure) this may be true. However, under normal processing, it is more appropriate to consider regrind as a changed material.

To help examine the concept, we must consider American Society for Testing and Materials (ASTM) standard test D 1238, Melt Flow Index by Extrusion Plastometer. In this test, the time required to displace a known amount of material under specific test conditions is converted to output in grams per 10-minute time period. This is not a measure of processability—the test conditions give a shear rate that is magnitudes less than the shear rates seen in some processes, and plastic flow is shear rate sensitive. Under fixed shear rate conditions, the test is a crude indicator of molecular size. The larger the molecules, the more difficult it is for them to flow, and the smaller the output in the timed test. Suppose we test two materials, A and B. Material A has an average Melt Flow Index of 2, and Material B has an average of 5. Our conclusion is that the two materials are different, and that the molecules in Material A are larger than those in Material B (they do not flow as readily). For our purposes, we do not care what the actual size difference is—we only care that there is a difference. Note that this approach can provide us with a raw material-receiving inspection test if we care to use it.

We suppose now that we receive raw material A from our supplier, and it has a measured MFI (Melt Flow Index) of 2. We process this material into a product and then test the MFI of the product. It would not be unusual to find the MFI has increased to 5. If we process this material and measure the MFI of the resultant product, it would not be unusual to find that the MFI has increased again, perhaps to 8. The numbers are arbitrary, the concept is not. Every time material goes through the injection molding process, the average molecular size will be reduced. The magnitude of the reduction will be a function of the original molecule size and the shear rate created in the process. That shear rate is a linear function of injection speed and an inverse cubic function of gate size. (The smaller the gate, the much higher the shear rate.) While the physical properties of plastic products depend on molecular size, many products can tolerate 30% or so regrind content without an undue sacrifice in properties. By the same token, there are some products that cannot tolerate any regrind content; they need the best properties they can get. Others can tolerate 100% regrind content and still provide acceptable performance. Also, we must recognize that the uniform addition of regrind will improve processability—the material flows more readily. We must recognize that virtually all plastics have additives in the form of process and shelf life stabilizers. The only difference between a virgin material of a given MFI and a regrind with the same MFI will be in additive content. Some stabilizers will be consumed in going through the process. This gives rise to the reprocessor, who puts additive content back in regrind materials.

13.1 The Injection Molding Screw

If we were to visit a typical injection molding operation and talk with the production control people, it would not be unusual to hear "we always put this job in this press because it runs better there." Really! Plastic knows what machine it's in? Not likely! The only things plastic molecules can recognize during processing are as follows:

1. Temperature—how much energy they have,
2. Pressure—how crowded they are against their neighbors,
3. Flow rate—where they are in the actual flow profile, and,
4. Cooling rate—how fast their energy is taken from them.

One of the reasons that a given job may run better in a given machine is that the design of the screw in that machine is better suited to the material being processed.

We remember that modern injection molding technology is a direct offshoot of extrusion technology.

Extrusion people specify a screw in several ways (injection molding people almost always take the screw given by the machine manufacturer with no questions asked).

1. Length-to-diameter ratio or *L/D* ratio. This is the nominal length of the screw divided by the nominal diameter in consistent units. Thus 72 inches from the midpoint of where the feed hopper would be to the end of the screw divided by a nominal 3-inch diameter screw would give a 24/1 *L/D*. Many extruder screws today are in the 30/1 to 36/1 *L/D* range.

However, that the higher *L/D*s serve to provide additional pumping hold true which means more pounds per hour throughput. The barrier to productivity in injection molding is almost always the ability (or inability) to cool plastic very quickly (because of its poor thermal conductivity, even if the mold cooling system is well-designed). *L/D*s in the range of 24/1 are suitable for injection molding.

2. The helix angle of the screw thread. Commonly, this is set at 17.7 degrees, because (a) it is close to the optimum for conveying and pumping efficiency, and (b) it provides a pitch exactly equal to the diameter of the screw. Pitch refers to the distance between a point on the screw thread and the same point one revolution downstream. This is shown in Figure 13.13, where pitch = diameter ($P = D$). Thus, if the *L/D* is 24/1, there must be 24 diameters of length or 24 turns of screw thread.
3. The screw is divided into three geometric sections:
   1. The feed section is a solid conveyor characterized by a constant, relatively deep screw flight depth (refer to Figure 13.1).
   2. A compression section where work is done on the material and its pressure increases, characterized by a uniformly decreasing screw flight depth. We will refer to this section as a transition section to emphasize that the function is to convert plastic behavior from solid to fluid.
   3. The metering section which acts as a fluid pump and is characterized by a constant, relatively shallow flight depth.

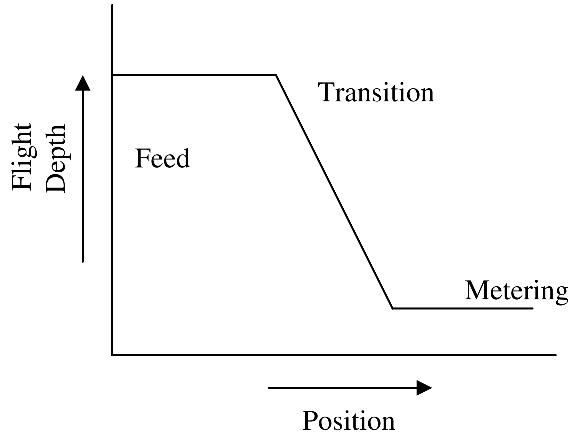


Figure 13.14 Flight depth vs position in a screw.

4. Compression ratio. A measure of the amount of work the screw is able to do. It is determined by the ratio of the feed section flight depth to the metering section flight depth. (Rigorously, it is the ratio of the volume of material contained in one turn of the feed section compared to the volume of material contained in one turn of the metering section, but most engineers simply use the linear ratio rather than go through the volume calculations.) A typical extrusion compression ratio is 4/1, but 3/1 is generally suitable for injection molding. (We must remember that extrusion is a continuous process, while injection molding is a batch process.)

These are shown in Figure 13.14.

(Note that the use of regrind requires a higher compression ratio to do the same amount of work that would be done using 100% virgin material. The bulk density of regrind will depend on the thickness of the product being ground as well as the screen size in the grinder.

However, it will always be lower than the bulk density of the original material. If the bulk density is reduced, the number of molecules contained in one turn of the screw flight will be reduced, thus reducing the amount of frictional heat generated.)

Now, if we have a conventional screw ($P = D$), and the screw has a 24/1 *L*/*D*, there must be 24 turns of screw flight (24 diameters = 24 pitches).

The question is "how many of the 24 turns should be allocated to the feed section, how many to the transition section, and how many to the metering section, or do we really care?" Well, we really care, and the allocation of turns will be a function of the material we plan to process in that machine.

A close look at extrusion industry practice will show the use of a "nylon screw" or a "polypropylene screw." This does not mean that these screws are made of nylon or polypropylene. It does mean that these screws are designed to process what we called "crystalline" materials—materials that have a melting point.

If we consider only thermoplastics, we process only two types of material: those that melt and those that do not melt. If we were to examine the arithmetic of screw design, we would find that longer metering sections improve pumping capability. This accounts for the high *L*/*D* ratios used in the extrusion industry. In many applications, profitability is based on throughput capacity. Higher throughput is generally not an advantage in injection molding. The problem molders have is cooling the existing throughput.

Screw configurations for these two types of materials are suggested below (assume 24/1 *L*/*D*, conventional helix):

	Crystalline	**Amorphous**
Number of turns feed	7–11	3–7
Transition	3–5	7–9
Metering*	10–12	10–12†
Total turns	24	24

*Except acetal, where shearing heat may cause unpleasant degradation, we must use a shorter metering section.

†Except PVC, where shear heat may cause undesirable degradation, we must use a shorter metering section.

Note that this is not to advocate new screws for one's molding machines. Rather, it is to advocate knowing the geometry of the screws one has and utilizing that geometry to one's advantage. When a screw is worn or damaged, it is time to be concerned with replacement screw geometry.

This discussion has been directed toward screws for thermoplastic materials. Screws for thermosetting materials will differ in that the compression ratio must be kept low—very close to 1/1. A 1.1/1compression ratio will be only marginally acceptable. It will generate enough heat in some materials that polymerization may take place in the barrel. This disrupts production because it requires removing the nozzle to purge the polymerized material.

14 Microcellular Injection Molding

Mark Berry
PPD Tech, 10 Buttonwood Rd, Bedford, NH 03110, USA

14.1 Introduction

Plastics have been produced as foams since their earliest development, with the objective of attaining the physical properties unique to foams, such as their thermal insulation properties and their inherent light weight. It was accepted that most mechanical properties, such as tensile strength would be significantly lower with the foamed version of a given material. More recently, microcellular foaming processes have been developed with the primary objectives of reducing material usage and increasing productivity with little or no loss in mechanical properties.

There is wide range of microcellular-foamed products now in every-day commercial use and the traditional perception of where foamed materials can be used to advantage has changed significantly over the past decade. Applications range from structural and mechanical components in printers, to automotive fan shrouds and precision electrical components. While weight reductions of 30−75% are common with microcellular extrusion, a different set of characteristics has supported the adoption of the microcellular injection molding processes. While weight reductions of 5−15% are common for engineering components, reduced cycle times (10−30%) and the reduction in molded-in stress and improved dimensional stability have also become important factors in the growth of the technology. The microcellular molding processes have also been combined with other technologies to yield unique results. For example, "core-back" molding adds the element of a controlled expansion and subsequent pressure drop in the cavity that promotes cell development and results in a high degree of foaming (Figure 14.1). When this method is used with fillers, such as a mineral or glass fiber, a low weight, high strength structural component is possible. Some automotive door panels are now made with this technique, such as on 2011 Mazda models, where the panel weight was reduced by 30% with equal or better strength [1]. Other processing methods have been combined with microcellular molding in attempts to minimize the inherent cosmetic issues associated with foam processing. These methods include gas counter pressure and rapid heat cycling.

While the focus of this chapter is on injection molding, microcellular extrusion is also briefly discussed—primarily in the context of the historical development of the technology. Common traits are discussed as well as how the two processes differ, relative to the most important processing parameters that apply to each version of the microcellular process.

Thermoplastic foams can be produced with chemical foaming agents (CFA) which release the foaming gas when the CFA decomposes at a given temperature or with physical foaming methods, which introduce the foaming agents directly into polymer melt stream. These physical foaming agents have also been called physical blowing agents (PBAs). While physical foaming methods have been used for some time, with a range of different gases, this chapter discusses

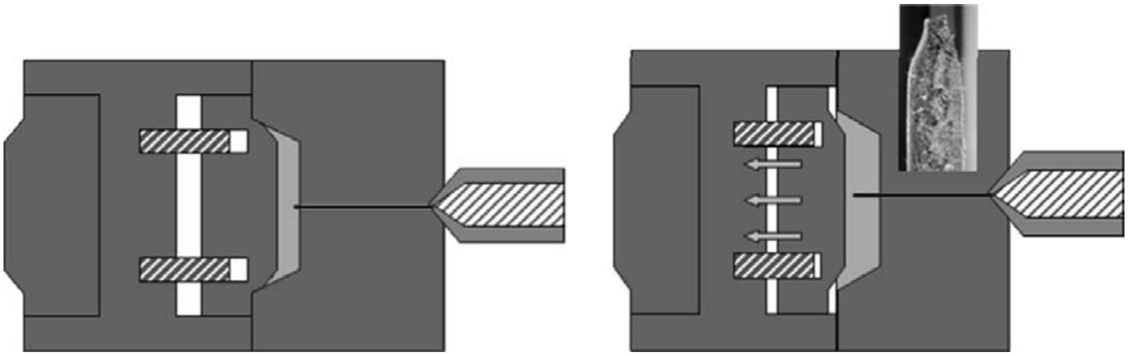


Figure 14.1 Core-back technology, which combines MuCell® process with a secondary expansion process. SCF laden plastic is injected with high pressure and minimal initial cell growth. The mold volume is then rapidly increased to initiate uniform cell growth.

the more recently developed microcellular processes based on the use of nitrogen (N_2) or carbon dioxide (CO_2), in the supercritical fluid (SCF) state, as the physical foaming agent. In this chapter, "PBA" will be used to describe non-SCF physical blowing (foaming) agents and "SCF" will be used to describe a physical foaming agent that is specifically used in the supercritical fluid state.

There have been several microcellular processing technologies developed and introduced since the mid 1990s. Most techniques follow the original work and theories developed at MIT [2]. Trexel, Inc. became the exclusive licensee of the original MIT patents and their MuCell® process was the first commercial technology introduced, based on the MIT work. The MuCell® process has experienced the most commercial success to date and therefore more information is available from users of that process. However, other microcellular foaming processes based on the use of SCF are also discussed. The precise definition of the term "microcellular" has varied some, with earlier research targeting cell sizes of 5–20 microns. In industry, the standard for "microcellular" cell size has generally been accepted as a cell structure with cells less than 100 microns in size.

14.2 Background

The current microcellular processing technologies started with work done at MIT, associated with the MIT-Industry Polymer Processing Program. Initiated by a request by Eastman Kodak, the original work pursued the objective of developing a process which could reduce material usage without loss of properties and maintain or improve manufacturing efficiency [3]. It was felt that if foam was developed with an extremely small cell size and a very uniform distribution, there should be very little loss in mechanical properties. Dr Nam Suh's group developed the original theories which were built on the core concepts of

- Producing a single phase solution of the physical blowing agent and the polymer.
- Developing an extremely large number of cell nucleation sites, distributed evenly throughout the plastics.

The technique that was developed was based on mixing an inert gas, which has been pressurized into the SCF state (Figure 14.2), into a single phase solution with the polymer. The SCF state provides the fluid with increased diffusivity and solubility. After the SCF is in solution a rapid pressure drop is caused, which yields many nucleation sites, each of which attracts gas molecules. Cells grow as gas molecules migrate to the nucleation sites. Cells stop growing when the polymer cools enough that its melt strength stops further expansion. Excess gas leaves the polymer over a few hours, leaving the base polymer unchanged. The steps of these mechanisms are illustrated in Figure 14.3. This method produced foams with cell sizes in the 5–10 micron size range.

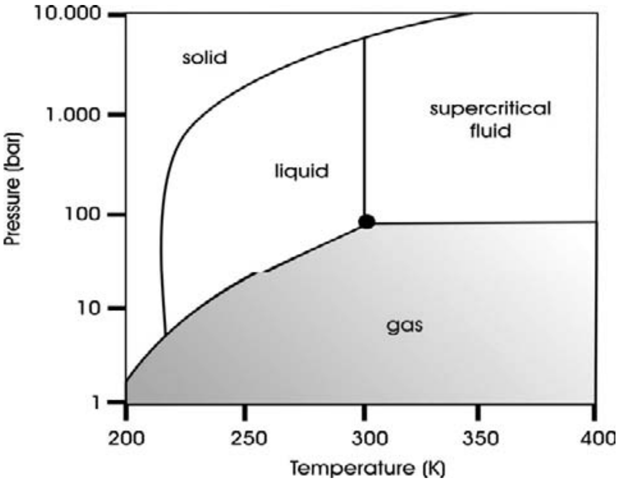
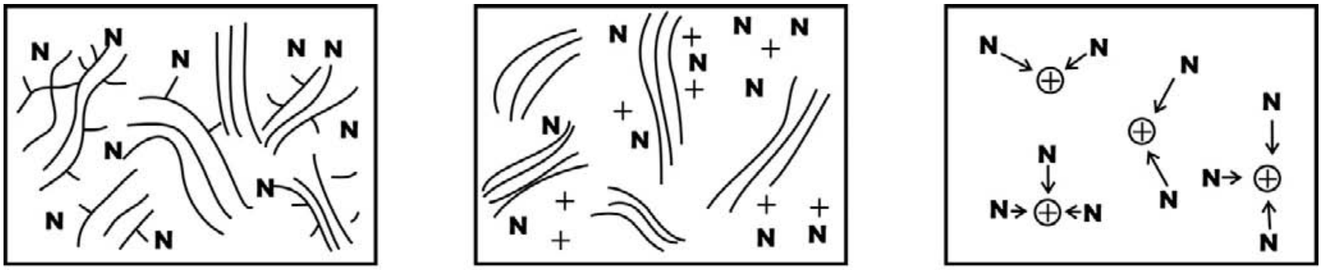


Figure 14.2 Carbon dioxide pressure–temperature phase diagram. In the supercritical fluid region, the CO_2 becomes denser than gas and can approach the density of the liquid CO_2. At the higher densities, the solubility of the CO_2 increases significantly as well.

Dr Suh's group first developed a batch process and then by 1989 was working on a continuous process. With the batch process, dissolution of the SCF into the polymer occurred over an extended period of time in a pressurized vessel and the rapid pressure drop was accomplished with the quick and complete release of the pressure.

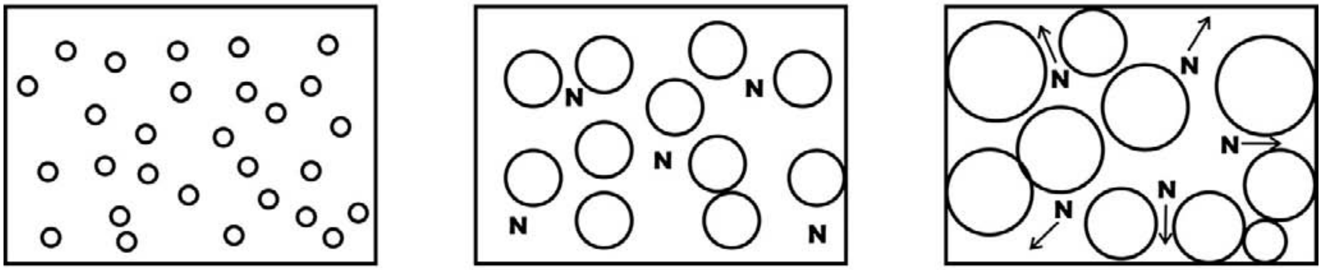
Of course, continuous processes have a more complex situation relative to mixing the materials into solution and with developing the required rapid pressure drop. The dissolution of the SCF into the polymer must occur in a matter of seconds. This necessitates physical mixing of some kind. The rapid pressure drop, necessary for a large number of nucleation sites must also occur in a controlled manner. Nucleation and the subsequent onset of cell growth should first occur at the die lips for an extruder and as close as possible to the mold cavity for injection molding. Trexel, Inc. was formed to commercialize these microcellular concepts with the processing equipment and technology capable of a controllable industrial process. The first MIT patent was issued in 1984. Seven US Patents and four International patents followed over the next 8 years (see Appendix). With exclusive rights to MIT patents Trexel named the technology "MuCell®" and originally targeted extrusion, with a business model based on exclusive licensing and co-development projects. The extrusion side of Trexel's business was acquired by Zotefoams plc, in March 2011 and is operating as MuCell Extrusions, Inc. Injection molding capability was added in 1998, with initial target applications being technical parts with wall thickness less than 4 mm. Trexel has been granted many US and International Patents related to the technology and equipment (see Appendix).



1. SCF Mixed with polymer

2. Nucleation

3. Migration of SCF to sites



4. Cells grow, adding Nitrogen

5. Cell growth stops when melt strength increases enough to prevent further growth

6. Excess SCF molecules migrate to atmosphere

Figure 14.3 After dissolution of the SCF the rapid pressure drop yields nucleation sites, which attracts gas molecules. Cells grow as gas molecules migrate to the nucleation sites. Cells stop growing when the polymer cools. Excess gas leaves the polymer.

14.3 General Discussion of Foam Processing

As noted, plastics foam processing has existed practically from the beginning of plastics processing. CFAs have long been used as the source of the foaming gases, with the foaming agent mixed with the material, typically at the hopper. As the material moves forward in the barrel, the temperature rises, eventually reaching the decomposition temperature of the CFA, where one of the byproducts is the desired gas (N_2 or CO_2). There are several different chemicals used, with selection based on gas choice and the degradation temperature required. The thermal decomposition can be exothermic, typically yielding N_2 or endothermic, yielding CO_2. Azodicarbonamide is a commonly used exothermic CFA. There are many endothermic CFAs including sodium bicarbonate. Nucleating agents are also added to facilitate the development of cells. While foaming is accomplished, this type of process tends to produce a heterogeneous nucleation with a limited number of sites. Cell sizes typically range from 250 microns to 1 mm in size [3]. The major advantage of CFA-based foaming is the lower equipment costs required. The major disadvantages are the larger and non-uniform small cell sizes, the typically higher cost over the longer term and the residual chemical byproducts that remain in the product. The latter issue of residual chemicals is a major reason care should be taken in the selection of a CFA, in that there can be compatibility issues related to the interaction of the residual chemicals with the polymer or with the additive packages typically used with plastics. Over the years many CFAs have been developed in attempts to add a wider selection of operating temperature ranges and a more controllable release of the gas as well as compatibility with the many different types of plastics. CFAs have been used to provide foamed parts with conventional injection molding machines, typically, with no other machine modifications other than the addition of a shut-off nozzle, or perhaps with the use of valve-gated mold. Sometimes a very small amount of CFA is added to minimize or eliminate a sink mark.

Physical foaming generally refers to processes which supply the physical foaming agent directly to the polymer. The fluids that are used have been called PBAs and these would include the chlorofluorocarbons originally used with urethanes. Environmental concerns resulted in the phasing out of CFCs to be replaced with other hydrocarbons such as HCFCs and Pentane. This chapter does not discuss these materials or processes, but rather focuses on physical foaming with the inert gases nitrogen (N_2) and carbon dioxide (CO_2) as applied to the thermoplastic extrusion and injection molding processes.

Structural foam injection molding has relied on CFAs as well as direct addition of the PBA, usually N_2 or CO_2. Historically, structural foam molding was most used in large, thick-walled products, with the major objective of reducing material usage. Cell sizes tend to have a wide range including very large cells, particularly in very thick sections. Some systems add the PBA directly to the barrel and may utilize an accumulator or a separate injection plunger [4].

There are some common traits of all foam injection molding, including structural foam molding and microcellular molding. The most important common trait may be that all of the processes are "short-shot" processes. With standard solid injection molding, the cavity is filled nearly completely with the screw movement under "velocity control." At some point, just short of compete fill, the screw movement control is switched to pressure-based control. This is done because the material has already started to shrink and material must be forced into the cavity to compensate for this shrinkage. This last bit of filling requires a fairly high pressure to keep the material moving and to "pack" out the cavity with material. With foam molding, this last bit of filling is accomplished with the growing cells, rather than the "packing" of more plastic through the gate. This is the primary reason that foam injection molded parts have much lower molded-in stress and fewer stress-related issues such as part warpage.

Another common trait of all foam molding is that addition of the foaming agent, e.g., N_2 or CO_2, also reduces the melt viscosity of the polymer. The degree of this effect depends on the specific polymer and foaming agent and also the amount of the agent. For instance CO_2 can reduce the melt viscosity of an amorphous polymer such as polycarbonate by more than 25%. The viscosity reduction for a semi-crystalline polymer such as PA6, with a well-defined Tm, would typically be less.

14.4 General Discussion of Microcellular Processing

Both microcellular extrusion and injection molding have a common process parameter that is quite different from the standard processes. That variable process parameter is "% SCF," which is the amount of physical foaming agent (N_2 or CO_2) in solution in the melt, typically measured as a percentage based on mass. Typical ranges for injection molding are from 0.75 to 2% for N_2 SCF and from 2 to 4% for CO_2. Higher SCF levels result in greater reductions in melt viscosity as well as smaller and more uniform cell sizes. It is also true that if a molded part or the mold is not properly designed that higher SCF levels could lead to processing issues and a loss of mechanical properties. The areas of concern are very thick sections in the part and poorly cooled areas in the mold, both of which can lead to very large cells which affect product properties.

While virtually every thermoplastic material can be foamed, the specific characteristics that can be attained with microcellular processing (extrusion or injection molding) are very much dependent on the type of material, type of SCF, and the product design.

Different types of polymers, such as amorphous materials and semi-crystalline materials behave very differently in foaming processes. The addition of fillers or additives also has a significant effect on how a material foams. Fillers appear to increase the number of nucleation sites, which has a major impact on the number of cells that form and their sizes. Each type of filler affects nucleation differently, with fiber reinforcements such as glass fiber increasing the number of nucleation sites significantly and particulate fillers such as mineral fillers increasing nucleation sites to a lesser degree. Additives such as impact modifiers also affect the microcellular processes and can present challenges maintaining a small cell size, since these additives tend to reduce the melt strength of the polymer. The exact combination of SCF and polymer is very important with both processes and sometimes the choice of SCF is determined as much by the specific process goals as it is by any affinity between a specific SCF and type of polymer. CO_2, which is more commonly used with olefins, also is the most soluble in most polymers. Since more CO_2 can be dissolved in the polymers it can be used to provide a greater reduction in melt viscosity. Therefore if a particular process could benefit the most from viscosity reduction, say with a very thin-walled product, CO_2 may be chosen as the SCF. N_2 which is most often used with engineering polymers would typically be specified if attaining the maximum level of foaming is the highest priority.

The melt strength of the cooling polymer melt is a critical factor for both processes. The cells have a very short time to nucleate and grow, and the polymer must have melt strength low enough to allow the cell to grow and high enough to prevent failure of cell walls that would result in many cells combining into large voids. The melt strength should ideally increase quickly as the foaming polymer cools, so as to limit the cell size to the smaller sizes associated with minimum property loss. Based on the above it should be clear that process cooling is a critical factor for both extrusion and molding. With any extrusion process, post-die cooling rates are the critical factor determining output. With microcellular extrusion, the cooling rates also greatly affect the type of cell structure and product quality that is attained. With microcellular injection molding, cooling has the same effect on cells and quality. If the part or mold is not designed for good cooling, at the very least the cycle time may be affected significantly. With the worst case, would be the inability to effectively mold the part at all, without fracture of the part or the runner at ejection from the mold.

With microcellular extrusion, management of the pressure drop is a major focus in process development and die design. There is a significant pressure drop as the melt exits the extrusion die and experiences atmospheric pressure. Ideally nucleation first occurs at that point and the cells grow for a brief period of time before the melt cools enough to result in enough melt strength to prevent further cell expansion. While the standard process parameters such as melt temperature, output, and cooling rates are important, die design plays a major role in controlling the pressure drop that the molten plastic experiences as it passes from the barrel into and through the die. This pressure drop determines where cell nucleation occurs, which subsequently controls the number of the cells and the cell sizes attained, which combine to determine material properties and the amount of weight reduction achieved. Die design guidelines used by microcellular extruders are typically closely held information. The parameters that affect pressure drop and subsequently the cell nucleation rates in injection molding are also complex but the important design parameters are more commonly known and available to users.

14.5 General Discussion of Microcellular Injection Molding

As discussed previously, the major objective of the physical foaming equipment and methods is to dose the SCF foaming agent into the polymer melt and mix the two components into a single phase solution prior to injection into the mold. With the onset of injection of the polymer/SCF solution into the mold, the microcellular molding process is not significantly different from standard (solid or compact) injection molding. However, the major process parameters will be modified to reach specific foaming objectives. For instance, as noted previously, foam molding is typically a short shot process. Injection is typically stopped at 90−95% of the stroke that would have applied to the same part if produced with standard molding. Injection Hold (Pack) times are typically very short, just long enough to ensure maintenance of a uniform screw position. With the solid molding process, the screw would continue to move forward for several seconds under pressure-based control, packing the cavity with additional material. The final filling of the cavity with the microcellular process is accomplished by cell growth rather than packing by the screw (ram). The pressure-based "hold time" for microcellular molding will typically be 0.5−1.0 second, just long enough to stabilize the screw position prior to the next screw recovery cycle.

As with microcellular extrusion, the standard injection molding process parameters such as melt temperature and cooling temperatures also affect the cell sizes and the level of weight reduction achieved as well as the other typical characteristics, such as shrinkage. The fill rates and pressure levels that develop in the injection process have an additional major effect on microcellular molded parts as compared to standard molding in that they affect the cell structure. As described in the original research, the rate of pressure drop and subsequently the number of nucleation sites will determine how many cells are formed and how uniform they will be.

With injection molding, the nucleation process can be complex, necessitating attention to material flow all the way from the screw tip to the end of fill in each cavity. At the start of injection, the shut-off nozzle is simultaneously opened and material exits the high pressure area (within the nozzle) and immediately experiences atmospheric pressure (~1 bar) as the material starts to travel into the sprue. This pressure drop will initiate nucleation and cells will start to grow as the material flows. As the sprue and runner(s) fill, pressure rises and at some point nucleation and cell development are both greatly slowed or stopped. The majority of cell nucleation and growth occurs as the molten plastic passes through the gate restriction into the cavity, experiencing a significant pressure drop as well as shear. From the above discussion it should be clear why valve-gated hot runner systems which deliver the high pressure melt directly to the cavity provide the best situation relative to control of cell growth and cell size distribution.

14.6 Process Monitoring and Control Methods for Microcellular Injection Molding

Cavity pressure has become well accepted as the basis of a process monitoring or control strategy for solid injection molding [5] and the use of in-mold temperature sensors has also gained acceptance, with the primary objective of sensing the melt front and to time the filling of the cavity [6]. Each type of sensor has been used successfully to both monitor process consistency and as a signal for switch over from velocity to pressure-controlled filling. If used for switch over control, the correct location of either type of sensor in the cavity is very important. With microcellular injection molding, the cavity filling and packing characteristics are quite different than standard injection molding with the biggest difference being that cavity pressures are significantly lower since the process is essentially a "short-shot" process, with the final filling and packing phases being provided by cell growth rather than by movement of the injection ram (Figure 14.4). With the very low pressures near the end of fill (Figure 14.5), there would be concern that while monitoring the cavity pressure may indicate a consistent process it may not be effective as a control of the switch over point.

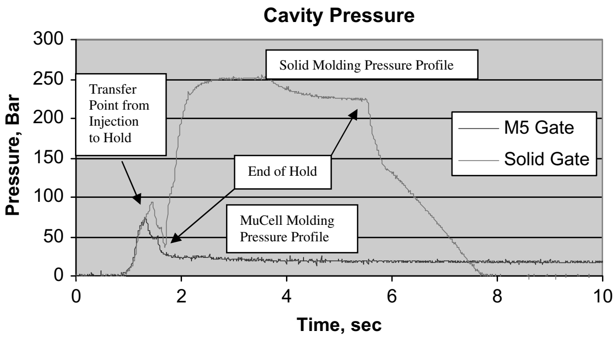


Figure 14.4 Cavity pressure plots (9) for the same part molded in solid PA6 with 30% glass fiber and also with microcellular (MuCell) process. Pressure transducer was located behind ejector pin near the gate.

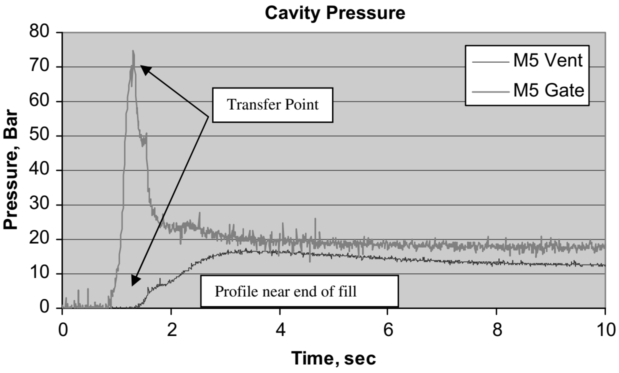


Figure 14.5 Cavity pressure profiles of solid molded part near gate and near end of fill.

Melt temperature and fill rates have been demonstrated to be very important process variable for microcellular injection molding. Recent work has studied the use of fast response thermocouples along with traditional pressure transducers to determine their effectiveness in providing practical process monitoring tools for the microcellular molding process [7]. Behind the ejector pin pressure transducers and fast response exposed thermocouples were located near the gate and also at the end of fill for a commercial two cavity drill handle mold, running PA6 with 30% glass fiber. Melt pressure and melt temperature profiles were collected as well as the time to reach peak pressure and melt temperature. The objective was to determine if these types of sensor have the potential to be used to:

1) indicate a steady state process
2) predict product quality (part weight and dimensions)

It was determined in this case that both in-cavity (behind ejector pin) pressure transducers and temperature sensors can be utilized to monitor microcellular injection molding and should be able to be developed as a basis of a process control model. For the pressure transducer, the gate location appeared to track part weight and dimensions more closely than at the end of fill, across the range of process changes.

The "time to peak temperature" values from the end of fill location tracked part weight and dimensions better than the peak temperature value itself. Therefore, the end of fill location appears to provide the most effective location for this type of temperature sensor and the variable "time to peak temperature" appears to be more predictive of changes in part characteristics than the actual melt temperature value.

The peak temperature vs. time to peak temperature scatter plot appeared to provide a unique process characterization for each set of process conditions which could define a process window. The peak melt temperature near the end of fill, which indicates the arrival of the melt front to that location, should provide an effective basis for controlling the switch over point (Figure 14.6).

For both types of sensors, there was less correlation to part weights and dimensions at the highest SCF level, indicating that a complete control strategy should include the monitoring and control of the process variables that affect the amount of SCF delivered to the molding machine. In the case of MuCell® processing, this would be % SCF, controlled by SCF flow rate, SCF dosing time, and SCF pressure drop, as it enters the barrel.

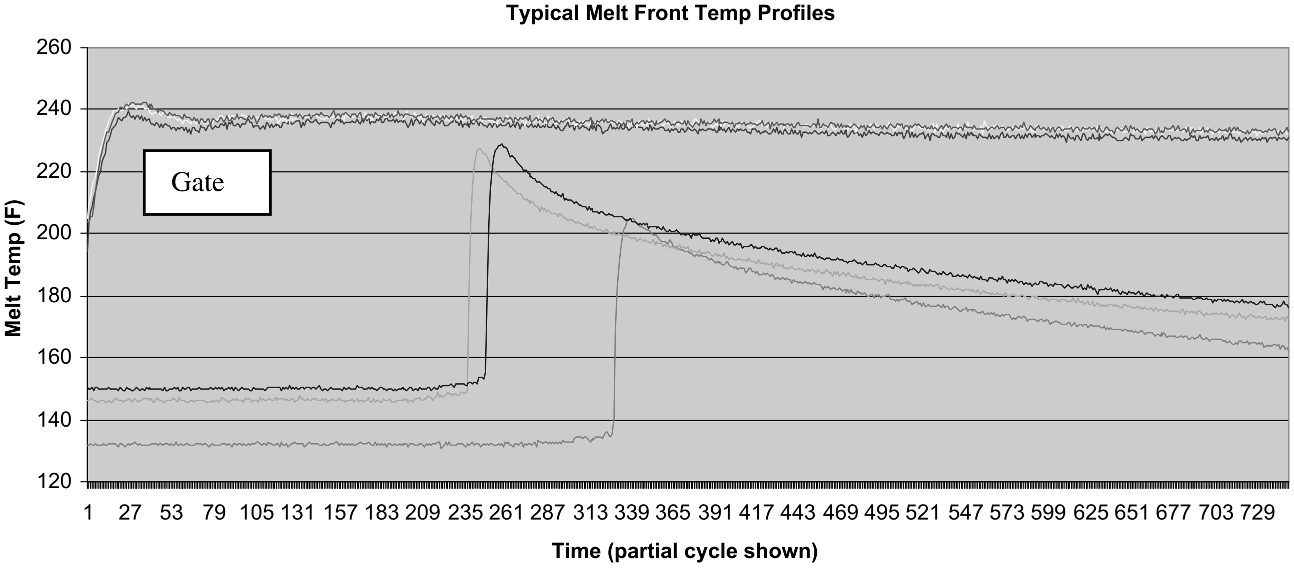


Figure 14.6 Peak temperature profiles at gate and near end of fill for three sets of MuCell process conditions. The "time to peak temperature" changes with process conditions and should provide a reliable trigger for switchover from velocity control to pressure controlled hold time.

14.7 Equipment Requirements for Microcellular Foam Injection Molding

Physical foaming processes for microcellular products, are typically based on the inert gas, (N_2 or CO_2) first being pressurized to the SCF state. Then the SCF is introduced directly into the barrel of the extruder or injection molding machine at a point where the plastic material is already melted. The amount of SCF that is used in a given process is dependent on the type of polymer, type of SCF, and the desired results. Therefore, any system must have adequate control systems to deliver a precise amount of SCF consistently over an extended run and from run to run. This can be accomplished by controlling flow rate and dosing time or by managing the mass of the SCF delivered to the barrel in each dose of SCF.

It is necessary to keep the gas in the SCF state from that point on, as the SCF is mixed into a single phase solution with the polymer. Therefore, the screw, barrel, and nozzle must be designed to maintain that elevated pressure level in the mixing area during the entire process. While extrusion screws use flight design to maintain the pressure, injection molding screws typically will have a second check ring located on the screw to establish a high pressure zone in the front portion of the screw. The main difference between the operation of extrusion screws and injection molding screws is that the extrusion screw rotates at a fixed position. A reciprocating injection molding screw moves back during rotation, thus linear movement driven by the plastic pellets moving forward in the screw flights. With SCF pressures at 100−200 bar, as the pressurized SCF/plastic single phase solution would migrate backward toward the hopper unless it is physically prevented from doing so. The center check ring or similar check device prevents this backward migration. With standard solid molding there is some back pressure typically applied to the screw during screw rotation, with typical pressure levels of 10−15 bar. With the SCF in solution, as the plastic melt passes through the front check ring and deposits in front of the screw tip, the screw would be driven backward from the pressure exerted on the screw tip by the single phase solution unless additional measures are taken. The screw position must also be maintained when the screw rotation stops, waiting for the next injection cycle. The screw position can be maintained by applying a constant hydraulic back pressure, typically in the range of 70−200 bar or with electric machines, by using screw position control functions.

14.8 Trexel's MuCell® Technology

With the MuCell® injection molding process, the SCF is dosed during screw recovery (rotation in preparation of the next shot). The SCF is delivered from one of several types of systems. The original and most commonly used system brings the gas pressure up to SCF pressure levels by utilizing two pumps. The SCF is then delivered to the barrel through an injector via a manifold system (Figure 14.7) that monitors the pressure in the barrel and the SCF pressure. To maintain a precise amount of SCF for every shot, the mass flow rate, dosing time, and the pressure drop are controlled.

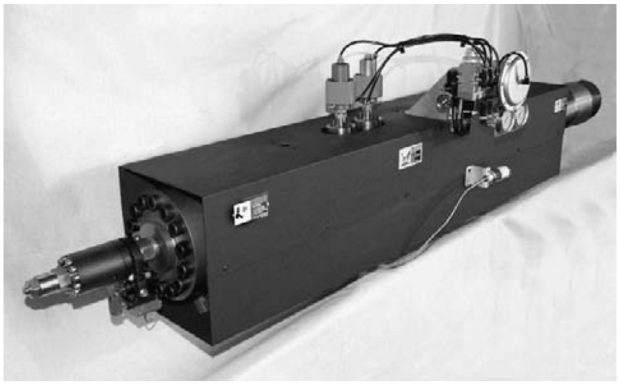


Figure 14.7 Trexel's MuCell SCF delivery manifold and SCF injector, shown on a MuCell modular (retrofit) barrel and screw assembly. Note shut-off nozzle.

The SCF is dosed into a specific area where the screw is specially designed to introduce and mix the SCF into the molten polymer with screw rotation (Figure 14.8).

In the time between the screw recovery phase and the start of injection, a constant back pressure is maintained on the screw, to maintain the singe phase solution. This is accomplished by adding a constant hydraulic pressure during the screw's idle time or relying on the position control function with electric machines to counter the pressure being applied to the screw tip by the gas laden polymer. A shut-off nozzle is used to prevent the pressurized material from drooling from the nozzle

14.9 Other Physical Foaming Techniques

- Sulzer Optifoam

The Optifoam process is developed by the Institute of Plastics Processing (IKV) in Aachen, Germany. The technology, which is available for injection molding [8] and extrusion [9], introduces the SCF into polymer at the nozzle. For extrusion, this occurs constantly and with injection molding, the SCF is delivered during the injection stroke. The Optifoam nozzle delivers the SCF to the passing polymer via a sintered metal coaxial device (Figure 14.9). The polymer/SCF mixture is then mixed downstream in a static mixer on its way to the die or the mold.

- ErgoCell system from Demag

Demag introduced microcellular technology in 2001 which was also based on adding the SCF to the melt downstream from

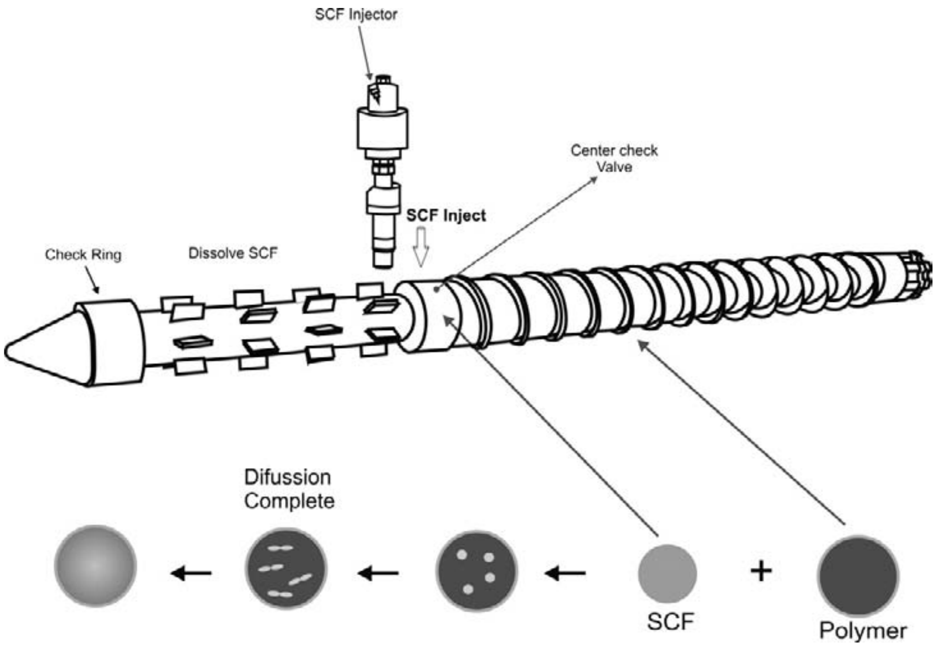


Figure 14.8 General layout of the MuCell screw, showing location of the SCF injector, middle check valve and the mixing area. The metering area, directly below the injector actually has a different (proprietary) screw flight design than shown, as it is designed to “wipe” SCF from the injector and advance it forward into the mixing zone.

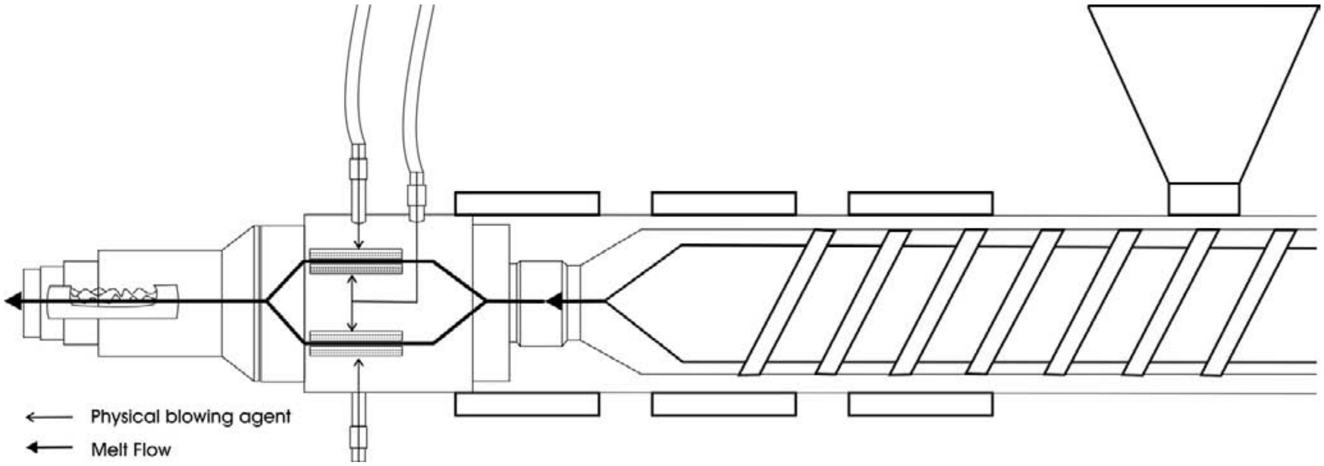


Figure 14.9 Sulzer OptiFoam nozzle delivers the SCF to the passing polymer via a sintered metal coaxial device. The polymer/SCF mixture is then mixed downstream in a static mixer on its way to the die or the mold.

the screw. A module is attached to the front of the screw which meters and mixes the SCF and polymer between the barrel and the nozzle. The mixer is driven by screw rotation during the plasticizing step, with the SCF being metered and mixed in the module at this time. While special licensing agreements were established to ensure non-infringement with Trexel’s patents, it is not clear to the author that the technology is still being offered by Demag since its merger with Sumitomo.

- ProFoam (IKV—in development)

IKV has published technical papers [10]describing an alternative approach to microcellular molding that does not require the foaming agent (N_2 or CO_2) to be in the supercritical state. Rather than dose the blowing agent into melted plastic in the barrel or in front of the barrel, under high pressure, the profoam process introduces the gas to plastic pellets before they enter the barrel of the molding machine. This approach is similar to typical bead foaming processes where the blowing agent is diffused into the plastic pellets over an extended period of time—perhaps 12 or more hours.

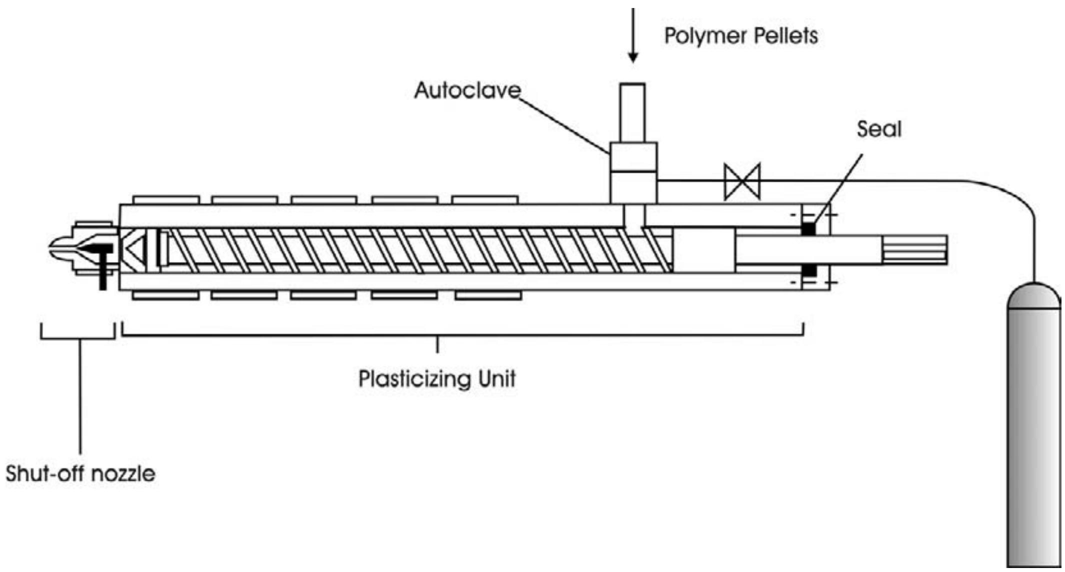


Figure 14.10 IKV ProFoam plasticizing unit. This approach, in development, utilizes an autoclave above the feed throat of the molding machine. The screw and barrel are sealed to allow the pressurized plastic/gas mix to remain in solution while being melted.

Of course with injection molding the absorption of the gas must occur much more quickly and this is the focus of their current work. Their approach is to install an autoclave above the feed throat of the molding machine and to use temperature and pressure to manage the rate of absorption and control the amount of blowing agent that is added. The screw and barrel are sealed to allow the pressurized plastic/gas mix to remain in solution while being melted (Figure 14.10).

14.10 Typical Objectives of Microcellular Injection Molding

- Weight reduction

Weight reductions of 3—15% are typical, with the exact amount that is attained dependent on the materials, product design, and mold design. The primary controlling material variables are type (amorphous vs. semi-crystalline, filler, or additives) and % SCF. The most important product design factors are thickness and factors that affect flow length. The longer the flow, the less weight reduction is possible. The most important mold design factors are venting and gate location. Inadequate venting cannot only trap the usual volatiles and the excess gas in the melt front, it could also result in the need for higher pressures to overcome the resistance to filling. This would have an impact on cell growth and the weight reductions that can be achieved. The gate size will affect pressures, shear, and flow rates all of which can affect the cell structure. The gate location is important for several key reasons. First, it will determine the flow length that is required to fill the part and this has a major impact on how much weight can be reduced. Second, it is best to avoid flowing from a thick section into a thin section, since the final filling occurs with cell growth and this is more easily controlled when flowing from thin to thick sections.

- Cycle time reduction

Cycle time reductions of 5—30% are typical, with the major contributors being the reduced weight and the minimized hold times (0.5—1.0 second typical). The primary controlling variables are part design and mold cooling. The design rules for optimizing cycle times follow the guidelines for standard solid molding. The most common issues limiting cycle time reduction are excessively thick areas and poor mold cooling in those areas.

- Less molded-in stress

The reduced viscosity, lower injection pressures, and the minimized hold times all contribute to a much lower amount of molded in-stress. This usually leads to reduced warpage and improved dimensional stability. It should be noted however, that if the root cause of warpage is fiber orientation, the reduced stress will not improve this warpage.

- More uniform shrinkage

While a thorough analysis is beyond the scope of this chapter, it has been demonstrated that the shrinkage of an injection molded microcellular part will be slightly different. There are several factors that affect the change.

Perhaps the greatest factor is the significant reduction in injection pressure. A highly packed molded part is ejected with a given set of dimensions, "frozen" into a position, exhibiting a specific shrinkage on the low side of the published range, but actually is quite highly stressed to exhibit that shrinkage. With exposure to heat, that part may experience stress relief and actually shrink more, with the final shrinkage more toward the middle or high part of the published range for that material. The same part, molded as a microcellular product will typically start out shrinking more close to the final shrinkage value. However, there are many factors involved in determining shrinkage, including the amount of cell growth and the types of fillers. It is suggested that prototype testing with the specific material/filler and weight reduction levels should be done prior to molding any new design.

14.11 Limitations of Microcellular Injection Molding

While there are ongoing improvements in these areas, the following summarizes the general limitations of microcellular processing.

- Cosmetic concerns
  - Splayed surfaces
  - Transparent parts not possible
- Some property loss
  - Roughly proportional to weight loss

Other considerations

- New process parameters to consider:
  - Gas levels
  - Back pressure
  - Minimum hold times
- Mold modifications:
  - More venting typically needed
  - Possibly more cooling
- Equipment costs

14.12 Best Target Applications

- Target wall thickness, less than 4 mm
- Filled semi-crystalline materials, such as PA66 with X % glass fiber or filled PBT
- Filled amorphous materials, such as polycarbonate or polystyrene
- Unfilled semi-crystalline materials, such as PA, PBT, PET, POM
- High heat materials such as PEI, PEEK, PES
- Thin-walled packaging in polypropylene
- Filled PP, such as Talc-filled PP copolymer.

14.13 More Challenging Situations

- Unfilled amorphous materials with rubber additives present more of a challenge to get maximum expected benefits. There has been significant work and improvements in this area for automotive applications, with a focus on material developments to better accommodate the foaming process.
- Very thick parts; Parts with wall thicknesses greater than 6 mm have been developed successfully, but cycle time reductions are typically not attained.
- Class A glossy surfaces are not yet attainable. Development work continues in many areas, attempting to solve this problem.
- Polyethylene does not appear to work well with microcellular molding.
- Liquid crystal polymers do not appear to be compatible with this type of foaming
- Parts with existing molds which are poorly cooled with "hot spots"; areas that never really cool down during normal molding cycles.

14.14 Commercial Examples

- **Automotive**
  - ○ Under the hood components in filled engineering materials
    - ■ Fan shrouds, radiator parts, air flow meter
  - ○ HVAC components in Talc-filled PP
    - ■ Housings, flapper doors
  - ○ Door lock mechanisms, PA6 with GF, POM, and filled PP
  - Interior: Door trim (talc-filled PP) with vinyl overmold, trunk liners
- Business machines
  - ○ Printer platens and paper guides (filled PPE, filled PC), ink cartridges (PET with GF), plotter housings (filled PPE), printer carriages
- Other
  - ○ Thin-walled packaging (PP)
  - ○ Electrical enclosures
  - ○ Power tool components.

14.15 Future Trends

As with most new technologies, it is anticipated that costs for equipment will continue to fall over time, with new developments such as the integration of gas delivery and control system into molding machine, where common control systems can be utilized. Materials such as Rhodia's and BASF's PA6 and PA66 have already been offered that are designed to improve cosmetics for microcellular-foamed parts. This trend is expected to continue. It is also expected that other techniques such as rapid heat cycling, gas counter pressure, and mold surface treatments, that address the inherent cosmetic challenges with foamed plastics will continue to be developed and applied.

Microcellular foaming of materials with long glass fiber reinforcement has also been introduced and successfully applied to structural components and this is certainly an area that should see growth in the future. Other combined technical solutions that utilize microcellular molding are also in their nascent stages, such as Engel's Dolphin technology for soft touch car instrument panels. This equipment- and materials-based technology molds a rigid base and then over-molds a soft microcellular-foamed TPE layer onto the base. "Core back" mold movement is used to increase the soft foamed layer from 2 mm to 6 mm thick.

The author anticipates steady growth for microcellular injection molding in the automotive area as weight and environmental concerns become even more important drivers in new product design. The same concerns also will affect design choices in other areas such as thin-walled packaging which will likely result in consideration of microcellular molding technology.

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Appendix

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U.S. Patent No. 5, 158, 986, issued 10/27/92 entitled "Microcellular Thermoplastic Foamed with Supercritical Fluid," by Sung W. Cha, Nam P. Suh, Daniel F. Baldwin, Chul B. Park.

U.S. Patent No. 5, 866, 053, issued 02/02/99, entitled "A Method for Providing Continuous Processing of Microcellular and Supermicrocellular Foamed Materials," by Chul B. Park, Nam P. Suh, Daniel F. Baldwin.

U.S. Patent No. 6, 051, 174, issued 04/18/00, entitled "A Method for Providing Continuous Processing of Microcellular and Supermicrocellular Foamed Materials," by Chul B. Park, Nam P. Suh, Daniel F. Baldwin.

Sampling of Related Trexel Patents (US Only)

U.S. Patent No. 6, 294, 115, issued 09/25/01, entitled "Microcellular Articles and Methods of Their Production," by Kent Blizard, Kelvin T. Okamoto, Jere R. Anderson.

U.S. Patent No. 6, 593, 384, issued 7/15/03, entitled "Polymer Foam Processing with Low Blowing Agent Levels," by Jere R. Anderson, Kelvin T. Okamoto, Kent G. Blizard.

U.S. Patent No. 6, 602, 063, issued 8/5/03, entitled "Discontinuous Blowing Agent Injection Pump for Polymer Processing," by inventor Juan Cardona.

U.S. Patent No. 6, 616, 434 issued 09/09/03, entitled "Blowing Agent Metering System and Method," by Theodore A. Burnham, Jeffrey L. Ng.

U.S. Patent No. 6, 659, 757 issued 12/09/03, entitled "Valve for Injection Molding," by Roland Y. Kim, Theodore A. Burnham.

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Sampling of Related US Patents

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15 Extrusion Processes

Eldridge M. Mount, III
EMMOUNT Technologies, LLC, 4329 Emerald Hill Circle, Canandaigua, NY 14424, USA

15.1 Introduction

Extrusion is widely used for the continuous and intermittent manufacture of polymeric products because it permits the preparation of highly uniform polymer melts at high rates [1,4–7]. This is necessary because the low thermal conductivity and high viscosity of polymers prevent the easy and high rate melting in bulk containers using external heat sources (i.e., melting in a stirred tank or bucket). If polymers are placed in a tank or bucket and heated, the outer portions melt and remain hot, while the inner portions remain cool. This results in large temperature gradients in the bucket of polymer and long heating times resulting in poor temperature homogenization and degradation of the outer portions, while the inner portions slowly heat and melt. Rather, polymers are efficiently melted by the viscous dissipation of mechanical energy in a device called an extruder. The use of an extruder allows the rapid melting of the polymer in a thin film of melt, which is continuously removed exposing fresh solid for melting [1,4–8]. In addition, the extruder feeds the solid polymer into the extruder and pumps the molten polymer out for use in subsequent manufacturing processes. In this context, the extruder becomes a unit operation in the polymer-processing industry. It is the primary device used to produce molten polymers at high rates necessary for efficient and inexpensive molten polymer production.

There are two broad categories of extruders: single-screw and twin-screw extruders. The single-screw extruder has existed for many years and still today it is the primary form of extruder, due to the ease of production and lower equipment costs, as well as its ability to handle high torques during polymer processing. Twin-screw extruders were primarily used for polymer powder extrusion and compounding, where high-quality dispersive mixing or well-defined residence times for devolatization, temperature-sensitive polymers, and reactive extrusion (polymerization and polymer modifications). However, the twin-screw technology has continued to evolve and today the torque capabilities of twin-screw extruders have been considerably increased and they are now used for high-capacity applications such as biaxially oriented polypropylene and polyester films.

For the twin-screw extruder, there are also several distinct subcategories with non-intermeshing and fully intermeshing twin-screw technologies. Further, the twin-screw extruders can have both the screws either co-rotating or counter-rotating. In single-screw extruders, multiple extruder combinations, termed tandem extruders, have been developed to separate the solids conveying and melting from the melt pumping functions. In a tandem extrusion system, one extruder feeds and melts the polymer and then transfers the melt to a second, generally larger diameter, extruder, which conditions and pumps the molten polymer to the next step in the process. Tandem extrusion systems become economically better than a single extruder as the processing rate begins to exceed 2500 kg/h where large-diameter (*D*) >250 mm and longer-length (*L*), and >36 length to diameter (*L*/*D*) ratio single-screw extruders would be required. In this instance, two smaller-diameter and shorter *L*/*D* extruders can be used in place of one large diameter machine. In addition, it is possible to further optimize the overall functioning of the extrusion system relative to a single-screw extruder obtaining higher rates at reduced melt temperatures. As output rates begin to exceed approximately 4000 kg/h it becomes necessary to add a second melting extruder to feed the larger diameter pumping extruder. At output levels above 4000 kg/h, the generally more expensive twin-screw extruders can be less expensive than the three-extruder tandem extrusion combination and in these instances twin-screw extrusion systems are becoming more common, and generally the preferred extrusion system on large polypropylene biaxially orienting film lines.

15.2 Single-Screw Extruders

A single-screw extruder (Figure 15.1) consists of a hollow cylindrical barrel fitted with external heaters. The inner barrel surface is coated with a hard metal liner such as Xaloy® to limit wear rates of the barrel and a compatible alloy hard wear surface can be added to the screw flights [27]. A screw is fitted into this cylinder with a specific geometry determined by the polymer and the desired thermal condition of the melt. The screw design chosen will determine the ultimate performance of the extrusion system and it is considered the heart of the extrusion process. The screw is driven by an electric motor through a gear reducer sized for the speed and power requirements of the screw. The typical

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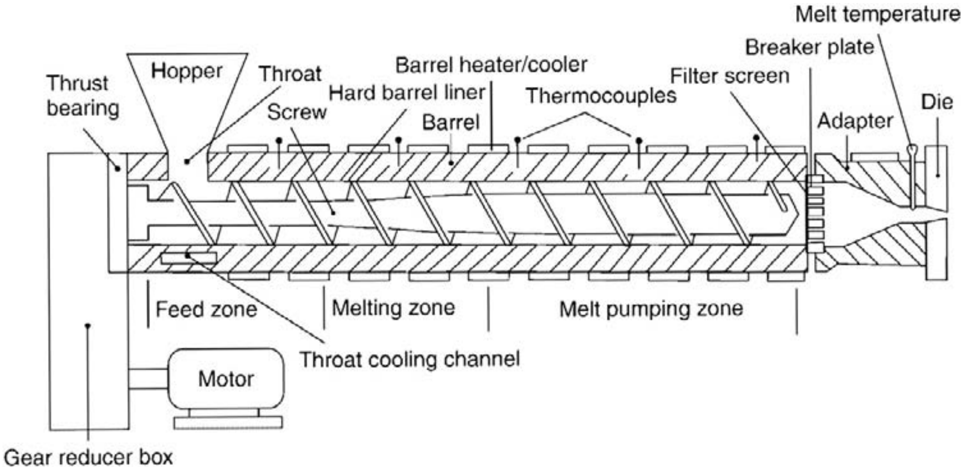


Figure 15.1 Cross section of an extruder showing principle components.

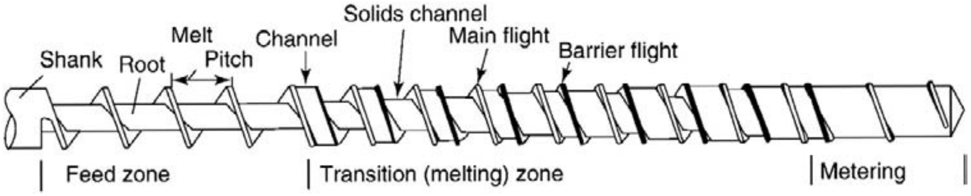


Figure 15.2 Schematic of Barr barrier flight screw with flight interchange.

barrier screw shown in Figure 15.2 takes advantage of the melting mechanism in the extruder to increase efficiency. Most of the energy required to melt the polymer is supplied by the motor [8,9]. Barrel temperature is maintained by electric heaters, which often contain channels for cooling water.

The solid polymer is introduced into the feed throat of the extruder and conveyed into the screw by its turning motion [4,5]. It is compacted into a solid plug, which is melted by rubbing it in contact with the hot barrel surface. Molten polymer is collected from the barrel surface by the screw flights and pumped toward the end of the extruder. At the end of the screw, the polymer is completely melted. The melt is mixed by the screw rotation, which generates enough pressure to push the melt through a die and to the next step [10,11]. The condition or quality of the melt is extremely important for product quality and process stability. The extrusion conditions affect crystallization behavior and molecular weight of the polymer in its final product form.

The melt is produced by the viscous dissipation of mechanical energy into a very thin layer of molten polymer located between the compressed solid plug and the heated barrel surface [5] (Figure 15.3). Owing to the high viscosity of the polymer melt, typically 50−1000 Pa·s (500−10,000 poise), large amounts of mechanical energy are dissipated in the melt film between the solid plug and the barrel surface as the motor turns the screw, forcing the polymer plug against the hot barrel surface. The mechanical energy is converted by viscous dissipation into heat in the thin melt film, which raises the temperature of the melt film. The increased heat energy generated in the melt film is transferred by thermal conduction and convection to the solid polymer plug, the barrel, and the melt pool. Excessive temperatures or mechanical work can cause thermal, oxidative, or mechanical degradation of the polymer.

A new generation of energy-efficient screw designs has been developed, which minimize the melt temperature by mixing the collected melt with the solid particles of the compacted bed [12,13]. This is accomplished by purposely disrupting the melting mechanism of Figure 15.3 at some point, by changing the screw geometry to mix the solid with the melt. This transfers thermal energy to the low-temperature unmolten solid by conduction of excess energy from the high-temperature melt resulting in a lower average temperature above the melting point of the polymer. However, it is not yet homogeneous in temperature and this is accomplished by screw design sections, which remix and shear the melt to make it homogeneous in temperature. Screws of this type are generically called “energy transfer” screws and are best represented by the ET® and Double Wave® screw designs.

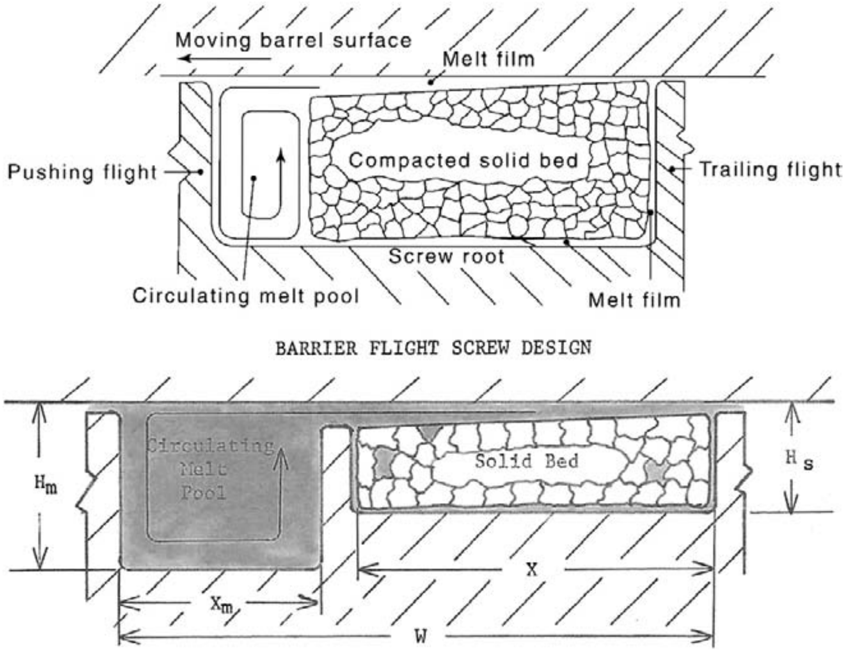


Figure 15.3 (a) Melting mechanism of single screw extruders as determined by Maddock. (b) Schematic diagram of barrier screw cross section showing separate solids and melt channels separated by the barrier flight as defined by Barr.

15.3 Single-Screw Extruder Mechanisms

This section is designed to give an overview of the principal mechanisms of single-screw extrusion. The main mechanisms are solids conveying, melting or plastication, and melt pumping. The manner in which these three mechanism are combined represents the extrusion model for the single-screw and will be discussed later in this chapter. It is important in the understanding of extrusion that the reader understands the operating mechanism of each of the three primary functions, which the extruder preforms, that is, conveying, melting, and metering. Ultimately, extruders are melting limited devices [8,45] and it is important to understand how melting differs from the solids conveying and metering to make the best use of an extruder screw design.

Plastication is a term, which represents the mechanical conversion of the solid polymer into a polymer melt. Because, not all polymers contain crystals they cannot melt in a classical thermodynamic sense, these noncrystalline polymers are glassy or amorphous polymers, which will pass through a temperature where they change from a solid glass to a liquid melt. This temperature is termed the “glass transition temperature” (T_g). Semicrystalline polymers are characterized by a distinct melting point but will also have a T_g for the noncrystalline portions of the solid and the T_g will be lower than the melting point. Figure 15.4 shows

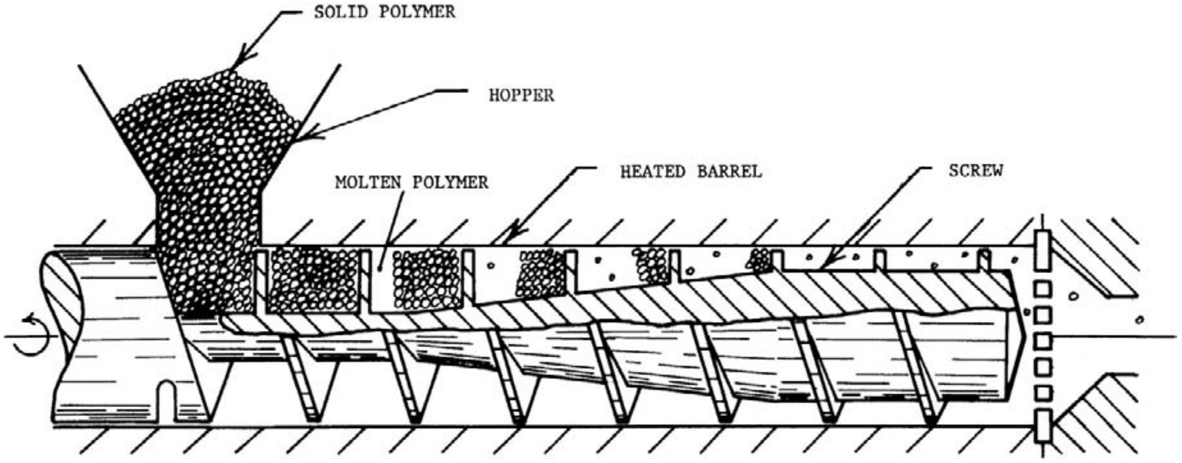


Figure 15.4 Cross section through an operating extruder.

a cross-section of an operating single-screw extruder. In Figure 15.4 we see that the solid polymer is fed to the extruder from the hopper in a granular form. The screw must capture the polymer falling into it from the hopper and convey it into the screw. As the polymer is fed forward it is compacted by the forces generated by solid conveying frictional forces. As the solid is compacted into a compressed solid plug, it is rubbed against the extruder barrel. The rubbing action generates heat, which combines with the energy conducted into the barrel from the barrel heaters and raises the barrel surface above the melting or softening point of the polymer. As the barrel temperature reaches the melting point of the polymer, a thin film of polymer melt forms on the barrel (Figure 15.3). As the barrel moves relative to the solid, the energy of the motor is dissipated in the melt film and is conducted into the solid melting the polymer. The molten polymer is scraped from the barrel and captured by the screw flight and pumped toward the metering section and to the die. As the melt pool is formed, it pressurizes the screw flight and pushes the solid against the trailing flight creating the melting system as shown in Figure 15.3.

In this transition section the screw must convey solids, melt the polymer, and pump the melt, which is formed by melting. At the end of the melting section the solid should be completely converted to a melt and the metering section creates a circulating flow of melt by the action of scraping the melt from the barrel and forcing it down to the bottom of the screw flight. Melt is conveyed by two mechanisms in the metering section: drag flow and pressure-driven flow. The balance of the two flows determines the final output of the metering section. The pressure flow is controlled by the pressure difference from the inlet of the metering section and the die restriction at the end of the extruder.

In the following sections, we will examine each of the individual mechanisms and then examine how they have been combined to describe the overall extrusion mechanism. For many years in the early development of extrusion equipment the melting mechanism as shown in Figure 15.3 was unknown. Work had previously been done by research groups at DuPont to describe the individual mechanisms of solid conveying [28] and metering [29], which could be studied independently. Then, in the early to mid-1960s Bruce Maddock performed freezing experiments where the extruder was run with a mixture of polymer with some pigmented pellets of the same polymer until a steady state was reached. Then, the extruder was rapidly stopped and the barrel cooled rapidly to solidify the polymer. Next, the barrel was reheated to release the polymer from the barrel and the screw was pushed from the barrel. The helical solid formed in the screw channel was then cut in cross-section and examined and the mechanism shown in Figures 15.3 and 15.4 was deduced. This experimental work led to mathematical modeling of the extrusion and melting mechanisms by Tadmor [30] at Bell Telephone and others [31—33] and led to rapid advances in the understanding of extrusion and improved methods of screw design. These single-flight screws were ultimately limited in output by solids exiting the metering section resulting in poor melt homogeneity. This then led to the use of the Maddock mixer, which is a dispersive mixing element invented for gel reduction, at the end of the melting or metering section to capture unmelted polymer exiting the melting section or at the end of the metering section (Figure 15.23G). These mixers held the remaining solids out of the metering section and insured complete melting with an improvement in overall output with better melt quality. The experimental discoveries of Maddock also led to the invention of the Barrier screw design by Barr [34], which gave higher extrusion outputs with a lower melt temperature than could be obtained with standard single-screw designs. This was then followed by direct experimental studies of the melting mechanism by several workers [35,41]. Further advances in extrusion screw design were then made by purposely disrupting the extrusion melting mechanism after a portion of the polymer was melted and mixing the solid polymer and the hot melt in the HPM double wave® and the Barr ET® screw concepts. These new ideas led to a further increase in output with a reduction in melt temperature with improved homogeneity of the melt.

15.3.1 Solid Feeding

First, we will consider the feeding of polymer to the screw from the extruder hopper. The screw at the entrance of the extruder is a volumetric feeder and with each turn of the screw a volume is swept out, which is related to the cross-sectional area of the screw flight, hopper discharge area, and the number of revolutions of the screw. The amount of polymer taken into the screw will depend on the bulk density of the polymer granules and the rate at which they can fall into the screw as the flight passes under the hopper. As the screw flight passes under the hopper it pushes the solid pellets forward and captures them at the leading edge of the barrel opening (the feed throat). After the flight passes the trailing edge of the hopper opening polymer pellets fall into the open screw channel and are then pushed forward by the pushing edge of the screw flight. Extruders may be manufactured with a circular, a rectangular feed opening, or a tangential feed pocket. The efficiency of the screw filling will depend on the geometry of the opening and the speed of the screw. The screw speed sets the time for polymer to fall into the screw and the flight can also push polymer away from the opening (slinging) lowering the amount of polymer picked up by each screw revolution. In this section of the extruder the screw flights are undercut more than the nominal diameter of the screw to prevent wedging of solid polymer between the screw flight and barrel causing the screw to stall the drive.

15.3.2 Solids Conveying

As the polymer pellets are transported into the screw they are compressed by the feeding forces and eventually form

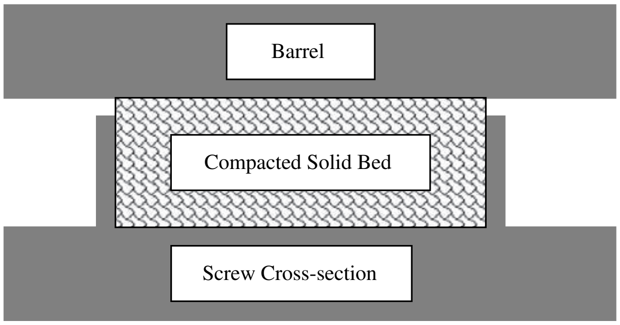


Figure 15.5 Fully compacted solid bed in screw feed section.

a solid plug, which completely fills the screw channel (Figure 15.5). At this point the feeding is controlled by the relative friction of the polymer against the screw and the barrel creating an unbalance torque, which drives the plug forward. Similarly, we will see from a deeper examination of the mechanism that the feeding is optimized by making the polymer stick to the barrel and slip on the screw. In order to test this, obtain a section of threaded rod and a nut. After screwing the nut onto the rod imagine that the rod is the screw and our fingers as the barrel. Without touching the nut rotate the rod and we will see that the nut simply turns with the rod. In this case we can see that the polymer (represented by the nut) is sticking to the screw and slipping on the barrel (hands off!). Next, touch the nut to prevent it from turning, that is the polymer is sticking to the barrel. As the rod turns the nut will begin to slip between the rod and the nut and will advance along the screw threads. This is the case where the polymer is sticking to the barrel. This is exactly what happens in the solids conveying of polymers except that there will be some slippage of the polymer (nut) against the barrel (our fingers), so it will both rotate and advance along the thread tracing out a long helical path with a helix angle of theta (θ). One can appreciate as well that the relative amount of slippage between the barrel and the screw will determine the torque required to move the polymer (or nut) forward. Thus, lubricating the rod will make it easier to move the nut while a dirty or rusty rod will increase the amount of force required to move the nut forward.

Next, we will consider the actual motion of the polymer inside the extruder. As the screw turns, the polymer is pushed by the screw flight, which will supply the energy to move it down the helical screw channel of angle ϕ as it is constrained by the screw flights. However, the motion of the solid is resisted by the frictional forces between the solid and the barrel and between the solid and the screw surfaces, which prevent the polymer from simply moving down the channel like a nut. Because the screw is turning inside the stationary barrel, as the solid moves down the channel it is rotated and it makes a helical motion relative to the extruder barrel. The angle at which it moves relative to the barrel with each screw rotation is termed the solids conveying angle (θ). Figure 15.6 shows the relative motion of the solid plug in the screw channel and relative to the barrel surface.

By knowing the velocity at which the solid plug moves along the screw flight in a given time it is possible to calculate the volumetric solids conveying rate in terms of the screw geometry and the solids conveying angle. A derivation of this was performed by Darnell and Mol (Equation 15.1).

$$\frac{Q}{N} = \frac{\pi^2 Dh(D-h)\tan\theta\tan\phi}{\tan\theta + \tan\phi} \tag{15.1}$$

where :
Q = volumetric through put
D = screw diameter
h = channel depth
N = screw speed

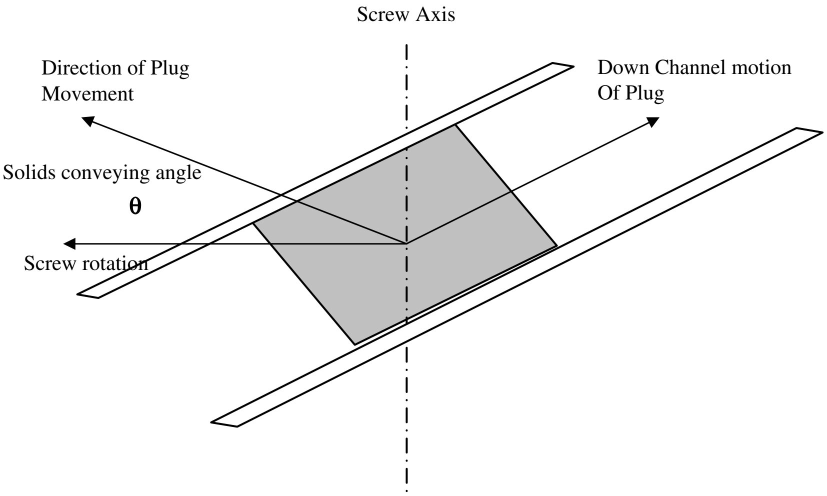


Figure 15.6 Motion of solid plug relative to barrel surface, angle θ, and down the channel relative to the screw and flight surfaces.

The mass flow rate, G, can then be calculated by multiplying the volumetric flow rate, Q, by the density of the solid bed (Equation 15.2)

$$G = Q \times N \times \rho_{sb} \qquad (15.2)$$

Equation (15.1) shows us that in order to be able to estimate the solids conveying rate we must be able to calculate θ as the solids conveying angle.

The early analysis of solids conveying in an extruder evolved through several simple models based upon simple concepts such as the frictional forces between the polymer and the metal surfaces is credited to Decker [36] and Maillefer [37] and the concept of the differential torque at the screw and barrel surface was introduced by Simonds [38]. The rigor of the derivation was significantly improved by Darnell and Mol of DuPont and their analysis is most often cited as it gives a good description of the behavior observed. The model is based upon the force and torque balance developed on the solid plug, which is assumed to completely fill the screw channel. The following are the basic assumptions used for the derivation of the model:

1. The polymer forms an elastic plug with internal pressure.
2. The elastic plug contacts all sides of the screw channel.
3. Pressure may be constant or increase with channel length.
4. The coefficient of friction (COF) of the polymer against the metal surface is independent of pressure.
5. The solid bed does not deform.
6. Single-flight screw in the feed zone.
7. The width of the screw flight is negligible.
8. The radial clearance between the flight and barrel is negligible.
9. The COF is the same at all polymer metal surfaces on the screw.

This set of assumptions describes the condition of plug flow of the solid in the feeding section of the screw.

In order to fully understand what is driving the solids conveying we need to examine the forces, which are acting on the plug. For in the end it is the imbalance in the forces, which will cause the plug to move forward toward the end of the extruder. Figure 15.7 shows a section of the solid plug as it is assumed to be in the feed section. In Figure 15.7, it is easy to see that the plug contacts all surfaces of the screw and the barrel surface. There are two primary directions that must be considered in the development of the forces. (1) The plug can only advance toward the end of the extruder by sliding along the screw channel because it is constrained by the screw flights. All frictional forces developed by the plug sliding along the screw will be along the direction of the screw flight helix angle (ϕ). (2) The plug is being rubbed against the barrel due to the rotation of the screw and the frictional force developed will be along the solids conveying angle θ, the direction of motion of the solid relative to the barrel surface. In addition to the frictional force, there is also a force due to changing internal pressure along the screw, which will impact on the solids flow rate. It takes some time to analyze the motions to fully understand the compound motion of the solid. The real motion of the solid is down the screw channel and the motion against the barrel is the relative motion of the sliding plug induced by the screw rotation.

Since we will not repeat the derivation of the previous work, we need to understand several key points. First, the energy to move the solid forward into the extruder is supplied by the pushing flight; all the other forces as shown in Figure 15.7 are resisting the motion and are the result of the polymer moving in the screw channel. The forces are broken down into components along the direction of the screw flight with some forces acting parallel to the screw axis and torques developed from the forces acting perpendicular to the screw axis. For the reader interested in better understanding the derivation of the model the original paper of Darnell and Mol [39] and the chapter on solids conveying in the book by Chung [40] are recommended.

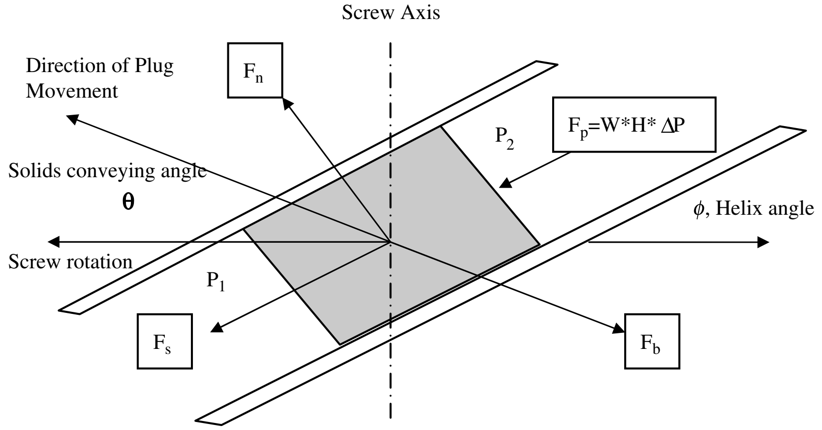


Figure 15.7 Force diagram for the solids conveying forces acting on the solid plug of width W, length ΔZ and thickness H.

Equation (15.3) gives the result of the analysis of the solids conveying controlled by friction:

$$\cos\theta = K\sin\theta + \frac{\mu_S}{\mu_B}K_2 + K_3\frac{H}{L\mu_B}Ln\left(\frac{P_2}{P_1}\right) \tag{15.3}$$

where K, K_2, and K_3 are complex constants based upon screw geometry and μ_s is the COF between the polymer and the screw given in Equation (15.4):

$$\begin{aligned}
\mu_b &= \text{coefficient of friction to the barrel} \\
\mu_s &= \text{coefficient of friction to the screw} \\
K &= \frac{E(\sin\phi + \mu_S\cos\phi)}{(\cos\phi - \mu_S\sin\phi)} \\
K_2 &= \left(\frac{2HK}{t}\tan\phi + K\sin\phi + \frac{2HE}{t} + C\cos\phi\right) \\
K_3 &= (E\cos\phi + K\sin\phi) \\
E &= \frac{R - \frac{1}{2}H}{R} \\
C &= \frac{R - H}{R}
\end{aligned} \tag{15.4}$$

Note that for the constant K that as μ_s decreases the value of K, which causes K_2 and K_3 to decrease as well.

If we examine the form of Equation (15.3) we see that the solids conveying angle θ appears on both sides of the equation and so must be solved iteratively. Examining the equation further we note that as the magnitude of the right side is made smaller then the value of θ will increase and the screw will feed at a higher rate. Conversely, as the right side of Equation (15.3) increases, then the value of θ will decrease and the screw will feed at a lower rate. We can now make some observation as to the effect of the various parameters on the capacity of the solids conveying of a screw.

1. As the feed depth (H) increases, θ will increase.
2. As the feed length (L) increases, θ will increase.
3. As the pressure at the end of the feed section (P_2) increases, θ will decrease.
4. As μ_s the COF between the polymer and screw decreases, θ will increase.
5. As μ_b the COF between the polymer and the barrel increases, θ will increase.

Thus, we can see the source of our earlier statement that for a given screw if we make the polymer slip on the screw and stick to the barrel we will improve solids conveying. For a new screw we can improve solids conveying by making the feed section deeper and/or longer.

15.4 Melting Mechanism

In this section we will discuss the mechanism of melting in a single-screw extruder and review the methods developed for estimating the rate of melting. In Figure 15.3, we saw the basic melting mechanism discovered by Bruce Maddock. It is customary in the development of these models to assume that the screw and solid bed are stationary and the barrel is moving at a velocity V_b relative to them, which is why Figure 15.3 shows the maximum velocity occurring at the barrel surface when in fact the barrel is stationary. This greatly simplifies the mathematics and should have no impact on the derived models. Examining Figure 15.3 closely we see that the compacted solid bed is surrounded by molten polymer. The solid, which was fed into the screw has been tightly compacted by the forces feeding the solids and as soon as the metal surfaces of the screw and the barrel exceed that of the melting point of the polymer the solid begins to melt as it moves along the screw. The lower melt films between the solid and the screw will be ignored for now as the melt formed in these regions, while important, does not contribute much to the high rate of melting observed in the extruder. These lower melt films are important in regards to polymer degradation along the screw as well as in supplying some fraction of the overall screw melt output. It is also thought that these films might impact the stability of the extrusion process, so they must be considered in the development of an extrusion model but the discussion of the melting model will be focused on the upper melt film between the solid bed and the barrel surface.

Returning to the physical description of the melting system of Figure 15.3, it is in this upper melt film where the high rate of melting observed in extruders is generated. As the solid melts against the barrel, a melt film is formed, which is moving at the velocity of the barrel and is stationary at the solid−melt interface. As the melt exits the edge of the solid bed a fraction of the melt film will be pulled or dragged along by the relative motion of the barrel. Not all of the melt film can be dragged out as the velocity varies across the melt film at the trailing edge of the solid as it enters the melt pool. This velocity profile ultimately determines the melting rate. All of the melting models, which have been developed have attempted to determine this thin film velocity profile and then to calculate the melting rate from it. Once the melt film is dragged out from under the solid the screw flight scrapes the melt film from the barrel and forces it down along the screw flight to the screw root. At the screw root the melt is forced to move toward the solid, which forces it up toward the barrel, where it meets the melt film exiting the solid bed. This constrained motion is what forms the circulating melt pool, which is shown in Figure 15.3. It is the motion of the screw flight that drives the circulating flow in the melt pool and pressurizes the melt. This melt pressure forces the solid against the trailing screw flight maintaining the observed melting mechanism and minimizes the growth of the melt films between the solid bed and the screw surface.

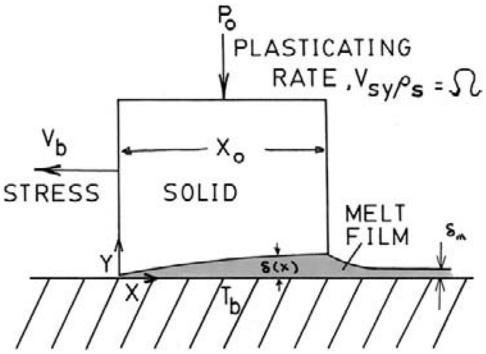


Figure 15.8 Mass balance around melting solid plug at the barrel surface.

In a mathematical analysis of the melting system the mass balance around the melting system (Figure 15.8) shows that the amount of melt dragged from under the solid and left on the barrel has to equal the rate at which the solid is melted. In Figure 15.8, we see that at steady state, the solid moves in the y-direction, toward the barrel surface, at a velocity V_{sy} as the melt is dragged away by the barrel. The melting rate is designated as Ω and is given in units of mass/time/area (lb/h/in.^{2} or kg/h/cm^2) and can be calculated from the solid velocity into the interface (V_{sy}) times the solid density (Equation 15.5).

$$\Omega = V_{\mathrm{sy}}\rho_{\mathrm{solid}} \tag{15.5}$$

The rate at which material is dragged from under the solid can be calculated by integrating the velocity profile (averaging the velocity of the melt across the thickness of the melt film) at the end of the solid bed times the melt density.

$$\Omega = \rho_{\mathrm{mb}} \int_{0}^{\delta(x)} v(x,y)dy$$

making the equation dimensionless and rearranging yields :

$$M = \frac{\Omega}{\rho_{\mathrm{m}} V_{\mathrm{b}}} = \frac{\delta_0}{X_0} \int_{0}^{\delta(1)} v(1,y)dy \tag{15.6}$$

where M is defined as the dimensionless melting efficiency, δ_0 is the characteristic length in the y-direction (film thickness), and X_0 is the characteristic length in the x-direction (solid bed width).

The equations, which describe the transfer of heat to the solid and the flow of melt due to the motion of the solid relative to the hot barrel surface are used to calculate the velocity profile in the film and then the flow rate of melt out from under the solid. From this, we can see that the mathematical problem is one of determining the velocity profile, $v(x, y)$, in the melt film under the solid bed. This is not an easy problem to solve due to the complex relationships, which exist between the various differential equations that describe the conservation of mass, momentum, and energy in the flow, and the temperature and shear rate dependence of the viscosity, which ties all of the conservation equations together. The methods used to obtain solutions to the melting calculations are beyond the scope of this chapter, but the results obtained can be examined to better understand what controls melting. The interested reader is directed to the book by Chung [8] for a discussion of the development of an iterative model developed by Tadmor and an analytical melting model based upon direct experimental melting measurements developed by Mount, Watson, and Chung [35]. Figure 15.9 displays the results obtained from the analytical melting model, which compares experimental melting rate data and the calculated melting rate from the model [35,41]. The good agreement signifies that the model incorporates all of the important characteristics of the flow problem and we will examine the relationship obtained for the melting rate to better understand the melting process.

Understanding the motion of the melt we now want to better understand the mechanism, which generates the energy used to melt the polymer. As the solid is forced down the screw channel by the solids conveying it, it is rubbed against the barrel surface generating frictional heat if the barrel surface is below the melting point. However, as soon as the barrel surface is above the melting point of the polymer, a film of liquid polymer will form, which will resist the motion of the solid due to the melt viscosity of the film. This viscous resistance will cause motor power to be consumed in

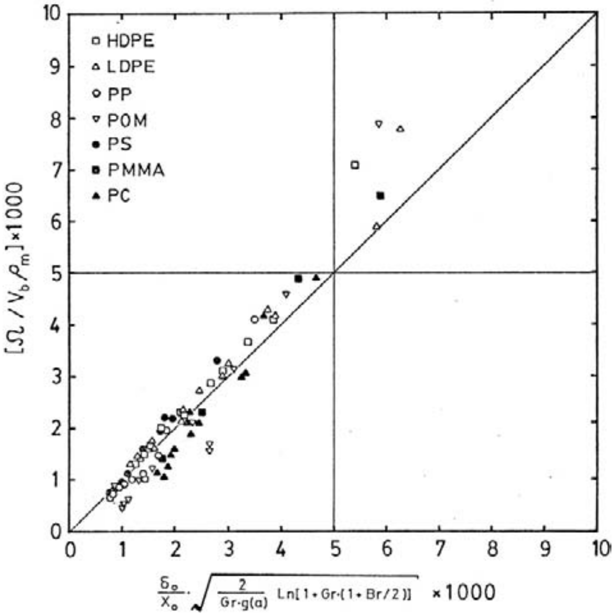


Figure 15.9 Comparison of experimental results and calculation from analytical melting model (41).

the turning of the screw, which will be dissipated in the melt film in the form of heat. The rate of heat generation will be proportional to the viscosity of the melt film and the square of the rubbing velocity of the solid (ηV^2). Thus, the higher the melt viscosity and the faster the screw speed, the greater the rate of heat generation and consequently the melting rate. In this process, the electrical energy of the motor has been converted into mechanical energy to turn the screw, which has been converted to thermal energy in the thin melt film raising the temperature of the melt film above the solid plug. This viscous dissipation of energy in the melt film is the principal source of the high melting rate observed in extruders because it raises the rate at which energy can be conducted to the solid to be used for melting. Energy can also enter the melt film from the barrel walls by conduction from the barrel heaters, but this is a small fraction of the heat needed to generate the amount of material typically melted in an extruder. Without the viscous dissipation mechanism the melting rate of the extruder will be too low for economical production because the insulating properties of the polymer give too low a melting rate for most processing. That is why ram type extruders are seldom used for polymer processing; the melting rates without viscous dissipation are too low.

Figure 15.10 shows the energy balance around the melting solid plug in relationship to the barrel, the melt film, and the solid plug. As the screw turns the energy conducted from the barrel wall and the energy dissipated in the melt film is conducted through the melt film toward the solid bed, as well as being carried toward (convected) the melt pool by the motion of the screw. The energy, which enters the melt pool is lost to the melting of the polymer resulting in higher melt temperature and lowers the energy efficiency of the melting process. The energy, which is conducted to the melt−solid interface is used to melt the polymer creating new melt. In many models it is assumed that some of the energy entering the interface is conducted away and is lost to melting, however, direct melting rate experiments of Mount [41] do not show the effect of this heating and it can be assumed that all of the energy conducted to the solid−melt interface is consumed in melting.

From this we can see that conditions, which increase the convection of energy into the melt pool will lower the energy efficiency of melting. The two principal sources of higher convection rates relative to conduction are screw speed and screw diameter. As the screw speed is increased the melt is in contact with the solid for a shorter period of time and, therefore, has less time for conduction. This is off-set somewhat by the thinner melt film, which permits better conduction, but we find that as screw speed increases we obtain fewer pounds of polymer melted for each unit of energy expended by the motor (lb/HP-h or kg/kW-h). In the case of larger screw diameters the solid bed becomes wider due to the increase in channel width of the larger screw. This results in a longer flow path above the solid bed and as a consequence the melt film becomes thicker as the melt is generated along the solid bed width. As the film becomes thicker the energy dissipated has a longer distance to be conducted to reach the solid interface and as a consequence less energy is conducted to the interface relative to the amount convected into the melt pool again lowering the energy efficiency of the melting process as the screw

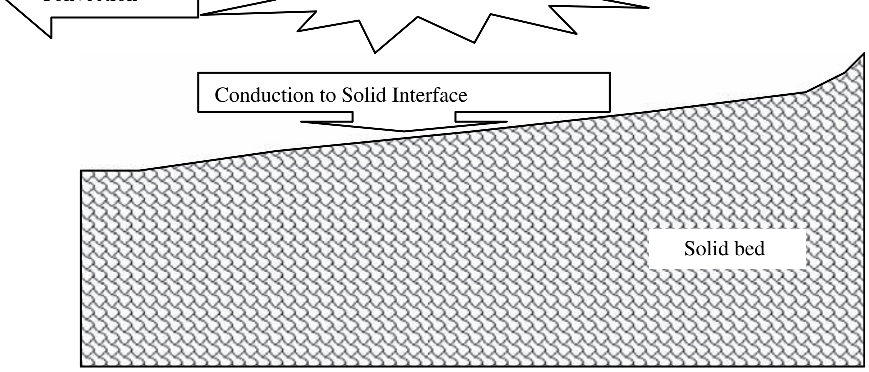


Figure 15.10 Energy balance in melt film of polymer melting by sliding on a hot barrel surface.

diameter is increased. And indeed it is found that for the same screw technology larger diameter screws produce lower melting energy efficiencies (Lbs/hp-h) and result in increased melt temperatures.

Having discussed the mechanism in terms of a word picture we will now look at the solution obtained for the melting efficiency (Equation 15.6) developed by Mount, Watson, and Chung [35]. In obtaining the solution the governing equations were put into dimensionless form and simplified. Table 15.1 lists the dimensionless groups and their definitions. In order to perform the simplification of the problem of finding $v(x, y)$, the dimensionless groups were calculated from the experimental study and the final equations and boundary conditions were developed and solved to develop the expression for the integral using the principle of superposition. In this case, solutions were obtained for various combinations of dimensionless terms by letting other dimensionless groups go to zero and solving the remaining equations. The less complex solutions are then combined such that as any dimensionless group becomes zero, the less complex results are recovered. The interested reader is again invited to review the procedure in Chung [8] and Mount et al. [35].

The final solution containing all of the important dimensionless groups can be written as Equation (15.7), which has replaced the integral with the expression derived in terms of all of the principal dimensionless groups.

$$M = \frac{\delta_0}{X_0}\sqrt{\frac{2}{G(a)}\,\frac{Ln\left(1 + 5/6Gr\left(1 + \frac{Br}{2}\right)\right)}{5/6Gr}} \tag{15.7}$$

Table 15.1 Definitions of dimensionless groups, k_m thermal conductivity, T_f the flow temperature (T_g or T_m), ρ_m the melt density, ΔH the enthalpy change, C_{pm} the heat capacity, b exponent of viscosity temperature change, n the power law index, η_0 the viscosity

Parameter	Name	Definition
δ_0	Characteristic melt film thickness	$\sqrt{\frac{k_m(T_b - T_f)X_0}{\rho_m \Delta H}}$
Gr	Graetz number (convection related)	$\frac{C_{Pm}(T_b - T_f)}{\Delta H}$
Br	Brinkman Number (dissipation related)	$\frac{\eta_0 V_b^2}{k_m(T_b - T_m)}$
a	Reduced temperature and shear sensitivity	$\frac{b(T_b - T_f)}{n}$
$G(a)$	Characteristic function of parameter a	$\frac{a(1 - e^a)}{a + 1 - e^a}$
σ	Reduced pressure	$\frac{\delta_0^2 P_0}{\eta_0 V_b X_0}$
α	Aspect ratio (δ_0/X_0)	$\sqrt{\frac{k_m(T_b - T_f)}{\rho_m \Delta H X_0}}$

This expression shows the importance of the viscous dissipation through Br, the convection through Gr, and the temperature and shear dependence of viscosity (a) on the velocity profile integration. In the development of this expression one of the most significant discoveries was the importance of $G(a)$ on the solutions. In earlier work by Tadmor there were noted large discrepancies between experiment and predicted results for the amorphous polymers in comparison to semicrystalline polymers. Consequently, an additional energy loss was added to the solution to decrease the over prediction of the amorphous polymers. In the work of Mount, Watson, and Chung [35] it was discovered that the principal source of overpredicting the amorphous polymers was due to the greater modification of the velocity profile by the temperature sensitivity of the amorphous polymers viscosity relative to that of the semicrystalline polymers [41]. This was shown graphically with the comparison experimental data with predicted results of intermediate models without the $G(a)$ term (Figure 15.11). These models without $G(a)$ gave large overpredictions of the melting rate. In comparison to a model, which contained only the $G(a)$ term gave highly reduced errors (Figure 15.12) and removed the separation in the data for the semicrystalline and amorphous polymers. This implies that the shape of the velocity profile is dramatically affected by the temperature dependency of the polymer viscosity by the temperature profile.

Therefore, in the estimation of the melting rate the model of Mount [35,41] will permit the most accurate estimation for use in both understanding the mechanism of melting and estimating the magnitude of the melting rate.

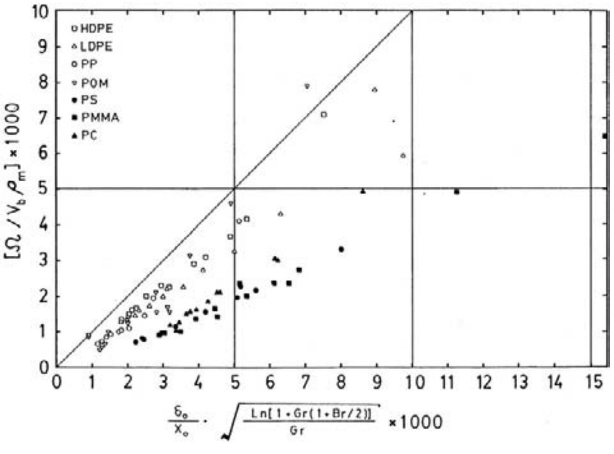


Figure 15.11 Intermediate model predictions without G(a) versus experimental results (41).

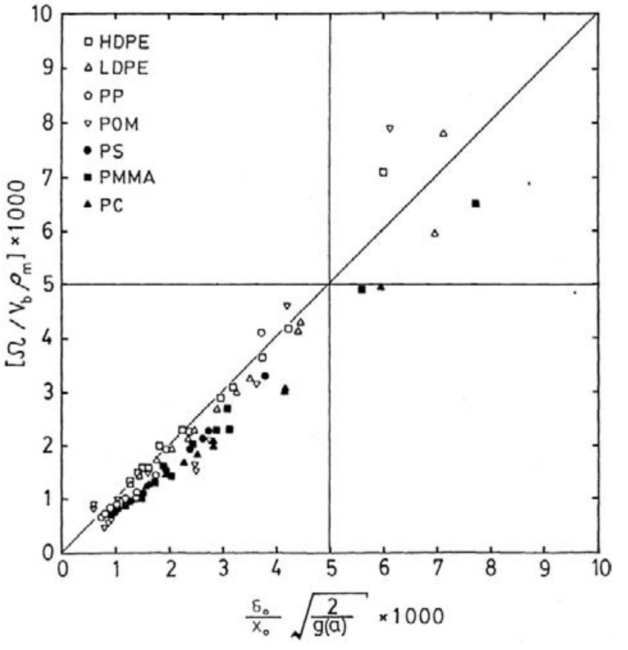


Figure 15.12 Comparison of model predictions for G(a) alone versus experimental data (41).

15.5 Metering Mechanism

The metering section of a single-screw extruder functions as a pump to move molten polymer out of the screw and through the remainder of the melt system. Extruder head pressure is the pressure, which must be generated by the extruder screw to force melt through the breaker plate, transition and/or adapter, and die. With the breaker plate, screens, and die attached to the extruder, the quantity of material forced through the die openings combined with the viscoelastic properties of the resin, at the particular melt temperature, determines the amount of pressure resisting the flow.

In general, the metering section is a constant-depth single spiral helix as shown in Figure 15.4. The polymer is found to have a complex flow pattern with some material passing directly along the spiral path of the screw flight while other material traces out a helical path as it moves along the screw channel (Figure 15.13). This complex flow pattern is due to the combination of the drag and pressure flow, the two driving forces for flow in the metering section. Imagine that the screw was not rotating and that a pressure was applied to the melt at the inlet of the screw channel forcing polymer to flow to the end of the extruder. This is just the pressure flow for melt in a rectangular duct. Next, imagine that the screw is stationary and that the barrel is rotating around it. Melt, which is contacting the barrel will be moved (dragged) with the barrel toward the screw flight. If there is no clearance between the screw flight and the barrel wall the melt will be scraped off the barrel and pushed down the screw flight until it reaches the screw root where it will be forced to flow across the screw flight toward the opposite screw flight. When it reaches the opposing screw flight it will be forced upward toward the barrel surface and when it reaches the barrel surface it will be moved toward the scraping screw flight by a new section of the barrel and begin the process again but a little further down the barrel (Figure 15.13). Now, the material contacting the barrel also drags the fluid below it along due to the momentum transfer to the melt from the barrel. It is this relative motion of the barrel to the screw that creates flow across the screw channel, which is called drag flow. It is the drag flow mechanism, which allows the screw to develop pressure to move the fluid through the screw even against a flow restriction such as a die. In the analysis of the screw flow it is customary to combine the actions of the drag and pressure components to obtain the combined flow model for the metering section. As in the case of the melting calculations, the output of the metering section is obtained by integrating the velocity profile of the melt at the end of the

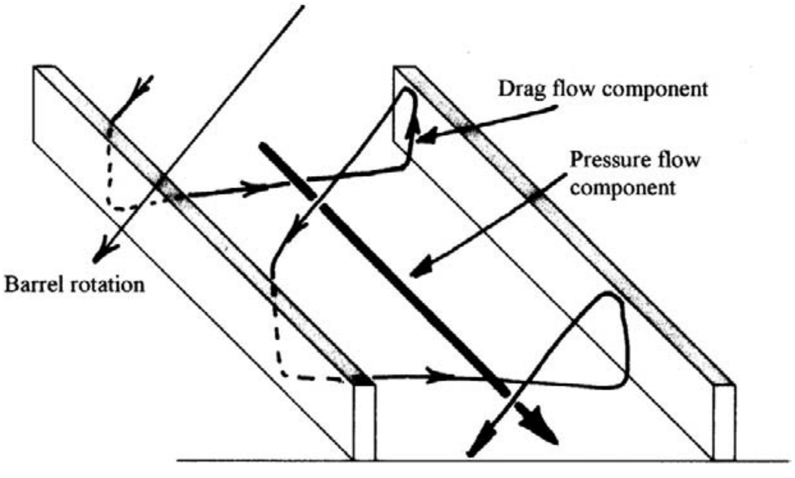


Figure 15.13 Circulating flow of melt in metering section.

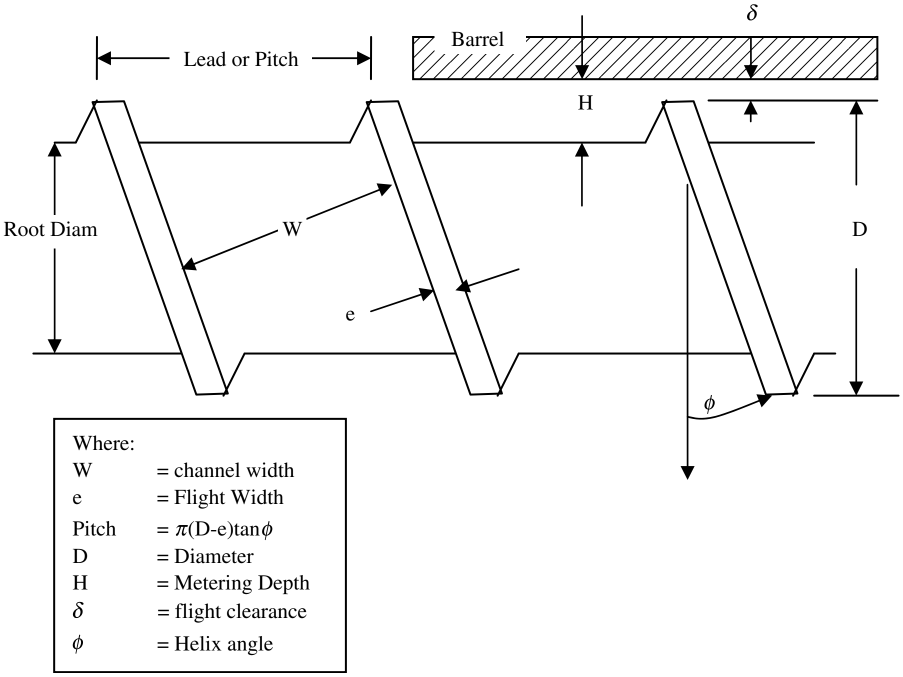


Figure 15.14 Geometry of typical metering screw.

screw channel. The work of the theoretician is to obtain the expressions describing the output so that it can be estimated.

Figure 15.14 shows the geometry of a typical metering section of a single-screw extruder and shows the typical screw dimensions. Figure 15.15 shows the coordinate system used to describe the metering section, which has been unrolled and laid flat. While this assumption of a flat metering section with no curvature will lead to errors, if the ratio of the depth to the diameter is small, then the error is found experimentally to be not too great. An analysis of this error is given by McKelvey [42] as in the mathematical analysis of the metering section it is customary to assume that the screw channel is much shallower than it is wide so that the edge of the screw channel can be neglected and that there will be no leakage of melt over the screw flight (zero clearance).

If this is done, then the differential equation for a Newtonian fluid, which describes this simplified flow theory [43] can be written as in Equation (15.8).

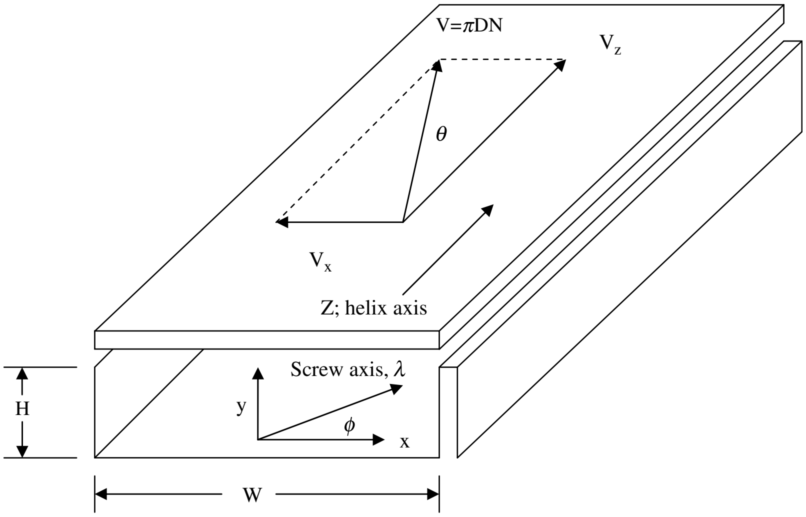


Figure 15.15 Unwound screw channel showing coordinate system and principle velocity components, directions and dimensions.

$$\frac{1}{\mu}\left(\frac{\partial P}{\partial z}\right) = \frac{d^2 v_z}{dy^2}$$

with boundry conditions : (15.8)

$$v_z(0) = 0$$

$$v_z(H) = V_b$$

Yielding the following velocity profile (Equation 15.9)

$$v_z = y\left(\frac{V_z}{H}\right) - \frac{y(H-y)}{2\mu}\left(\frac{\partial P}{\partial z}\right) \qquad (15.9)$$

The output of the metering channel is obtained by integrating the velocity profile obtained (Equation 15.9) across the depth of the metering section (Equation 15.10),

$$Q = W\int_0^H v_z dy \qquad (15.10)$$

which yields Equation (15.11) for the metering section output.

$$Q = \frac{V_z WH}{2} - \frac{WH^3}{12\mu}\left(\frac{\partial P}{\partial z}\right) = Q_D - Q_P$$

where : (15.11)

$$Q_D = \frac{V_z WH}{2} \quad \text{drag flow term}$$

$$Q_P = \frac{WH^3}{12\mu}\left(\frac{\partial P}{\partial z}\right) \quad \text{pressure flow term}$$

This simple result shows how the drag (Q_D) and the pressure (Q_P) flows combine to give the overall metering section output (Q). In general, the drag flow is found to be positive and half the volume of the screw channel swept out each unit of time. For the pressure flow, the discharge pressure gradient diminishes the flow and the flow rate is very sensitive to the channel depth (H^3) and the viscosity ($1/\mu$) level. As the channel depth increases, at constant pressure gradient and viscosity, the magnitude of the pressure term opposing the drag flow is increased and the overall output drops. Also, as the viscosity drops, at constant pressure gradient and channel depth, the pressure term (Q_P) increases and the output (Q) drops. Figure 15.16 shows the impact of channel depth on output for various pressure gradients for a polyester melt.

Equation (15.11) shows very well the interrelationship between the screw design parameters (H, W, screw speed $V_z = N\pi D$), material properties (viscosity is really a function of temperature and shear rate ~V_z/H) and operating conditions of barrel temperature and screw speed. These interrelationships can be used to troubleshoot a metering section, which can be understood through the impact of any particular change of materials or operating condition on the drag flow and pressure term.

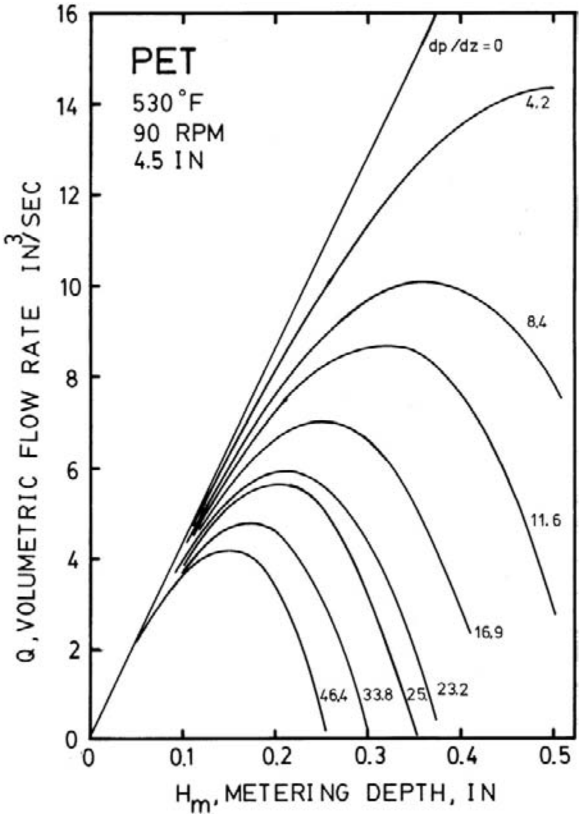


Figure 15.16 Impact of pressure gradient (d*P*/d*Z*) on metering section volumetric output (*Q*) as a function of metering depth.

To better understand the impact of the pressure flow it can be instructive to examine the impact of the discharge pressure on the calculated velocity profiles in the screw channel. Figure 15.17 shows the velocity profile in the z-direction (down the screw channel) and the direction λ parallel to the screw axis (Figure 15.14). The λ direction is the direction of flow toward the screw exit and represents the true net flow toward the discharge. The comparison is made for drag flow, two intermediate ratios of pressure to drag flows (Q_P/Q_D: 1/3 and 2/3) and closed discharge where the screw pumps against a blind die. For drag flow, Figure 15.17a, the velocity profile is a straight line with slope V_z/H (an average shear rate). As the pressure gradient increases it changes the shape of the velocity profile, as in Figures 17b and c, which can be understood to be decreasing the flow relative to the drag flow profile, i.e., the velocity is lower at all positions except the barrel surface. Indeed in Figure 15.17c the velocity profile shows what appears to flow back along the screw root, which is sometimes called backflow. However, as can be seen for flow in the λ direction, toward the screw exit, all components of the velocity profile are positive, so there is no true "backflow" into the extruder. At closed discharge (Figure 15.17d) there is no net flow in the discharge direction and the polymer circulates in the screw channel in a closed loop. Figure 15.18 is an alternative representation, which

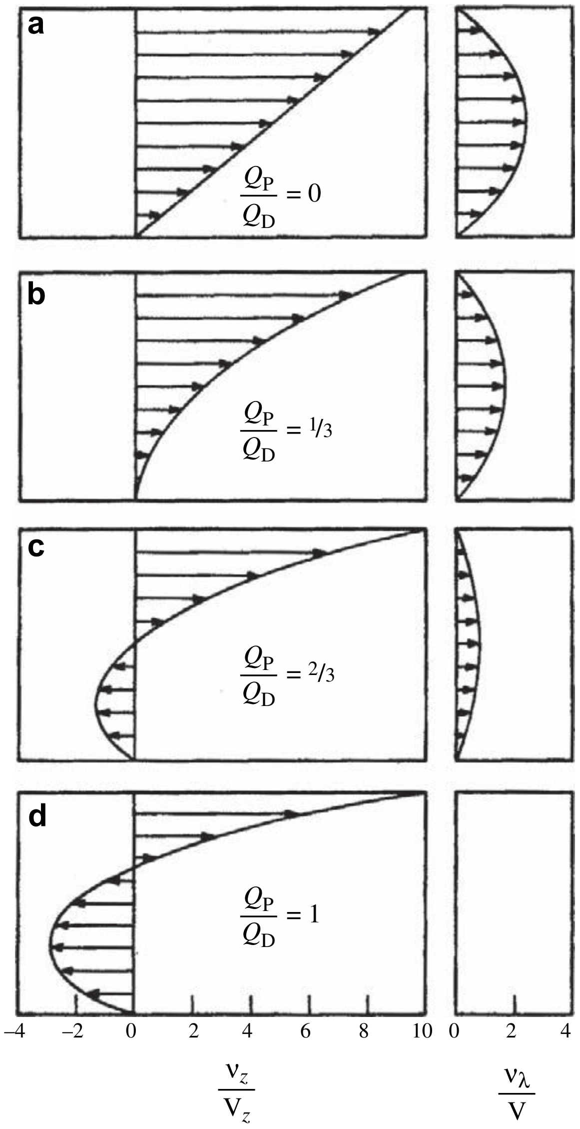


Figure 15.17 Comparison of the reduced velocity profiles for the down channel (z) and the axial (λ) directions showing the always positive axial flow towards the screw exit for all values of Q_p/Q_d less than 1 (Redrawn from McKelvey: Reference 10).

shows the helical nature of the flow described above for drag flow and several ratios of pressure to drag flow.

A more complex analysis taking into account the finite width of most real screw channels yields Equation (15.12) [10]. The shape factors have the same form of the solution as Equation (15.11) with the addition of shape factors (F_D, F_P), which depend only on the screw geometry factor *W*/*H* and modify the results due to the rectangular shape of the screw channel (Equation 15.12) and are shown graphically in Figure 15.19. As can be seen from an examination of Figure 15.19 as the screw channel becomes squarer (*H*/*W* approaches 1) the output drop can be as much as 50% because the flights decreases the flow due to the melt being restrained by the contact with the screw flight and reducing the flow in the down channel direction. Therefore, wider, shallower screw channels can be understood to pump more efficiently than narrow, deep channels as defined by the ratio of *H*/*W*.

$$Q = \left(\frac{V_z W H}{2}\right) F_D - \frac{W H^3}{12\mu}\left(\frac{\partial P}{\partial z}\right) F_P = Q_D F_D - Q_P F_P$$

where :

$$F_D = \frac{16_z W}{\pi^3 H} \sum_{g=1,3,..}^{\infty} \frac{1}{g^3} \tanh(g\pi H/2W)$$

$$F_P = 1 - \frac{192H}{\pi^5 W} \sum_{g=1,3,..}^{\infty} \frac{1}{g^5} \tanh(g\pi H/2W) \tag{15.12}$$

However, polymer fluids are not Newtonian and the Newtonian models will not accurately estimate the true metering rate from a screw. Real polymer melts shear thin, which is often times estimated with a power law viscosity model in the model development in order to improve the calculated output, especially for larger extruders. For the case of a power law fluid the approach of Middleman [44] for a one-dimensional flow yields a plot of dimensionless output versus dimensionless pressure (Equation 15.13) for various values of the power law index (Figure 15.20), which may be used to estimate the output of a metering section for a power law fluid.

$$\begin{aligned} \Pi_Q &= \frac{Q}{V_z H W} \text{ reduced output} \\ \Pi_P &= \frac{\Delta P H^2}{\mu V_z Z} \text{ reduced pressure} \end{aligned} \tag{15.13}$$

In the characterization of the function of the metering section it is customary to measure the output as a function of wall temperature, screw speed and inlet, and discharge pressure, where the inlet pressure is customarily assumed to be zero. If the discharge pressure is zero (no die or restriction at the extruder flange), then the flow will be pure drag flow and this condition is defined as open discharge. In open discharge the screw will discharge half of its volume independent of the fluid type (set pressure gradient to 0 in Equation 15.11). If we measure the output of the extruder as a function of screw speed and discharge pressure it is then possible to compare the results of the test to that of open discharge and learn a little more about the internal conditions of the extruder at the point of the metering section inlet. This is done by dividing the measured output by the calculated value of Q_D shown in Equation (15.11). If the value obtained is <1.0, then the pressure gradient is positive across the metering section. If however, the value is >1.0, then the pressure gradient is negative and the pressure at the inlet to the metering section is greater than that of the discharge. A value of 1.0 would imply that there is no net pressure flow and the metering section inlet pressure is the same as the discharge pressure.

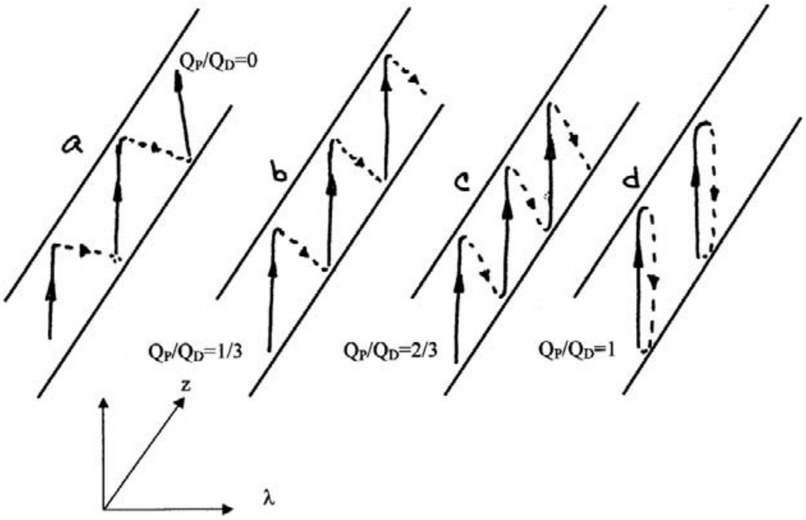


Figure 15.18 Particle paths in screw channel at various values of Q_P/Q_D, (redrawn from McKelvey, reference 10, p 244).

Information of this sort about the pressure levels at the end of a melting section at the inlet to the metering section can be helpful in troubleshooting the potential of excessive wear due to poor melting or overfeeding in the solids conveying section.

15.5.1 Single-Screw Extrusion Model

In an operating extruder the beginning of the screw can be fully described by the solids conveying model and the end of the screw can be described by the metering models because at the beginning and end of the extruder only one function is being performed. However, in a large portion of the screw, the transition section, the polymer is being melted as it is pushed along by the solids conveying forces, and the melt produced by melting is pumped toward the metering section and out of the extruder. It is this large portion of the screw where all three primary mechanisms are operating where the true extrusion model must be used. In its broadest terms, at steady state, the conservation of mass principle requires that the extrusion model says that the total mass of solid and melt, which enters into one section of the screw must equal the total mass of solid and melt, which exits the section of the screw, so the model must be able to calculate the relative amounts of solid and melt if they change in that section. In general, the solid will be melting, so the amount of solids exiting a section equals the amount of solids leaving plus the amount of solids melted in that section. This is shown schematically in Figure 15.21 and represented mathematically in Equation (15.14):

$$(\text{Solid mass})_{\text{OUT}} = (\text{solid mass})_{\text{IN}} - \text{amount melted} \tag{15.14}$$

From Figure 15.21 we can determine that the mass of solid is just the volume of solid times the density of the solid and that the amount of material melted is just the melting rate per

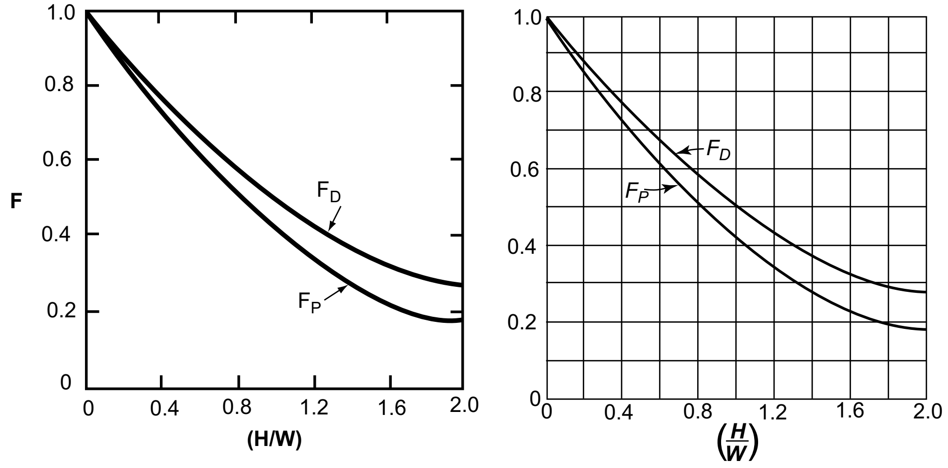


Figure 15.19 Metering form factors for drag flow (F_D) and pressure flow (F_P), (redrawn from McKelvey, reference 10).

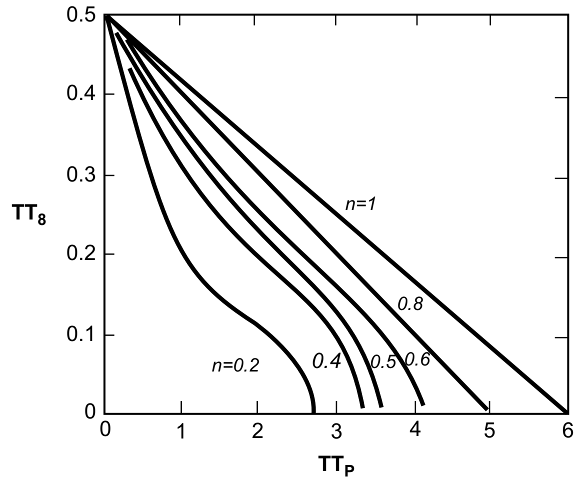


Figure 15.20 Plot of reduced output as a function of reduced pressure for various values of *n*, the power law index (redrawn from Middleman; Reference 11).

unit area (Ω) times the area of solid to barrel contact. Assuming that the solid is at the full height of the channel depth and the melt and solid separated as seen in the melting mechanism discussed earlier, Equation (15.14) can be rewritten as Equation (15.15).

$$\dot{G}_{\mathrm{out}} = \dot{G}_{\mathrm{in}} - \Omega A$$

where: (15.15)

$$\dot{G} = \rho_{\mathrm{solid\ density}} V_{\mathrm{solid\ velocity}} X_{\mathrm{solid\ width}} H$$

Generalizing to any two locations, 1 and 2, in the extruder and substituting in the definition of G the mass flow rate of solid followed by rearranging terms gives an extrusion model, which can predict the width of the solid bed at any location along the screw from knowledge of the melting rate, the solid bed barrel contact area, the solid density (function of solid temperature and internal pressure), the down channel solid velocity, and the physical dimensions of the screw channel.

$$\rho_{\mathrm{S2}} V_{\mathrm{sz2}} H_2 X_2 = \rho_{\mathrm{S1}} V_{\mathrm{sz1}} H_1 X_1 - \Omega A$$

$$X_2 = \frac{\rho_{\mathrm{S1}} V_{\mathrm{sz1}} H_1}{\rho_{\mathrm{S2}} V_{\mathrm{sz2}} H_2} X_1 - \frac{\Omega A}{\rho_{\mathrm{S2}} V_{\mathrm{sz2}} H_2} \tag{15.16}$$

From this simple mass balance it is easy to see which factors are important in determining the output of an extruder screw and for the calculation of a screw's performance. In addition, the melting area can be broken down into several areas such as against the barrel, along the screw flights, and the screw root and the melting rate for each of these sections added to the overall melting rate.

15.5.2 Single-Screw Designs

The screw is the heart of the extrusion process and the screw design controls the performance of the extruder in providing a homogeneous molten polymer at the required rate, pressure and melt temperature levels, and stability. The typical single-screw design consists of three primary sections: the feed, transition and metering sections, and a single-screw flight with a helix angle of 17.7°, which yields a screw pitch equal to the diameter of the screw and is called a "square pitch" design (Figure 15.22). The square-pitch screw design predates the discovery of the melting mechanism by Maddock. These single flight designs evolved in part as a compromise in optimum screw helix angles for feeding and metering, and due to the difficulty in manually machining screws with longer and or variable pitch screws. Variable screw-pitch single-screws for optimizing screw performance are more common today primarily due to advances in CNC machining, which make variable screw pitches easier to machine. In many variable pitch designs, the screw is made with a square-pitch feed zone, an increased pitch transition section and a square-pitch metering section.

After the melting mechanism was described in 1959 by Maddock, variable width barrier section was invented by Maillefer [47] and the constant width barrier section screw design was invented by Barr [48]. Other barrier screw

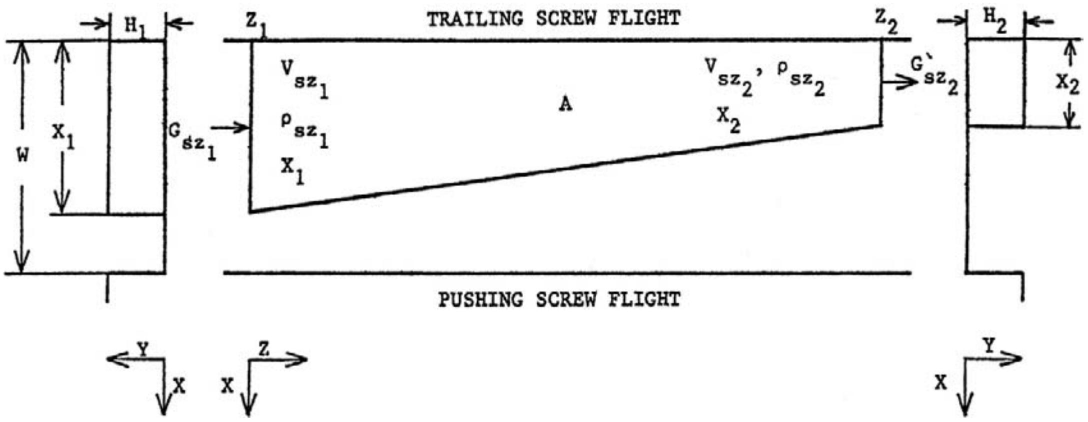


Figure 15.21 Mass balance around the melting solid plug showing the key variables needed in an extrusion model.

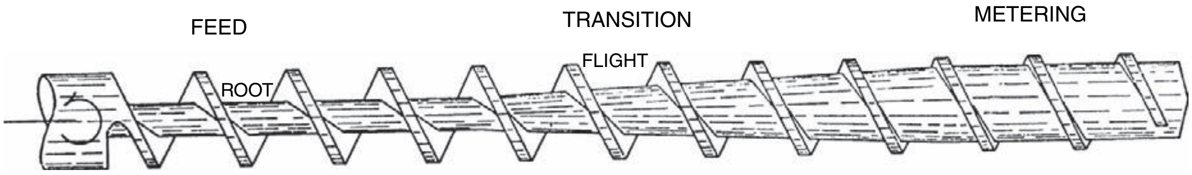


Figure 15.22 Schematic of a square pitch or general purpose screw design.

designs were patented by Geyer [49], Lacher [50], and Dray [51]. A good review of screw designs can be found in Chung [8].

Barrier screws increase output by increasing solid/barrel contact area.

15.5.2.1 Mixing

Mixing is another critical extruder function even when processing only one virgin polymer stream. The two types of mixing occurring in the extruder are distributive and dispersive mixing. As their names describe, distributive mixing evenly distributes particles throughout the melt while dispersive mixing breaks up agglomerates or large particles and disperses them evenly throughout the melt.

Distributive mixing is a low-shear process accomplished by repeatedly changing the flow directions by breaking the molten polymer into channels and recombining the melt. Distributive mixing is used with fibers, reinforcing fillers, shear-sensitive materials, and to provide uniformity of melt temperature. Dispersive mixing is a high shear stress process where molten polymer is forced through very small openings generating significant shear heat. Dispersive mixing is used in alloying different plastics, pigment dispersion, and mixing nonreinforcing fillers and additives, such as flame retardants, impact modifiers, lubricants, and so forth.

For single-flight screw designs, the extrusion goal of achieving a uniform melt temperature and homogeneous melt is best attained with the addition of a mixing head to the screw. The degree of mixing is determined by the residence time and the shear rate the fluid is exposed in the mixing section. Single-screw extruders without mixing sections do a relatively poor job of mixing and homogenizing; the spiraling flow in the metering section of the screw and the large variations in shear histories, depending on where the material is in the screw channel, do not lead to extensive mixing. The type mixing section to add to the extruder screw depends on the polymer being processed and type of mixing required. For the energy transfer screws, distributive mixing is purposely increased in the screw design by flight interchanges and the absolute need for a mixer for thermal homogenization is reduced. Mixers are often times added to add a high shear section to a screw for the purpose of improving particulate dispersion or breaking down high-molecular-weight gels. However, the incorporation of a distributive mixer will increase the discharge temperature from the screw. Some dispersive and distributive mixer designs [46] are shown in Figure 15.23.

Because polymer mixing flows are laminar, the number of changes in the flow direction determines the degree of distributive mixing. Distributive mixing sections divide the flow into a number of channels, recombine the flow, break the flow, etc. and improve temperature homogeneity. Typical distributive mixers added to screw designs are pins in the screw channel (15.23A), Dulmage (15.23B), Saxton (15.23C), and pineapple mixer (15.23D).

For example, consider the actions of the Dulmage, pineapple, or Saxton mixing sections shown in Figures 15.23A–C. Polymer exiting the metering section is pumped in a spiraling motion from the metering section (Figure 15.13). Once the material gets into the mixing section, the flow is broken up from one large channel or flow front into numerous small channels or flow fronts. Flow fronts recombine and are subsequently redistributed into small flow channels again and then recombined. Other distributive mixers have obstacles in the screw channel to change the direction of polymer flow to achieve the required degree of mixing.

Dispersive mixing requires high shear rates and high shear stresses that are achieved by forcing the melt over a restrictive barrier. Dispersive mixing sections require more energy than distributive mixing. The higher energy input will raise the polymer melt temperature or might cause degradation. Three common dispersive mixing sections are shown in Figure 15.23. The Maddock mixer (Figure 15.23G) contains numerous channels open on one end parallel to the screw length. Alternating channel openings face toward the metering section and the die end of the screw, respectively. Molten polymer, flowing into the channel from the metering section, is forced over a restrictive barrier into the next channel before exiting toward the die. All materials are forced over this restrictive barrier with low clearance between the flight and the barrel wall before it can exit the extruder. The Egan mixer (Figure 15.23H) is similar in operation to the Maddock, but has a helical configuration to the separate channels. A second example of a dispersive mixing section in Figure 15.23 is a blister ring (Figure 15.23J). The clearance between the barrel wall and the top of the blister ring is greater than the distance between a screw flight and the barrel wall. All molten polymers flow over the blister ring in a high shear environment.

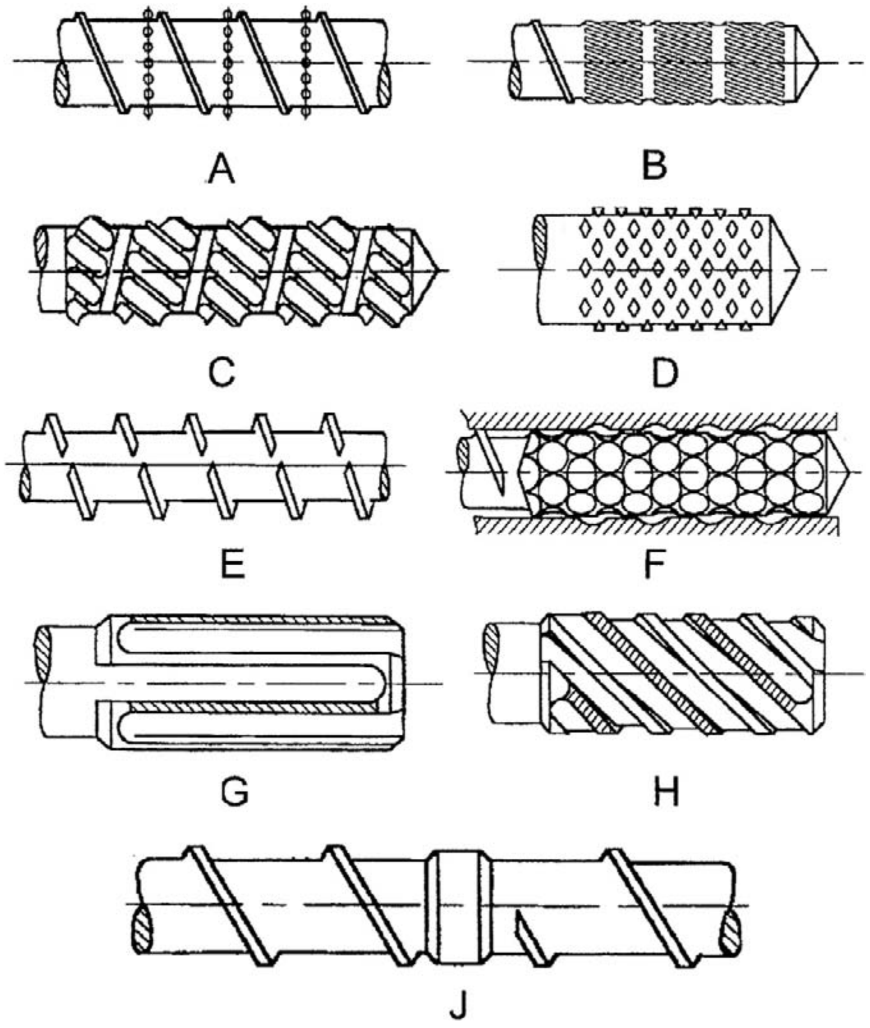


Figure 15.23 Various distributive and dispersive mixer designs (From Figure 2 of Reference 46).

The third example of polymer mixing due to screw design clearances is a barrier screw. All barrier screws have a secondary screw flight with a slightly smaller outside flight diameter from the primary flight (Figure 15.23). The secondary (or melt) channel initial width or depth is small compared to the primary (or solids) screw channel and may be varied along the length of the screw. As the flights revolve around the screw, the primary and secondary channel width can remain constant (Barr Design) or the secondary channel width may increase as the primary channel width decreases (Maillefer design). At the end of the barrier section, the secondary channel becomes the principal channel and the primary channel disappears. In all barrier designs, molten polymer must cross from the primary channel over the secondary flight into the melt or secondary channel (Figure 15.23). As the primary channel and screw flights disappear, the polymer crosses the barrier or secondary flight between the top of the flight and the barrel wall experiencing a high shear stress, which results in the dispersive mixing.

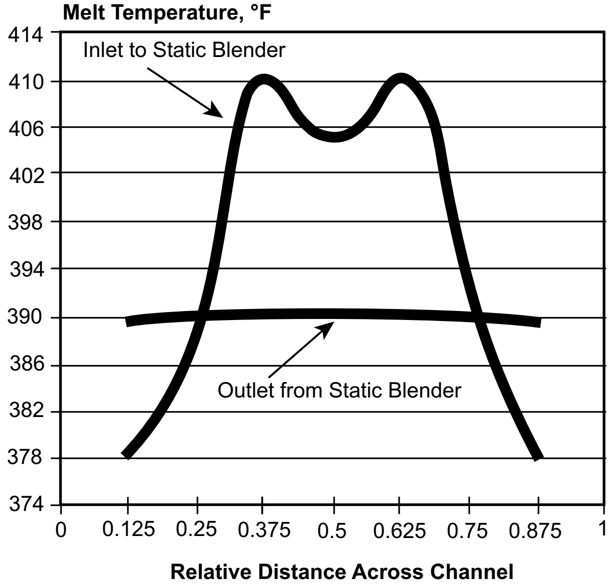


Figure 15.24 Melt temperature profile before and after a static mixer.

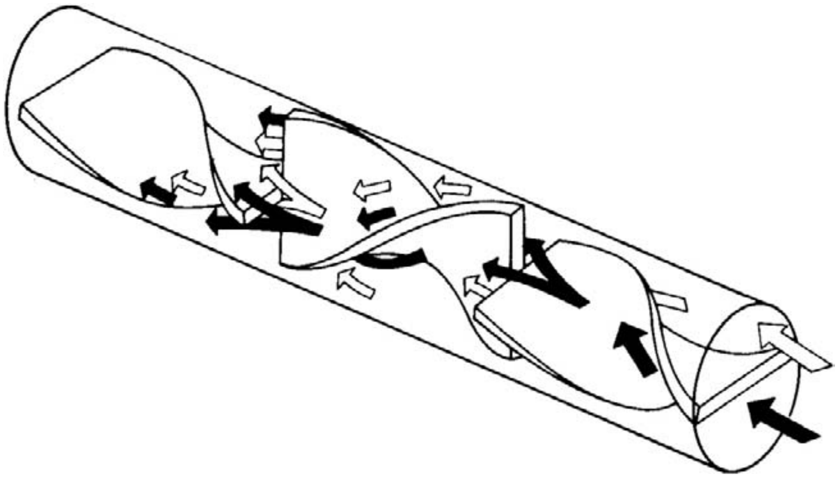


Figure 15.25 Polymer flow distributive mixing mechanism of the Kenics® Static Mixer.

Barrier flights in the metering section of the screw after the transition section are designed for dispersive mixing, while barrier flights in the transition zone are designed for improving the melting efficiency. The dispersive mixers shown will help to prevent solid polymer from entering the metering section and the die in the event of solid bed breakup. Large solid particles will not pass through the tight tolerances between the barrier and barrel wall and the high shear stresses can complete the breakdown and homogenization of small unmelted particles.

Another type of mixer is called a cavity mixer, with cavities in the end of the screw and barrel (Figure 15.23F) designed for distributive mixing. These types of mixers are inferior to the other distributive mixers listed in Figure 15.23 as they do not wipe the barrel, are not operator friendly because they are hard to clean, have no forward pumping capabilities, and generate large pressure drops [1]. Cavity mixers are normally added as extensions to the screw when mixing is inadequate.

Another approach to use when mixing or thermal homogenization is inadequate, and no mixing elements are present on the screw, is a static mixer in a transition pipe between the end of the extruder and the die. A number of static mixer designs are available that provide good distributive mixing by constantly dividing and recombining the flow stream. The Kenics®, Koch®, and Ross ISG® mixers are examples of commercially available static mixers available in many different configurations and geometries depending on the mixing requirements. Static mixers are installed in pipes where the fluid motion is essentially a plug flow and result in rearrangement of the flows but result in increased pressure drop in the melt pipe. Figure 15.24 shows the polymer temperature profile across a transition pipe at the entrance and exit of a static mixer [1] demonstrating that static mixers are excellent thermal homogenizers. In addition to improved melt temperature uniformity with a static mixer, homogenization of colorants and additives is improved, so lower concentrations may be used in the formulation to attain the same results. Static mixers are used extensively in fiber production. Figure 15.25 shows a Kenics® static mixer and the method by which it divides and recombines the flowing polymer.

The following are the general guidelines for single-screw mixing element design:

- Mixing section produces a minimal pressure drop with forward pumping capability.
- No material hang-up or dead spots exist where polymer can agglomerate and degrade.
- Mixing device completely wipes the barrel surface.
- Mixing device is easy to disassemble, clean, and reassemble.
- Reasonably priced, which is directly related to the difficulty of machining.

15.5.3 Twin-Screw Extruder Equipment

There are a number of different types of twin-screw extruders commercially available depending on the type of end-use application. Different models have two parallel screw shafts that either rotate in the same direction (called co-rotating) or rotate in opposite directions (called counter-rotating) with varying distance between the screw shafts. This results in screw configurations, which range from fully intermeshing to non-intermeshing. Figure 15.26 shows

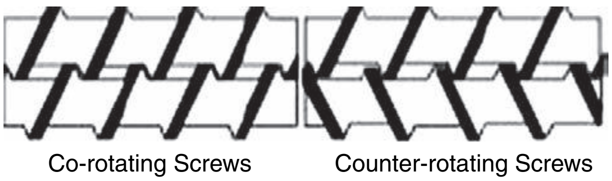


Figure 15.26 Comparison of fully intermeshing co and counter rotating twin screw extruder conveying sections.

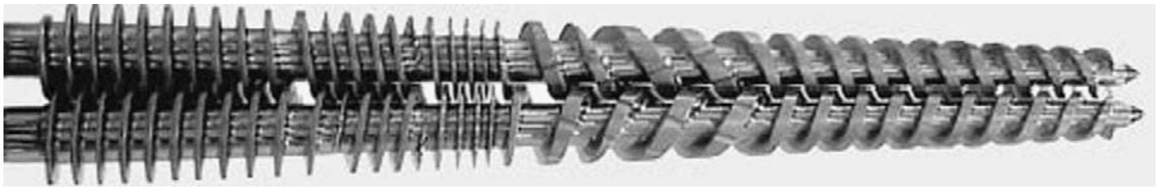


Figure 15.27 Screws from a fully intermeshing conical twin screw extruder.

a short segment conveying screw element in parallel co-rotating and counter-rotating screws that are fully intermeshing. In non-intermeshing extruders the screw lengths of the two shafts can be equal or one screw can be longer than the other to provide better melt pumping capability to the die as in a single-screw metering section. The other common type of twin-screw extruder is conical where the counter-rotating intermeshing screws are tapered rather than parallel. Figure 15.27 shows the screw geometry in a conical extruder. This section describes the different types of twin-screw extruders, their hardware, and how they differ from single-screw extruders.

The principal differences in parallel intermeshing and non-intermeshing twin-screw extruders depends on whether the screws are rotating in the same direction, co-rotating or in opposite direction, counter-rotating, and the distance between the screws. Figure 15.28 shows a schematic summarizing the different types of parallel twin-screw extruders and applications where the different types of twin-screw extruders are used. High-speed co-rotating twin-screw extruders are used for compounding resin with a wide assortment of additives (colorants, fillers, flame retardants, reinforcements, fillers, stabilizers), devolatilization to remove solvents, and reactive extrusion (chemical reactions done in situ in the extruder). Low-speed co-rotating and counter-rotating extruders are used by extrusion manufacturers to produce profiles and pipe. Counter-rotating twin-screws are used for compounding PVC and other resin systems. Non-intermeshing counter-rotating extruders are principally used for devolatilization and chemical reactions, i.e., grafting, polycondensation, addition, controlled cross-linking, and functionalization. Twin-screw extruders are finding homes in sheet and film extrusion where different formulation ingredients can be compounded and formed in the same extrusion. This eliminates the middle step of compounding and re-extruding to produce a final product.

Figure 15.29 shows a schematic of a parallel twin-screw extruder with four of the five major equipment components identified, the drive, feed, screw and barrel, and the die or head. The fifth equipment component not shown is the control cabinet. The drive system is composed of an electric motor, cooling system for the motor, coupling between the motor and gearbox, thrust bearing, gearbox, oil lubrication and cooling for the gearbox, and shaft coupling between the gearbox and the extruder screws. One feed port is located at the rear of the extruder in the first barrel section. Additional feed streams can be added in numerous locations along the barrel length through either gravity from a volumetric or gravimetric feeder, liquid feed using a pump with a liquid injection nozzle, and/or a side-feed extruder or stuffer to add polymer, additives, fillers, or reinforcements at a number of locations along the barrel. Screw and barrel sections are both modular. Barrel sections can be added or removed to make the extruder barrel longer or shorter to increase or decrease

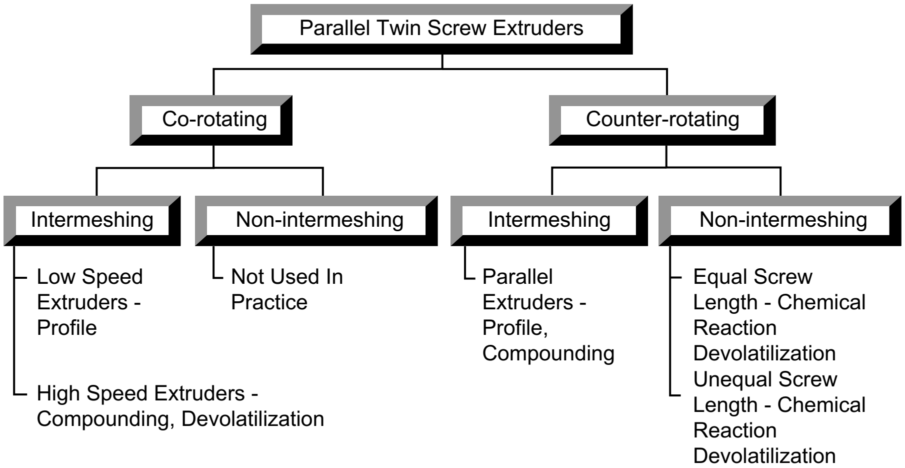


Figure 15.28 Comparison of intermeshing and non-intermeshing twin-screw extruders schematic summarizing the different types of parallel twin-screw extruders and applications.

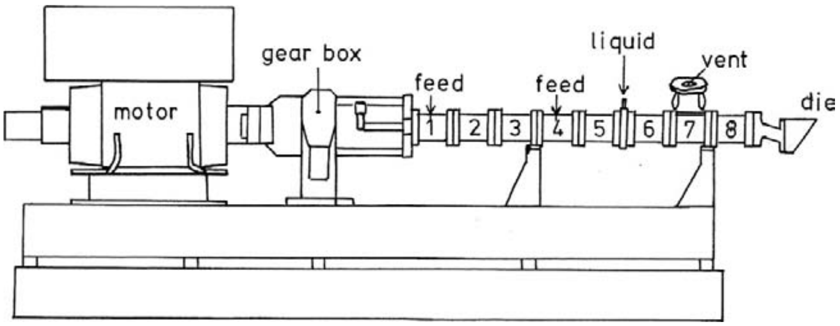


Figure 15.29 Schematic of a parallel twin screw extruder showing 8 barrel sections and with major equipment components identified.

compounding capabilities depending on the product application. A set of screw shafts is required for each extruder length that depends on the number of barrel sections. Additional barrel sections are normally added to increase process flexibility for downstream feeding or venting. Each barrel section is normally cooled with water and heated with cast heaters to control barrel temperature. Screws are modular with different elements combined in a strategic design to localize the feeding, melting, conveying, mixing, pumping, and venting at specific locations along the extruder barrel. Screw designs are easily changed or modified to optimize the processing depending on the materials being fed and the product requirements. The adapter between the end of the extruder and die can be equipped with a gear pump and a screen pack for melt filtration. Use of an automatic screen changer and gear pump between the end of the barrel and the die is becoming common in sheet extrusion lines. Melt temperature and pressure transducers are located at the exit of the extruder to monitor and/or control the process.

The difference between co-rotating and counter-rotating twin-screw extruders is the direction of screw rotation relative to each other. In co-rotating extruders both screws rotate in the same direction while in counter-rotating extruders one screw rotates clockwise, while the other screw rotates counterclockwise. With co-rotating screws both screws have either right-handed or left-handed thread depending on the direction of screw rotation while in counter-rotating extruders one screw has a right-handed thread and the other has a left-handed thread. Polymer flow in a fully intermeshing co-rotating extruder makes a pattern as shown in Figure 15.30, as the material does not pass between the screws. This generates a high- and low-pressure region for the material near the extruder apex as shown in Figure 15.30. Polymer flow in a counter-rotating extruder is forced between the two screws resulting in a high pressure region at the nip where the material is being forced between the screws and a low-pressure region at the nip exit (Figure 15.31).

In addition to the identification of twin-screw extruders based on the direction of screw rotation, the distance between the two screws varies from fully intermeshing at one end of the spectrum to non-intermeshing with distance between the screws at the other extreme. Material flow and the shear generated depend on the degree of intermeshing [53,54]. Screw designs (Table 15.2) are defined as either open or closed based on whether material can flow in a particular direction [54]. If material can flow in an axial or longitudinal direction from the feed throat to the die, the screw is open in the length direction. Theoretically, material can move from one channel to the next channel allowing flow in the lengthwise direction. If the screw is closed to material flow in the axial direction, the length is considered closed.

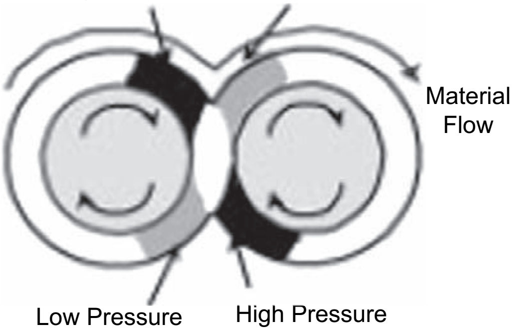


Figure 15.30 Schematic of co-rotating screws defining location of high and low pressure regions.

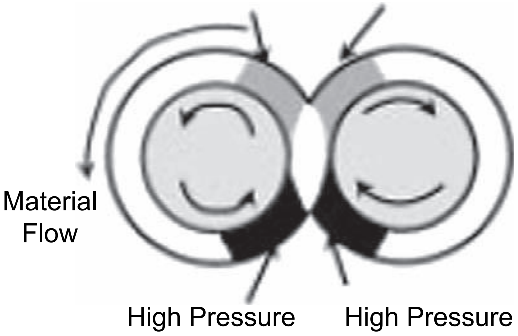


Figure 15.31 Schematic of counter rotating screws defining location of high and low pressure regions.

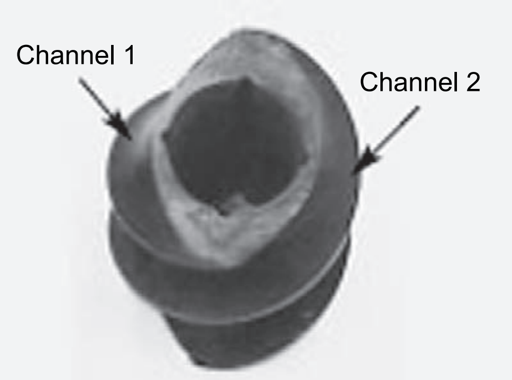
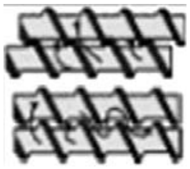
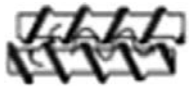


Figure 15.32 Two lobe conveying element showing the two separate channels and screw flights.

Partially intermeshing co-rotating screws are open to flow in both the axial and cross-machine directions. In the cross-machine direction the channel is considered open if the material can flow around a particular screw channel. Partially intermeshing counter-rotating screw elements have material flow both lengthwise in the axial direction and across the extruder as the material passes between the screws. Referring to Table 15.2, with fully intermeshing co-rotating screws material cannot pass between the screws because of the screw rotation [54]. As one screw is rotating down, the other screw is rotating up preventing material flow. Table 15.2 shows various twin-screw extruder configurations and those screw configurations that allow material flow axially and across the channel and those that do not. Normal leakage flow caused by the requirements for mechanical clearance between the two screws is not considered in the material flow behavior. Depending on whether the screw configurations are open to cross or lengthwise flow is directly related to the conveying, mixing, and pumping efficiency in a particular type of extruder.

If the axial length is closed, the pathway down the screw is divided into a number of isolated areas with no opportunity for flow in the axial direction. Open cross-flow allows a material path around the screw, the polymer flows in the radial direction, as it transfers back and forth between the screws. If the cross-direction is closed, material cannot flow between adjacent screws resulting in no flow in the radial direction. When both the length and cross-flow are open, good distributive mixing along with poor pressure

Table 15.2 Comparison of possible configurations for intermeshing twin screw extruders

Screw Distance	Material Flow	Counter-Rotating	Co-Rotating
Fully intermeshing	Closed to length and cross		Impossible
	Open to length closed to cross	Impossible	
	Open to length and cross	Possible, not practical	Kneading blocks and gear mixers
Partially intermeshing	Open to length closed to cross		Impossible
	Open to length and cross		
Non-intermeshing	Open to length and cross		

generation results. Good distributive and dispersive mixing but poor pressure generation occurs with the length open and the cross-material flow closed. If both the length and cross-flow directions are closed, good dispersive mixing results with good pressure generation. Non-intermeshing twin-screw extruders are open both axial and across the barrel regardless of whether the extruder is co-rotating or counter-rotating.

The relative comparison of processing parameters for the three basic types of parallel twin-screw extruders is displayed in Table 15.3 [55]. Definitions of the various processing parameters compared are as follows.

- *Practical residence time* is the time that polymer, additives, or other components of the formulation will spend in the extruder from feed to the die.
- *Residence time distribution* is the time range that different particles spend in the extruder from the shortest to longest time.
- *Dispersion* is the ability of the extruder to breakup large particles, agglomerates, or the melt in general and uniformly disperse it throughout the melt.
- *Heat transfer* is the ability of the barrel heaters to transfer heat into the material being processed to create a uniform temperature profile throughout the melt.
- *Venting* is the ability of the extruder to remove volatiles or moisture through a single or multiple vent ports along the barrel length.
- *Pumping* is the ability of the extruder to deliver a uniform melt pressure and material supply to the die.
- *Self-wiping* is the result of one intermeshing screw element removing polymer from the adjacent screw element.
- *Zoning* is the ability to provide specific areas or zones in the extruder to accomplish specific extrusion objectives such as melting, mixing, and feeding.
- *Output rate* is a measure of the throughput rate or pounds/hour that can be delivered by a specific extruder size or diameter.
- *Distributive* mixing is a measure of the degree of low shear mixing to provide a uniform distribution of all components and melt temperature in the extrudate.

Twin-screw extruders for plastic processing have evolved over the past 50 years from extruders with an over/under twin-screw arrangement or geometry to a side-by-side configuration providing better feed of low-bulk density powders and other materials. Early side-by-side extruders used three-lobe conveying elements (three separate flights around each element) coupled to motors with limited torque and small gearboxes. Three-lobe screw elements have been replaced with two-lobe elements (two flights and screw channels around each element, see Figure 15.32) increasing the free volume and throughput capacity of the extruder. Extruder equipment changes accompanying the two-lobe screws are larger motors that generate higher torque, higher torque screw shaft to transfer the increased power to the screw, and an increased centerline distance leading to more free volume within the extruder. Combining all the equipment changes, throughput rates for two-lobe twin-screw extruders have increased dramatically.

With intermeshing screw elements, the shaft centerline distance and screw diameter determines the free volume, the shear rates, and the characteristic outside to inside diameter of the screw elements (D_o/D_i). The channel depth of the conveying elements is a function of the centerline distance, the outside diameter, and the number of screw flights. The

Table 15.3 Comparison of key attributes for twin screw extruders

	Co-Rotating Intermeshing	**Counter-Rotating Intermeshing**	**Counter-Rotating Non-Intermeshing**
Practical residence time (min)	0.35–6	0.35–6	0.35–6
Residence time distribution	Variable	Variable/tighter	Variable
Dispersion	High	High	Good
Heat transfer	Excellent	Excellent	Excellent
Venting	Excellent	Excellent	Excellent
Pumping	Good	Excellent	Fair
Self-wiping	Excellent	Good	Fair
Zoning	Excellent	Excellent	Good
Output rate	High	Moderate	High
Distributive mixing	Good	Good	Excellent

channel depth must provide enough wall thickness between the inside diameters of the screw element and the shaft to transfer the torque from the motor and shaft to the screw elements. Deep channels were cut in the three-lobe elements to transfer the torque by means of one or two large keyways. In the two-lobe systems there is not enough wall thickness for these large keyways. Different systems have been developed to transfer the torque with the thinner screw element walls. The combination of the open channel depths between the screw and the barrel wall (less any channel space occupied by the intermeshing flight of the adjacent screw element) plus the space between the kneading blocks or other elements and the barrel wall makes up the extruder free volume. Extruder free volume is a measure of the amount of space available in the barrel for pellets, powder, reinforcements, fillers, and/or polymer melt with a specific screw configuration. Extruder free volume is given by Equation (15.17):

$$V_0 = A_0 \times L \tag{15.17}$$

where V_0 is the free volume, A_0 is the screw element open area and L is the length of the screw.

A_0 can be calculated for each screw element using Equation (15.18):

$$A_0 = A_b - A_s \tag{15.18}$$

where A_b is the barrel area and A_s is the screw area.

Greater free volume gives the extruder higher throughput capacity.

Free volume is directly related to the ratio D_o/D_i and the shaft centerline distance. The amount of free volume is balanced versus the extruder torque. Screw shafts must be able to transfer the available motor torque through the screws to process a specific quantity of material. As the extruder free volume increases, more open space will be available in the extruder barrel resulting from deeper screw channels. With deeper screw channels the amount of metal between the bottom of the channel and the screw shaft decreases providing less area to transfer the motor torque each screw element. Consequently, the ratio of the outer to inner screw element diameter reaches an optimum value. At low values of D_o/D_i there is very little free volume in the extruder and the distance from the screw shaft wall to the bottom of the channel is fairly large. In this scenario high torque can be transferred from the motor to the screw but only limited torque is required because the volume of material in the extruder is reduced. With high values of D_o/D_i, higher extruder free volume is available allowing more material to be processed. However, the thickness of the screw element wall between the bottom of the channel and the shaft wall has decreased making it more difficult to transfer the torque required for processing from the motor to the extruder. The centerline distance between the shafts becomes important because of the smaller distances that limit the thrust-bearing size in the gearbox reducing the amount of torque that can be transferred from the motor to the screw shafts. Larger screw shafts that can transfer more torque have less free volume in the barrel and a greater centerline distance. Consequently, less material is processed when larger diameter shafts are present. This becomes a balancing act as smaller screw shafts lead to more free volume while the shafts, thrust bearings, centerline distance, and keyways must be able to handle increased torque. Figure 15.33 shows graphically the relationship between D_o/D_i, torque, and free volume.

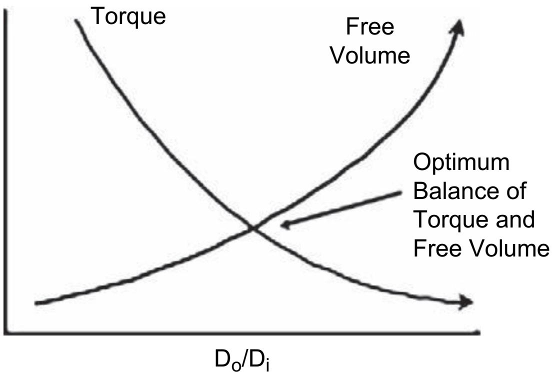


Figure 15.33 Graph of the relationship between D_0/D_i, torque, and free volume for twin screw extruder.

As extruders evolved from three-flight, three-lobe elements to two-flight, two-lobe elements the free volume increased. Increasing both the D_o/D_i ratio and the centerline distance raises the free volume more. The relationship of free volume relative to the number of lobes and the D_o/D_i ratio of various commercial extruders is shown in Table 15.4 [1]. Most manufacturers of co-rotating twin-screw extruders today have a centerline distance, a, and flight depth, h, given by Equations (15.19) and (15.20), respectively:

$$a = \frac{D_0 + D_i}{2} \tag{15.19}$$

$$h = \frac{D_0 - D_i}{2} \tag{15.20}$$

Table 15.4 Comparison of free volume for different D_0/D_i ratios

Type	D_o	D_i	Free Volume
3 Lobe	55	1.26	0.52
2 Lobe	57	1.44	0.86
2 Lobe	58	1.55	1.0
2 Lobe	60	1.54	1.0

As free the volume increases, the extruder torque had to increase to process the additional resin capacity. With thinner screw element walls between the screw shaft surface and the bottom of the channel depth the challenge was how to transfer the higher torque provided by larger motors and gearboxes to the screw elements. Early three-lobe machines had one large rectangular keyway on each shaft. With the introduction of the two-flighted two-lobe machines one keyway was still used with two key channels 180° apart on the inside of the screw element. As the inside screw element walls became thinner with the increase of the D_o/D_i ratio, the keyway was replaced by four round rods, hexagonal or octagonal shafts, or splined shafts depending on the extruder manufacturer.

Free volume increases require higher motor torque since most of the energy to melt plastic is supplied by the motor. As the amount of material in the extruder increases the quantity of energy to process the plastic must increase proportionally. Increasing the motor power provides more torque at constant screw speed. High screw speed translates to more power allowing more material to be fed per unit time.

Torque in rotational motion is the power divided by the angular velocity. The torque is then calculated by rearranging the power Equation (15.21):

$$\text{Power} = C \times \text{torque} \times 2\pi N \tag{15.21}$$

where

C = Conversion factor (1 hp = 33,000 ft-lb/min)
P = Power given in horsepower (hp)
N = Screw speed given in rpm
Torque = lb-ft

Starve-fed twin-screw extruders run at high rpm to generate enough power to convey, melt, mix, and pump the polymer to the die. In addition to increased free volume, modern twin-screw extruders have the capability of running at very high rpm. The specific energy, measured in kW-h/kg, is related to how much material can be processed based on screw speed and power input. As the screw speed increases, the available power increases, allowing more material to be processed. At low screw speed there is very little power available; consequently, if the extruder is overfed, the motor and drive will stall because the system torque and power requirements are exceeded. This means that when starting a starve-fed extruder, the screw is first started and material is fed slowly to the extruder. Once material exits the die, the screw speed is increased before more material is fed to the extruder while monitoring the torque. If too much material is fed, the power requirement is exceeded and the drive and motor will stall. The amount of material that can be fed depends on the power available and the screw speed. During operation, the screw torque is constantly monitored and must be maintained below a maximum value.

Related to the power and torque requirements is the degree of fill of the screw flights in the extruder. Since the extruder is starve-fed and the screw speed is running at sufficient speed to remove all the materials being fed, most of the screw elements are not full of material. (Depending on the screw elements and the screw configuration, some sections of the screws may be completely filled.) The percentage fill at any location along the extruder screw is a function of the feed rate, screw rpm, screw pitch, screw configuration, and pressure gradients along the screw. In calculating shear rates, the values change depending on the degree of fill. If the degree of fill is 30%, the total free volume available between the screw and the barrel wall is 70% as only 30% of the total volume available for polymer melt is occupied. Each conveying channel may only be partially filled with solid or molten polymer depending on the screw element pitch and the screw configuration.

Material in the extruder experiences a range of residence times based on the screw design, type of twin-screw extruder, *L/D* ratio, screw speed, and feed rate. The average residence time is defined by t_{mean} given by Equation 15.22:

$$t_{\text{mean}} = \frac{V}{Q} \tag{15.22}$$

where
V = Used volume (amount of free volume used)
Q = Total volume

Counter-rotating intermeshing twin-screw extruders have the narrowest residence time distribution followed closely by co-rotating intermeshing twin-screw extruders. Counter-rotating non-intermeshing twin-screw extruders have the broadest residence time distribution.

Some co-rotating twin-screw extruders operate with their screws turning in a clockwise direction while others operate in a counterclockwise direction. Discussions to this point have assumed a clockwise direction with right-handed conveying elements moving material from the feed throat to the die and left-handed elements moving material back toward the feed throat. If the co-rotating screws rotate in a counterclockwise direction, left-handed elements convey material from the feed throat toward the die while right-handed elements convey material back toward the feed throat. In the case of counter-rotating extruders, one screw rotates clockwise and the other rotates counterclockwise. Consequently, the screw elements on the clockwise rotating screw are right-handed elements to convey material toward the die while the screw rotating counterclockwise uses left-handed conveying elements to move the material toward the die.

Parallel co-rotating intermeshing twin-screw extruders are one of the more common types of twin-screw extruders that are presently available, and they are produced by a number of different companies.

15.5.3.1 Twin-screws: Screw, barrel, heating, and cooling

The screw and barrel are the heart of the machine where polymer is fed, melted, conveyed, mixed, devolatilized, and pumped to the die. Both the screws and barrel sections are modular and can be arranged in any configuration necessary to accomplish a particular extrusion objective. Barrel sections normally have either rectangular or circular outside dimensions depending on the manufacturer. They are assembled with either a rod through all the sections or with bolts holding the sections together. The barrel is supported at different locations along its length to prevent it from sagging. Each barrel section contains a thermocouple to control the heating and cooling input. Barrel sections have flanges on each end for alignment and connection to the next barrel. While it is a sizable task, barrel sections can be unassembled, reconfigured, and reassembled to move feed and vacuum sections. Some machines (particularly smaller ones) may have a clamshell barrel design where the barrel separates in the middle and the entire screw length is exposed. Clamshell barrels are one piece construction rather than modular sections that bolt together. Individual heating and cooling zones along the barrel provide temperature control similar to that of a water-cooled single-screw extruder.

Barrel sections like extruders come in different *L*/*D* ratios. Typical lengths depend on the screw diameters and the manufacturers of the different extruders. Some common *L*/*D*s are 2.5, 3, 4, 5, 6, 8, 10, and 12. There are a number of different types of barrel sections, those used for feeding with an opening on top, feeding into the side with a vent on top, or a solid barrel normally called a vent barrel, combi barrel, or closed barrel, respectively. The vent barrel has an opening on top that may be either circular or rectangular and is used to vent volatiles from the barrel or to feed different components of the formulation. The first barrel section in the extruder is opened on top for feeding all or part of the formulation into the extruder. It is cooled and normally has no heaters on any of the sides. The normal pattern bore (Figure 15.8) connects to an end plate that prevents the formulation from traveling backward toward the drive system, with the other end connecting to the next barrel section. Other vent or feed barrel sections have an opening on top with cast heaters contacting the barrel on the other three sides. Barrel sections containing a vent plug can be used to feed liquid through an injection nozzle, gravity feed polymer farther downstream, or to vent volatiles with the use of a vent stack. The vent stack can be open for atmospheric venting or it can be connected to a vacuum port to remove a higher level of volatiles through vacuum venting. The combi barrel has an opening on top for gravity feeding and an opening on the side for addition of material by a side-feed extruder. Combi barrel sections are cooled similar to other barrels but only two of the four sides are heated when the side-feed extruder is connected. If the side-feed extruder is not in use the port can be plugged and heated similar to the vent barrel. The last type of barrel section is a closed barrel with no openings on the top or side. This barrel is heated with cast heaters on all four sides and cooled similar to the other sections. If an atmospheric or vacuum vent is used the vacuum port covers half of the screw to prevent material from flowing out of the vent.

Barrels and screw are normally nitrided steel for long life. Through-hardened barrels are available and some barrels are lined with wear-resistant liners to increase life. Liners provide resistance to corrosion and abrasion. Other metal treatments are also available to increase service life.

Different types of cast barrel heaters are available depending on the application and temperature requirements. Aluminum heaters have a temperature range up to 660 °F (350 °C), while aluminum/bronze alloy heaters go up to 840 °F (450 °C).

Two types of barrel cooling are available: (1) cooling bores, with a number of holes bored around the barrel next to the barrel liner and (2) water cooling in the heater with a loop running around the heating element. Combining both types of cooling provides the maximum temperature control for the system. In some circumstances the screw shafts can be cooled for better temperature control if required. Water or oil is pumped in a tube down the center of the shaft and returned on the outside of the tube. This provides good heat transfer to the outside surface of the screw shaft and inside surface of the screw elements. Maximum cooling occurs at the extruder discharge end. Reversing the flow provides maximum cooling at the extruder feed end.

For a welding engineer counter-rotating non-intermeshing twin-screw extruder, the barrel section does not appear radically different from the intermeshing barrels shown previously and the drive system components are similar. The only slight difference is the apex area of the barrel where the metal on top and bottom of the bore extends farther toward each other due to the larger screw centerline separation distance.

Similar to the barrel sections, screw elements are modular and are inserted on to the screw shafts to provide the proper conveying, melting, mixing, downstream component addition, venting, and pumping to produce a commercially acceptable product. Specific screw designs are developed to accomplish various objectives. The following are important to understand the extrusion requirements before assembling the screw.

- Where along the extruder barrel do you want the material to melt?
- What location do you want to add ingredients downstream?
- How much and what kind of mixing is required to produce a homogeneous melt?
- What type of rate is required?

- Does the product need atmospheric or vacuum venting and at what location?

Before assembling a specific screw configuration, the following points must be considered;

- All elements must be cleaned on both outside and inside.
- The ends lapped to provide a good sealing surface between the elements.
- The shafts, keyways, or splines must be cleaned so elements slide on the shafts easily.
- Antisieze applied in a thin coat to all surfaces during assembly.

A specific screw design is developed for the process and documented. The design is used to assemble the elements in the correct order. Figure 15.34 shows a typical setup to use when constructing or assembling a new screw design. During screw assembly, antisieze application is essential to assure that the screw can be disassembled later. However, excessive antisieze must be avoided to prevent the formation of gaps between the elements where polymer will flow between the elements under pressure down to the shaft. Over time at high-temperature, polymer trapped between the screw elements and the shaft degrades and chars making screw element removal very difficult.

Screw assembly is critical; the elements must be placed on the shafts in pairs (element on shaft 1 must be the same as element on shaft 2). With multiple keyways, splined shafts, or polygon shafts there is only one correct position to install each element. The flights of each element must match the flight of the preceding and following elements to prevent dead spaces along the shaft creating a smooth polymer flow. If any element is out of place or a left-handed element is used on one shaft and right-handed one on the other, the screw shafts will not rotate and the screw elements have to be removed back to the mistake and then reinstalled. Identical kneading blocks like conveying elements have to be installed at the same place on the shafts or the shafts will not rotate.

Figure 15.34 Picture of the screw shafts and screw elements ready for assembly.

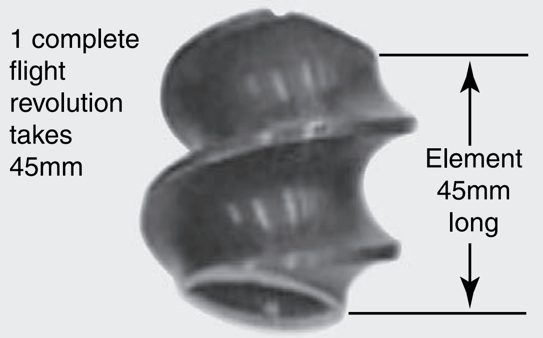


Figure 15.35 A 45/45 conveying element.

Next, the nomenclature used to identify different screw elements will be outlined. In a two-lobe screw design, each conveying element contains two flights with the elements sometimes called two-flighted elements. Two numbers identify conveying elements (independent of the diameter of the element) that represent the element pitch and element length. A 45/45 conveying screw element is shown in Figure 15.35. The top number represents the pitch or the length of screw element required for a given flight to make one complete revolution around the element while the bottom number represents the element length. Consequently, in Figure 15.35, the pitch is 45 mm or it takes 45 mm for a flight to complete one revolution about the element, and the element is 45-mm long. Many combinations of pitch and length are possible for conveying elements, for instance, a 60/60, a 30/30, or a 90/90. Conveying elements can be either right-handed or left-handed pitch to convey material forward or rearward in the barrel. Figure 15.36 shows a 60/60 right-handed element followed by a 60/30 left-handed conveying element, followed by another 60/60 right-handed conveying element. The left-handed element acts as a melt seal or a place to build pressure in the screw.

Mixing elements, called kneading blocks, have a number of disks in different spatial configurations around the element. An additional number is added to the kneading block nomenclature indicating the number of disks. A 45/5/30 kneading block (shown in Figure 15.37) has the first disk rotated 45° from the original disk with a total of five disks and

Figure 15.36 A left hand 60/30 conveying element preceded and followed by right hand 60/60 conveying element.

Figure 15.37 A 45/5/30 kneading element showing the 45 degree rotation of each block, the 5 elements and the 30 mm segment length.

an overall length of 30 mm. A 45/5/45 kneading block (shown in Figure 15.38) has the second block rotated 45° with a total of five disks in a 45 mm overall length. Similar to conveying elements there are right-handed and left-handed kneading blocks with the disks rotating in either a right-handed or left-handed pattern. Neutral kneading blocks have the second disk at 90° rotation from the first disk. These are designated as 90/3/15 where the second disk is 90° from the first, with three disks and a total length of 15 mm. There are many other special-purpose screw elements from different machine manufacturers that can be used in specialty screw designs.

Screws and barrels for conical counter-rotating extruders are significantly different from the parallel intermeshing co-rotating and counter-rotating extruders. Similar to single-screw extruders, the barrel is not segmented and modular but one piece. Likewise, the screws are one piece. Conical twin-screws are used primarily for rigid or unplasticized polyvinyl chloride (PVC) extrusion into profiles (window, siding, gutters, etc.) and pipe. Conical screws and barrels have a large diameter at the feed throat and get progressively smaller toward the die. A set of conical twin-screw extrusion shafts from CPM GmbH is shown in Figure 15.27. The outside view of a conical extruder looks similar to a single-screw extruder with heater bands, cooling, and barrel covers for safety.

Figure 15.38 A 45/5/45 kneading element showing the 45 degree rotation of each block, the 5 elements and the 45 mm segment length.

Both the root diameter and the flight diameter of the screw decrease from the feed section to the die. Material is compressed from the feed end of the machine to the die through a decrease in channel volume. With conical twin-screws the feed is often PVC powder, which has a low bulk density, compared to the melt density. Consequently, the channel volume change through the extruder is quite dramatic to properly compress and mix the formulation. Maximum channel volume occurs in the feed zone assuring a uniform material feed and conveying. The feed and plastication area of the extruder is where the formulation is fed and converted to a molten polymer. After the plastication flights, a restrictive area with smaller flight volume retards the resin movement forcing the resin to spend more time in the plastication zone while preparing the melt for devolatilization. Similar to parallel twin-screw extruders, this screw section acts as a melt seal for the devolatization area. The devolatilization zone has a larger pitch to provide maximum polymer surface area to remove volatiles. This part of the screw is only partially filled to assist removal of trapped air and volatiles from the melt. Finally, the melt is recompressed and pumped to the die in the metering zone.

Parallel twin-screw extruders have more surface area compared to conical twin-screws. However, the flight flanks in a conical have more surface area than in a parallel extruder and can transfer more heat to the material in the channel. The screw surface area is 40% larger compared to a parallel extruder. Due to the larger channel volumes, conical extruders generate less shear heat and more conductive heat compared to parallel twin-screw extruders, making them better for processing shear-sensitive materials such as PVC.

Conical twin-screws have a distinct advantage in transferring torque to the screws because of their one-piece design. Since much of the energy to melt the material is supplied by the motor and screw rotation, conical extruders have more strength in areas of the screw where it is required. Most screw wear will occur in the feed, plasticating, and restrictive areas of the screw.

15.5.3.2 Plasticating and melting

Two mechanisms exist to melt polymer in the extruder barrel [52−56]:

- Conductive heat transferred from the barrel heaters
- Shear heat supplied by the motor through the screw elements and shaft

Under normal operating conditions the extruder motor through shear heating supplies 80–90% of the energy to plasticate polymer. As polymer is conveyed down the extruder barrel, conductive heat is transferred to the plastic from the barrel walls. Resin and additives are compressed by reducing the pitch of the conveying elements as the material moves forward in the extruder barrel. Reducing the element pitch decreases the free volume, compressing the material while supplying some shear heat. As the formulation is conveyed forward in the first two or three barrel sections, it is preheated and compressed in the conveying elements. The particular melting point location is defined by the screw configuration and the objective to be accomplished with the material once melting is complete. Using a high *L/D* extruder with a large number of barrel sections, the location of the melting point depends on what other functions are to be accomplished downstream such as mixing, venting, liquid feed addition, or solid feed addition. Melting can be accomplished in a relatively short *L/D* after the material is added to the extruder, depending on the screw elements used in the screw configuration.

The melt seal developed by left-handed conveying elements prevents any air in the partially filled screws from passing downstream. The left-handed conveying elements force the flights just prior to it to be completely filled with polymer. Therefore, any air entering the extruder with the formulation is forced back through the feed throat. This can have a negative effect on polymer feeding particularly if it is a powder. Since the bulk density of the powder is normally low to begin, the addition of air blowing back out of the extruder, counter current to the powder being added, can lower the bulk density farther creating feed issues. One alternative is to put an atmospheric vent in zone 2 to remove any air being forced back toward the feed throat by the restrictive elements at the end of the melt section. The second problem associated with air coming back out of the feed throat is dusting and housekeeping from airborne powder or fines being blown back out of the feed throat.

In the event when the polymer added to the extruder is a powder, it may be advantageous to change the melting section to contain only kneading blocks that convey material toward the die and remove all reverse elements. Forward conveying kneading blocks do not create as tight a melt seal allowing some air entering the extruder with the feed to pass through the kneading blocks. The air can be removed downstream by either a vacuum or atmospheric vent. How melting is accomplished depends on the oxidative and thermal stability of the resin. In some situations, oxygen presence in the melt state causes resin degradation.

General screw design guidelines suggest conveying elements between the feed throat and the melting zone have reduced pitch to decrease the free volume and increase the degree of fill. Restrictive elements are used in the melting zone or at the end of the melting zone to work the material creating higher shear heat to melt the formulation. If the melt temperature rise in the melting section is too high due to the shear heat generated by the type and number of restrictive elements used in the melting section, conveying elements can be placed between sets of kneading blocks to assist in reducing and controlling temperature.

The screw design and elements used to melt the formulation depends on the formulation particle size (pellets vs. powder), the resin softening temperature or melting point (amorphous vs. crystalline), and whether the polymer viscosity is heat or shear sensitive. Other factors to be considered include liquid addition, lubricity of the formulation, and other additives present that may affect the screw's ability to feed and forward convey.

Melting in a counter-rotating parallel extruder is similar to that in a co-rotating twin-screw. The melting section is designed to shear and work the formulation in a given location in the extruder by using reduced pitch conveying elements, kneading blocks, and restrictive elements to localize melting.

In a conical twin-screw the material is compressed as the screw flight volume decreases. As the screw-root and flight diameters steadily decrease, the channel volume decreases, compressing the polymer. The reduced volume coupled with the intermeshing counter-rotating screws works the material as it travels between the gap in the two screws supplying the shear energy required to flux and soften the PVC formulations. The narrow screw channels provide conductive heat, which assists plastic melting. The large flights conduct heat from the barrel wall to the screw root, heating the polymer in the narrow channels and reducing the shear heating requirements.

15.5.3.3 Melt conveying

Once the material is melted it is conveyed forward in the barrel by the addition of conveying elements to the screw. Figure 15.39 shows a possible screw element configuration after the melting section to convey the melt forward to a mixing or downstream feeding section of the screw. This particular conveying section uses large-pitch elements to minimize the work and reduce the pressure on the melt. Conveying in a two-lobe intermeshing parallel extruder contains three distinct lobal pools of material around the screw elements that are moving down the screw in three distinct channels. Figure 15.40 shows an end view of the screw elements with an outline of a simulated barrel and the location of the three distinct lobal pools of molten polymer. As

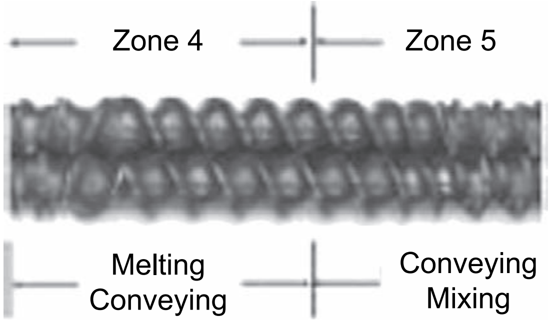


Figure 15.39 Section of twin screw profile with a reverse flight melting and conveying section (zone 4) followed by a conveying and mixing section containing kneading blocks (zone 5).

the polymer is conveyed down the extruder barrel each lobal pool is in a different screw channel. There are $(2n - 1)$ lobal pools where n is the number of lobes on the screw element. For a three-lobe screw element, there are five lobal pools.

15.5.3.4 Mixing

There are two types of mixing that occur in twin-screw extruders, regardless of whether they are co-rotating or counter-rotating, parallel or conical, or intermeshing or non-intermeshing [1,52–55]. Distributive mixing, as its name implies, distributes particles uniformly throughout the melt. Distributive mixing is a low-shear process and is accomplished by breaking and recombining the melt stream. The following are the normal applications for distributive mixing:

- Distribution of fibrous materials (e.g., carbon fiber, fiber glass, and aramid fiber)
- Fillers with high aspects ratios (mica)
- Mixing of shear sensitive polymers and additives

The second type of mixing is dispersive, which breaks up large particles and disperses them as smaller particles throughout the melt. Dispersive mixing is a high shear process used:

- To disperse
  - Pigments
  - Liquid additives
  - Non-reinforcing fillers
- Alloying or blending two or more polymer resin systems

Different mixing elements and screw geometries are used to accomplish each type of mixing. The degree of mixing is dependent on the following:

- Screw speed
- Degree of fill in the screw channels
- Temperature
- Screw geometry

Screw geometry affects the shear rate, which influences the resin viscosity.

Narrow kneading blocks provide good distributive mixing as material flows in and around the blocks, but not between the block and the barrel wall. Different types of kneading blocks are available, ranging from wide blocks to narrow blocks, forward or rearward conveying, and nonconveying (neutral block) or conveying configurations. Gear mixers (Figure 15.41) are supplied by several twin-screw manufacturers. Gear mixers are used for distributive and dispersive mixing. The number of teeth, the conveying angle, and the spacer width may vary slightly depending on the supplier but these mixing elements split the melt stream in a numerous places and then recombine it on the other side gear in the spacer area. Sometimes, three or four gear mixers will be used in succession to break and recombine the melt stream. Gear mixers are particularly useful when mixing liquid additives into the polymer melt stream.

Wider kneading blocks are used for dispersive mixing. With the narrow disks, molten polymer and additives flow around the disks but with the wider disks material in addition

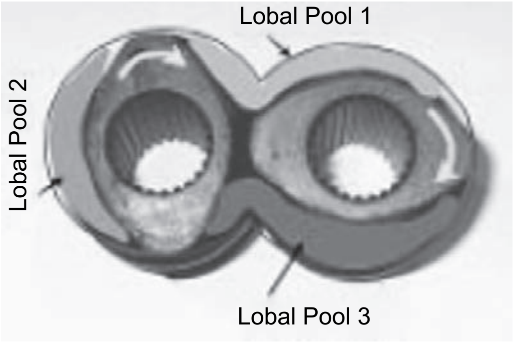


Figure 15.40 End view of intermeshing co-rotating twin screw conveying elements with in the barrel outline, showing the three separate lobal melt pools.

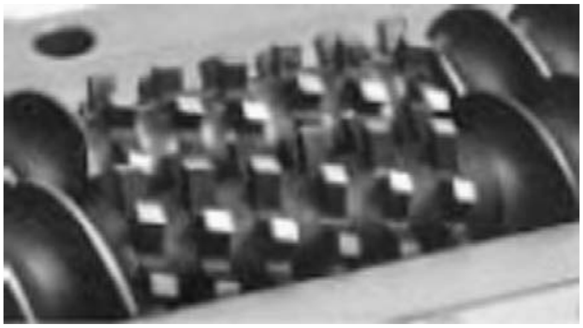


Figure 15.41 Picture of intermeshing gear mixers in a twin screw profile.

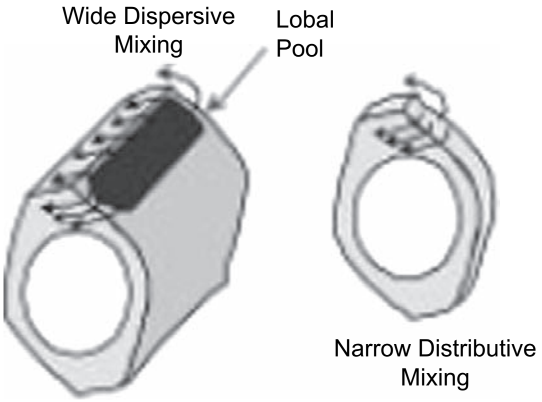


Figure 15.42 Schematic of two kneading blocks of wide and narrow design demonstrating the flow over the element tip between the barrel of wide kneading elements and the lower shear flow around the narrow kneading element.

to going around the disk also goes over the top of the disk, providing dispersive mixing. A global pool formed in front of a wide block goes through the small gap between the flight top and the barrel wall. As it passes over the block, dispersive mixing occurs. This is shown graphically in Figure 15.42.

Neutral kneading blocks can be used for either distributive or dispersive mixing, depending on each kneading block width. Neutral kneading blocks have neither forward nor rearward conveying attributes in the extruder. They come in different lengths with either three or five blocks. The kneading blocks are positioned 90° from each other. If the blocks are wide they provide more dispersive mixing while narrow blocks provide more distributive mixing. For example, in a 45 mm twin-screw extruder a 90/3/15 is only 15 mm long with three blocks or lobes that are 5 mm wide; this type of element provides good distributive mixing. On the other hand, a 90/5/60 in a 40 mm twin-screw is 60 mm long with each of the five blocks being 12 mm in width providing dispersive mixing. Numerous types of special elements are available from different extruder manufacturers to provide specialized mixing capabilities with their equipment.

Similar to melting, various mixing elements are combined to provide specific mixing capabilities and degrees of mixing for the formulations being processed. To minimize heat build-up in groups of kneading blocks due to shear, the blocks can be separated with conveying elements. The mixing section design depends on the following:

- Mixing type required by the formulation
- Screw mixing length available
- Polymer and additives temperature sensitivity
- Polymer and additive shear sensitivity in the formulation

Some mixing is accomplished strictly with conveying elements by going from a large-pitch to a small-pitch element back to a large-pitch element, and so forth. This repeated material compression and expansion does provide some mixing; however, kneading blocks and other mixing elements are much more efficient mixers.

In conical twin-screw extruders, a restrictive zone follows the plastication or melting zone. The restrictive zone seals off the plastication zone from the devolatilization zone. Mixing will occur in the restrictive zone compressing the polymer in the narrower channels. The restrictive zone compressive capacity is determined by its length and the channel volume. Mixing also occurs downstream in the metering section as the plasticated polymer is homogenized by the reduction in channel size.

15.5.3.5 Downstream feeding

Unlike single-screw extrusion, numerous materials, both solid and liquid, are fed downstream in parallel twin-screw extrusion. This provides maximum extrusion flexibility by allowing materials to be introduced into the melt at different stages or locations along the extruder barrel. Examples of downstream feeding advantages are as follows:

- Addition of fibrous material (glass, carbon fiber, stainless steel, aramid) to minimize fiber attrition.
- Addition of high aspect ratio fillers (mica) to minimize attrition in aspect ratio.
- Addition of shear or temperature-sensitive materials that may degrade if put through the entire extruder with the rest of the polymer system.
- Addition of liquid feed added to the melt as a plasticizer, liquid colorant, stabilizer, or lubricant.

High aspect ratio fillers and/or reinforcements can experience severe size attrition, resulting in loss of aspect ratio and properties, when added to the feed throat with solid polymer. Fibers conveyed in the feed section and compressed with solid pellets break while creating extensive screw wear. Downstream feeding allows the introduction of the high aspect ratio fillers or reinforcements into a melt, which assists feeding by acting more as a lubricant, conveying the material forward in the barrel. Mixing elements used after reinforcement addition downstream are relatively mild to provide sufficient mixing, while minimizing fiber attrition. When processing high-temperature polymers that require low-temperature additive addition, downstream feeding increases the possibility of successful addition without the accompanying additive volatilization or degradation. For example, assume a concentrate is being made with polycarbonate that used an additive with limited thermal stability. The polycarbonate is added to the extruder feed throat. After it is melted, the additive is added downstream to minimize the thermal degradation that is a function of time, temperature, and shear history.

Liquid addition in the feed throat can lead to feed problems, due to the liquid lubricity on the barrel wall in the feed zone. In addition, any restrictive elements used to melt or plasticate the polymer may prevent the liquid feed from passing through this section of the extruder. In that event, after a very short time the liquid feed will back up and come out of the feed throat of the extruder. Liquid is normally added more efficiently downstream by means of a liquid feed pump.

Downstream feeding introduces room-temperature material into a polymer melt that is substantially higher in temperature. If the downstream additive volume is relatively high compared to the polymer volume, this can substantially alter the polymer melt temperature. Care must be taken to assure that crystalline materials with sharp melting points are not cooled below their melting points, where portions of the polymer can actually solidify. In this situation, additional heat is required to remelt the crystalline material, and the solid polymer may damage high aspect ratio fillers or reinforcements, thereby causing higher attrition as the amount of lubrication from the polymer melt is reduced.

Downstream feeding of fillers, fibers, polymers for alloying or blending, additives such as flame retardants, stabilizers, lubricants, and colorants is done by gravity feeding, or using a stuffer box or side-feed extruder. By proper selection of large-pitch screw elements that are not full of polymer in the barrel section, prior to the addition of the additive ingredient, a vacuum or atmospheric vent can be used to remove the air introduced with the downstream addition. Otherwise the air has to be removed through the barrel section where the downstream feeding takes place. Air removal through the same port as feed addition occurs may lead to poor additive feed characteristics particularly with low-bulk density powders.

15.5.3.6 Die and adapter

However produced, the polymer melt generally flows through a filter and an adapter to a die and then into the next process step (usually shaping, drawing, and quenching). For uniform product, the mass flow through the die must be uniform across the exit plane. However, this is complicated by the nonlinear dependence of melt viscosity on both temperature and shear rate in the die [10,11] and must be considered in the design of the die. The viscosity behavior of a given material is determined by measuring the flow properties with a capillary rheometer over the temperature and shear rate range expected. Melt elasticity can cause flow instabilities, which affect haze and thickness [14,15] or the operation of downstream equipment. Exit melt velocity, flow characteristics, and quenching rate may impart and "freeze in" significant orientation to the polymer. In some processes, melt orientation is reduced by melt relaxation, while in others, it is maintained by quenching.

The extruder head assembly includes the breaker plate (or a screen changer holding the breaker plate), an adapter to connect the die assembly to the end of the extruder, and die. The breaker plate, shown in Figure 15.43, is a round disk containing a large number of holes that is placed between the end of the extruder and the adapter. The functions of the breaker plate are as follows:

- It stops the spiraling action of the polymer melt coming off the end of the screw by forcing the polymer in straight lines as it passes through the breaker plate.
- The breaker plate provides a seal between the end of the extruder and the die/adapter. If the sealing surface is damaged or if the surface has been refinished a number of times to remove nicks and/or dents and the breaker plate is then too thin to provide a good seal, molten polymer will leak around the gate between the die/adapter and the extruder. High pressure is generated in this area; so the sealing surfaces must be smooth and the pressure evenly applied around the seal to prevent polymer leakage.
- Screens are placed in the breaker plate to filter contamination from the polymer melt and to create pressure at the end of the extruder. The screen and breaker plate combination assist in providing thermal homogeneity in the polymer melt. Screens clogged with contaminants will cause high pressures at the end of the extruder reducing the extruder throughput. If the formulation

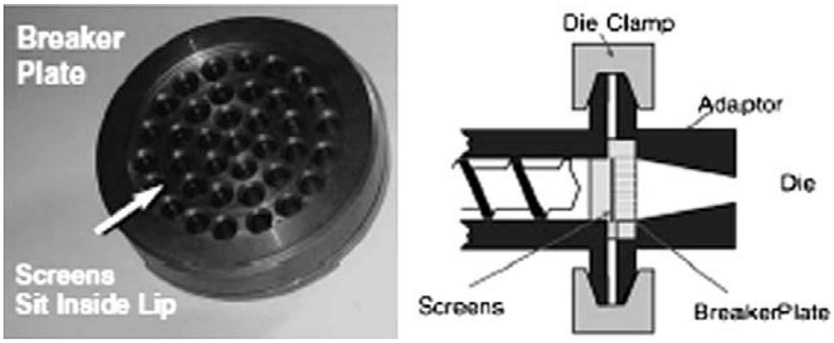


Figure 15.43 Picture of a breaker plate and a schematic of its location in the extruder head.

Table 15.5 Comparison of various filtration media

Characteristics	Square Weave Screen	Dutch Twill Weave Screen	Sintered Powder	Metal Fiber
Gel capture	Poor	Fair	Good	Very good
Contaminate capacity	Fair	Good	Fair	Very good
Permeability	Very good	Poor	Fair	Good

contains fillers or fiber reinforcements all screens must be removed.

Filtration is accomplished with wire mesh screens (square or twill weave), sintered powder, or sintered metal fibers. Table 15.5 shows a comparison of the various filtration media and their characteristics. Square weave screen (Figure 15.44) has every other wire over and under while twill weaves has every second wire over and under. Screen mesh is a measure of the number of wires per inch; the higher the mesh, the more wires per inch resulting in finer hole size and better contamination removal. Screen placement in a breaker plate starts with a coarse screen closest to the screw followed by a finer and finer mesh, with the last screen in the group being a coarse mesh to act as a support for the fine mesh screens. The last coarse mesh prevents holes from being blown in the fine mesh screens in front of the breaker plate holes when high pressure is present. A typical 20/40/60/20 screen pack has the order of screens from the end of the extruder screw: 20 mesh, 40 mesh, 60 mesh, and finally 20 mesh screen to support the 60 mesh.

Applications with high levels of contamination requiring numerous screen changes may need an automatic screen changer to run economically. Many types of screen changers are available with a wide range of sophistication depending on the application, the running time between the screen contamination, and the expense associated with shutting down and restarting the process. Continuous-operation screen changers index as the screens become clogged, replacing the dirty screens with new screens, without shutting down the process. Intermittent-operation screen changers require the process to be shut down, the screens changed, and the process restarted. Figure 15.45 shows a two-position hydraulic screen changer with one screen in the polymer stream and the second clean screen waiting to be transferred into the polymer stream once the first screen becomes contaminated. Hydraulic screen changers may move either slowly, requiring the process to be stopped, or very rapidly where they can be changed while running with only minimal loss in product and time. Other types of screen changers available for continuous processes are rotary screen changers and double-bolt screen changers. As screen packs become contaminated, the pressure at the end of the extruder increases decreasing the extruder output. If the pressure increases substantially during a run, either the extruder screw speed must be increased or the puller speed decreased to maintain product dimensions.

The die is attached either directly to the end of the extruder or with a transfer pipe or adapter that connects the die to the extruder. Polymer melt temperature in the adapter must be maintained. Transfer pipes like extruder barrels should have heater bands covering as much surface area as possible to minimize the possibility of hot or cold spots. Remember two of the extruder objectives to provide uniform melt temperature and the proper melt temperature. Transfer pipes normally have smaller diameters than the extruder barrel with a converging hole as material enters the transfer pipe from the extruder and a diverging hole as it exits the transfer pipe to the die. This helps maintain good polymer velocity through the transfer pipes and adapters.

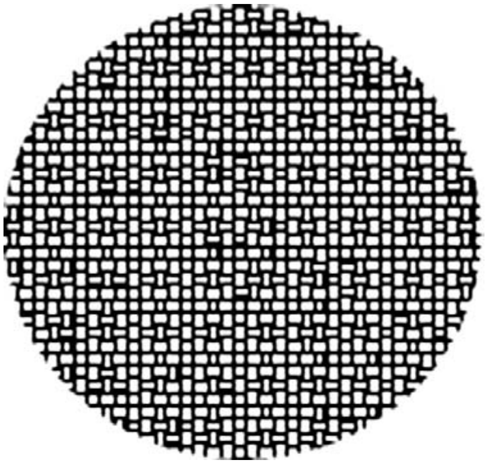


Figure 15.44 Square screen weave.

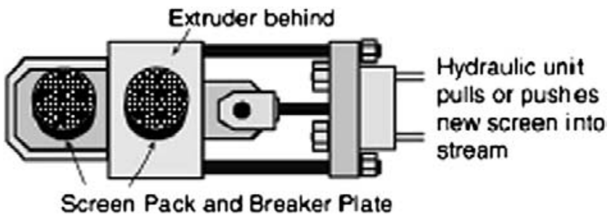


Figure 15.45 Two position hydraulic screen changer.

15.6 Shaping and Drawing and Extrusion Applications

In the last step in extrusion, the molten extrudate leaves the extruder and is then shaped into the desired cross-section required in the next step of the polymer process. This final exit section, attached to the extruder, is typically called the die. The shape of the die and its final product typically gives a name to a polymer process. As the melt enters the die, the polymer molecules are generally increased in velocity as the melt cross-section is changed, in the various die land areas, causing orientation of the melt. As the extrudate exits the die, the molecules that were oriented in the die land area relax and re-entangle causing die swell. If the extrudate is allowed to droll out of the die, then the cross-section swells becoming larger than the die opening due to the relaxation of the polymer molecules. Pulling extrudate away from the extruder requires the application of a force, by means of a puller farther down the line. This applied pulling force further orients the polymer molecular chains in the machine direction, or in the direction of the puller. Neck down or draw down of the extrudate is induced by this pulling action. The degree of draw depends on the speed of the puller relative to the average melt velocity at the die exit, which is determined from the extruder output and the dimensions of the die. Draw ratio is directly related to the molecular orientation resulting in higher tensile and flexural properties in the machine direction compared to the transverse direction.

With a given die cross-sectional area, there is only one ratio of puller speed to extruder throughput rate that produces a product with the correct cross-sectional dimensions. If the extruder throughput is increased, the puller speed must be increased proportionally to maintain the same finished product dimensions. Likewise, if the throughput is decreased the puller speed must be decreased proportionally to maintain the same finished product cross-sectional area. The draw ratio and molecular orientation can only be increased or decreased by changing the die cross-sectional area relative to the puller speed assuming the final product dimensions are kept constant. This is easily done with sheet dies, cast film dies, or blown film dies that have adjustable die lips. Profile and cross-head dies may have a fixed cross-sectional opening that is not adjustable; at a given throughput rate there is only one puller speed that yields a product with the correct final dimensions. A product that tends to crack or break in the machine direction (in the plant or in field applications) may have too much molecular orientation. A new die with a different cross-sectional opening is required to alter the draw ratio and change the molecular orientation to correct the problem. Higher draw ratios increase the tensile and flexural properties and the tendency to crack or split in the machine direction. Assuming that most polymer molecules are aligned in one direction, it is easy to slit the product along that direction, because there are a limited number of molecules in the perpendicular direction holding the product together.

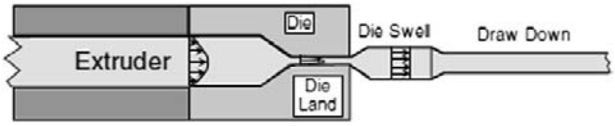


Figure 15.46 schematic diagram of die swell on exiting the die and subsequent draw down of the extrudate, which may hide the presence of the die swell.

Extrudate swells, commonly known as die swell, as shown in Figure 15.46, is not always visible at the die exit because the extrudate is pulled away from the extruder, causing draw down or neck down. If the extrudate is allowed to droll on the floor or is pulled from the extruder very slowly, die swell becomes very obvious. Polymer molecules in the die land area are oriented in the direction of flow. The extrudate velocity profile is higher at the center of the flow front and lower near the die walls. Immediately after exiting the die, the extrudate velocity profile is identical across the entire cross-section. Consequently, the velocity at the surface of the extrudate outside the die is identical to the velocity in the center of the extrudate. This change in the flow velocity profile gives rise to molecular relaxation outside the die and the resultant die swells.

When the extrudate exits the die, it has to be quenched and possibly sized (drawn through a fixture) to maintain its final shape. Depending on the extrusion process, different methods are available to quench the final product. Cast film and sheet are quenched on rolls and in water baths and blown film is quenched by air in a blown film tower. Solid profile, pipe, and tubing are quenched in calibration tanks filled with water and in some cases connected to a vacuum system. Polymer strands and monofilaments are quenched in air or water baths while wire coating is done horizontally in air or water. In small and large part blow molding, the melt is quenched in molds as the extruded tubular parison is inflated.

Numerous types of dies are available depending on the extrusion process and the type of product being produced. Compounders use strand dies to make continuous strands that are chopped into pellets. Sheet and cast film producers use flat dies. A schematic of a flat film or sheet die is shown in Figure 15.47. This produces a flat web of a specific thickness that passes through a three roll stack or lays flat on a cast roll. Blown film producers use circular dies as shown in Figure 15.48. Tubing and pipe cross-head dies are similar to that shown in Figure 15.49A where extrudate exiting the die passes through an annulus with internal supports called spiders, and then enters a vacuum sizing tank to set the tubing or pipe outer dimensions. Profile dies can be of all shapes and types depending on the complexity of the product profile. Wire coating cross-head dies (Figure 15.49B) are similar configuration to tubing dies except a wire, running

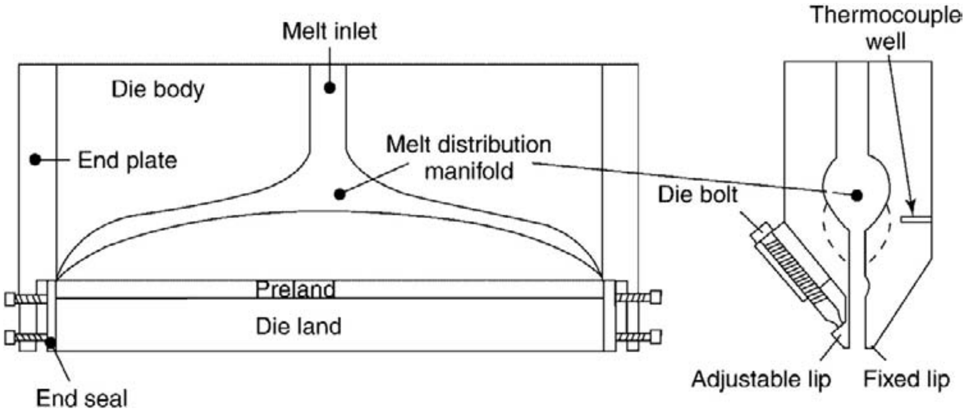


Figure 15.47 Schematic diagram of the coat-hanger design of a film or sheet die.

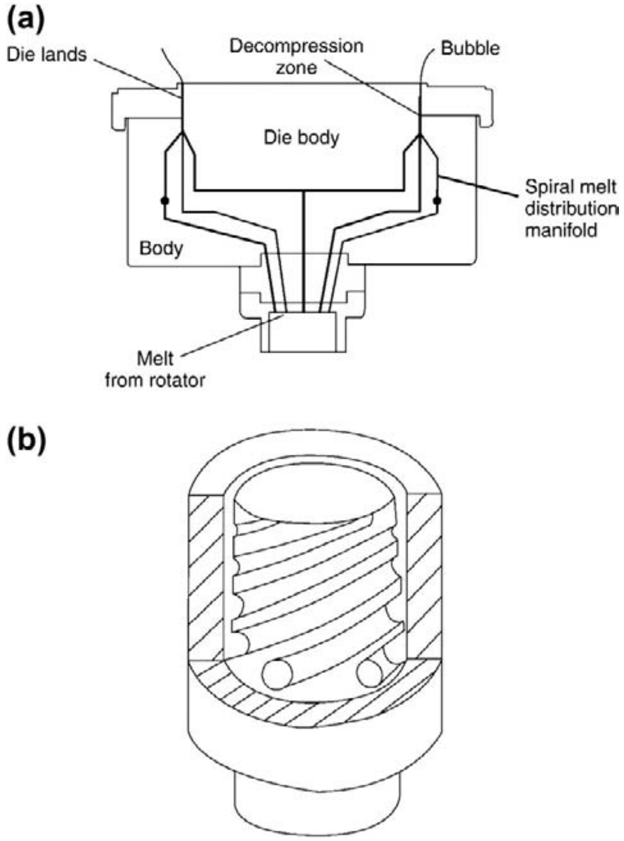


Figure 15.48 (a) Tubular (three-layer) spiral die; (b) detail of spiral melt manifold.

perpendicular to the extruder, runs through the cross-head die for coating and then exits to the cooling section.

In flat-die extruders, slot and coat hanger die geometries (Figure 15.47) predominate, whereas in circular die extruders, spiral dies (Figure 15.48) predominate. A die is usually constructed of tool steel and heated to maintain the desired temperature for optimum flow. Temperature uniformity is very important. A uniform flow through the die is determined by the design of the internal distribution manifold using the polymer shear viscosity data. For good melt distribution, this section must be designed to maintain uniform flow rate, pressure drop, and shear rate [11]. Independent flow adjustment at the die exit is usually provided by an adjustable die lip. An internal flow adjustment can be provided by a choker bar, but at present these are used less than previously. The die lip and chocker bar adjustments ensure a uniform flow by selectively changing the pressure drop of the melt across the die width before it leaves the die. Multiple temperature zones, standard on most dies, permit the selective alteration of the temperature across the die face, ensuring production of a flat sheet. This is necessary to counteract gauge variations caused by possible nonhomogeneous melt from the extruder, inadequacies in the die construction or design, and the physical limitations imposed in the machining of the internal configuration of the dies.

To ensure isothermal flow, die temperatures are maintained as close to the melt temperature as practical. Die gaps vary, depending upon the speed with which material is removed from the die lips, as this determines the shear rate. Die exit shear rate and shear stress control is important because of die swell and melt fracture. Die gap also determines the final film thickness. Die gaps for films are 0.25−2.5 mm (0.010−0.10 in.), which is small compared with the typical die width of 39−305 cm.

15.7 Coextrusion

Coextrusion technology has been developed in conjunction with new polymers, providing continuously formed layered polymer structures such as the film structures required for flexible packaging. Coextrusion is perhaps the most economical method of combining polymers into functional multilayer products such as films, sheets, profiles, bottles, pipes, wire coatings, etc.

Multiple melt streams from several extruders are combined either in a feed block (Figure 15.50) or in a multiple cavity die (Figure 15.51), resulting in a stratified flow from the die.

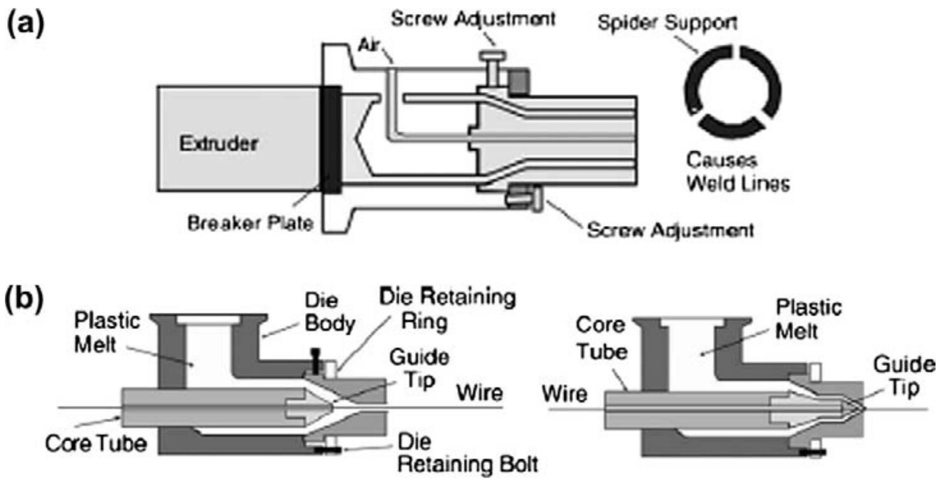


Figure 15.49 Schematic of a cross head die for tubing or pipe extrusion and the schematic diagram of two types of wire coating cross head dies.

A feed block may be used with a single cavity die or in conjunction with one cavity of a multiple cavity die to produce structures with many layers. Multiple cavity dies are used for films requiring several layers, which interact chemically to improve adhesion between the polymers but which may disturb the interface stability or noninteracting polymers, which must remain separate for as long as possible owing to poor rheological compatibility.

Coextrusion is promoted by the laminar flow of the melt in the feed block and die, which prevents the turbulent mixing of the various layers. The laminar flow is due to the low Reynolds numbers (low inertia between flow planes) that result from the high melt viscosities [10,11]. However, the generation of interfaces between the flowing materials requires that melt viscosities and melt elasticity between the layers be sufficiently matched to prevent the formation of flow instabilities [16−19]. Therefore, coextrusion requires superior equipment and process control throughout.

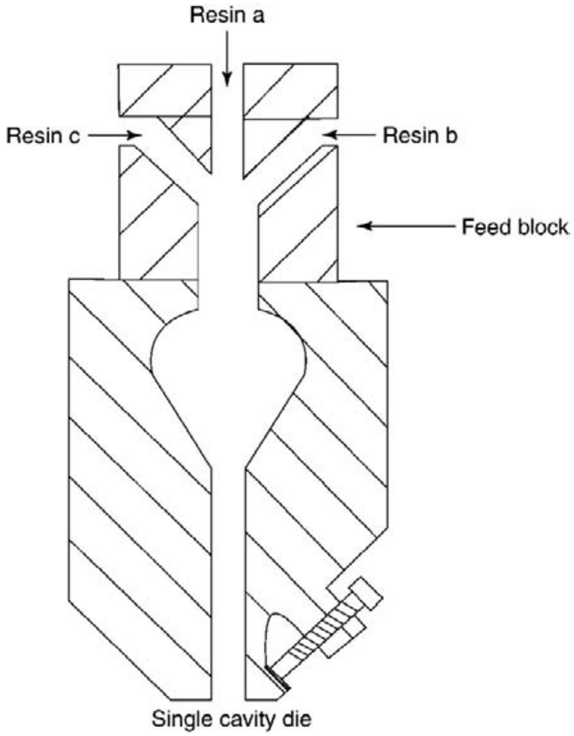


Figure 15.50 Schematic diagram of a flat die coextrusion system (single cavity die) using a feed block for three polymer streams.

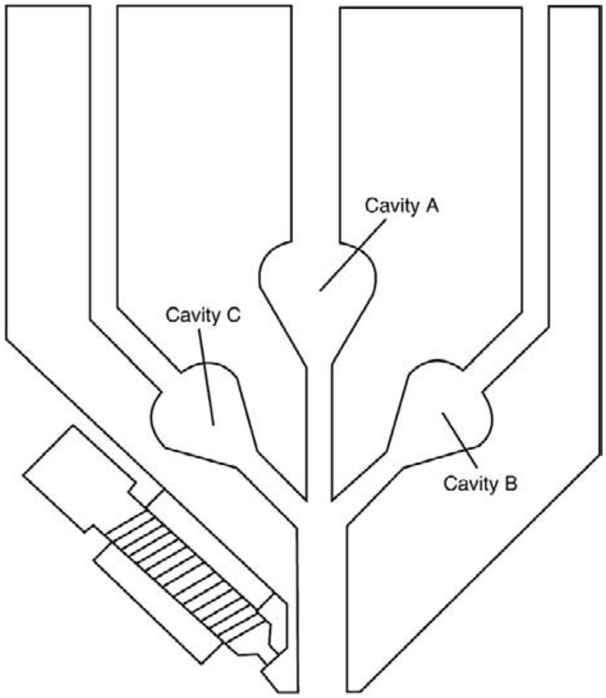


Figure 15.51 Multiple cavity coextrusion die showing three separate melt-distribution manifolds which join to form a three layer coextrusion at the die exit.

Multilayer spiral dies are becoming more common but are limited to rheological compatible polymers in the layers much as with the feed block method in flat dies. This is due to the long flow distances required for layer uniformity in the multilayer spiral dies, which makes them more prone to generate interfacial instabilities. Coextrusions with 5−13 layers are relatively common and products with as many as 1000 layers are known.

15.8 Extrusion Laminations and Coatings

In making multilayer structures, two or three melt streams from separate extruders can be combined and cast to form a multilayer structure. Alternatively, a melt stream and, a premade cast or blown film web or a quenched and oriented film web, may combined on a chilled drum providing the web with new surface functionality (Figure 15.52). This method is known as the extrusion coating process [2].

15.9 Solidification and Cooling

Extrudate cooling is normally done by water, air, or contact with a cold surface. Semicrystalline polymers, i.e., polyethylene, polypropylene, nylon, polybutylene, and terephthalate, have very sharp melting points and consequently very sharp solidification temperatures. Amorphous polymers on the other hand do not melt but enter a rubbery state above their T_g (glass transition temperature). As the temperature increases, polymer chain mobility continues to increase until the polymer flows and is easy to process. For cooling of amorphous polymers, part temperature needs to be below the material T_g to freeze the final part dimensions. Thick cross-sections can form a surface skin with the center still being molten. This allows the extrusion line to be run at higher rates; however, if product dimensional tolerances are very tight, the entire product should be cooled below the melting point if it is a semicrystalline polymer and below T_g if it is an amorphous polymer. Cooling from elevated to room temperature after the product is completely solid results in additional product shrinkage and dimensional changes.

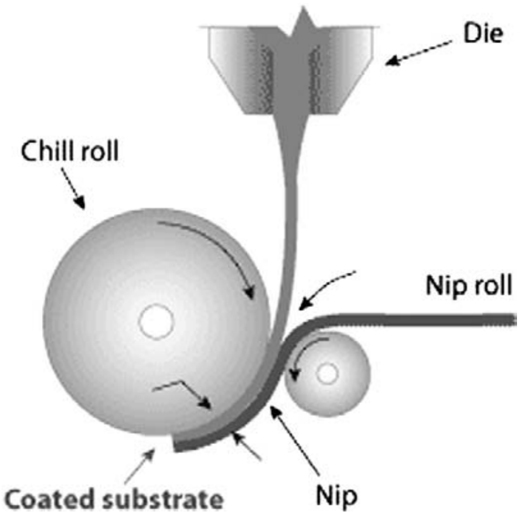


Figure 15.52 Schematic diagram of extrusion coating a preformed web.

Proper part cooling is critical in producing warpage free parts with acceptable dimensions and performance. Part warpage is caused by differential shrinkage. To minimize differential shrinkage, the part must be cooled uniformly on all sides. If one side or area of the extrudate solidifies before another, the part will warp bending toward the side that solidified last. If one side of the extrudate is dragged over an object in the cooling operation, molecular orientation is induced on that side of the part causing it to shrink differently from the other side leading to warpage.

Cooling rates with semicrystalline polymers are critical in developing the correct amount and size of crystals in the final product. Rapid quenching leads to small crystal development and low levels of crystallinity. Later heating or annealing (heated for a specific time and temperature above its T_g but below T_m) leads to additional crystal growth in the solid state. Accompanying this increase in crystallinity is a reduction in volume, a change in the part dimensions, and possibly the introduction of warpage. To maximize the degree of crystallinity, the extrudate should be cooled slowly. Rates of cooling can be critical in maximizing product performance and reproducibility. Cooling rates are determined by throughput rates, part thickness, and temperature of the cooling medium (water bath, roll temperatures, or air temperatures).

With some extruded products, the cooling rate and treatment during cooling are critical to obtain the final product properties required by the customer. In sheet or cast film, extrusion, roll temperatures, and surfaces determine the aesthetics of the product. Highly polished rolls run at relatively high-temperatures produce polished glossy surfaces. A matte finish on the product is attained by using rolls with a matte finish, while a matte finish on one side and a polished glossy surface on the other is produced by using a combination of matte finish and highly polished rolls. A vacuum sizing tank is used for hollow profiles or pipe and tubing where the extrudate is run through a set of sizers under water with a vacuum above the water. The fixture type and cooling required to maintain final dimensions depends on the application.

Drawing products in their solid state (monofilament production, uniaxially oriented film, or biaxially oriented film) maximizes molecular orientation and directional properties. In semicrystalline polymers, drawing can lead to additional crystallinity development through alignment of the polymer molecules. The ability to successfully draw and process the polymer into oriented fibers, films, and profiles is oftentimes dependent on the quenching conditions used to form the precursor fiber, sheet, or profile.

15.9.1 Drying

Some polymers require drying prior to extrusion to prevent polymer degradation. Resins produced by condensation reactions, with the removal of water during polymerization, i.e., nylon, polyester (polyethylene terephthalate—PET and polybutylene terephthalate—PBT), polyurethanes and polycarbonate are hygroscopic absorbing moisture rapidly from the air. In the presence of heat moisture degrades these materials to lower molecular weight (shorter chains) resulting in poorer property performance. Proper drying to eliminate moisture is critical in obtaining optimum property performance in the final product. Other materials, i.e., acrylics, Ultem®, polysulfone, Noryl®, ABS, and EVOH also absorb moisture from the air and must be dried prior to processing. Any moisture in the polymer is converted to steam in the extruder and depending on the quantity present can cause surface imperfections such as splay, holes in the product, or a foamy product. Some polymers, i.e., nylon, are shipped dry in moisture proof containers. With proper handling, these resins do not normally require additional drying prior to processing. However, if the seal is broken on the container or the bag is not completely resealed after opening, the product will absorb moisture and have to be dried prior to extrusion. Polyesters, nylons, polyurethanes, and polycarbonate are particularly sensitive to moisture and must be dried in dehumidifying dryers, transported with dry air, and blanketed with dry air or nitrogen in the feed hopper. Dehumidifying dryers with dew points of −40°F (−40 °C) are recommended for drying most polymers.

Formulations requiring both a dry polymer plus blending with other ingredients can lead to special handling requirements. Once moisture-sensitive resin is dried, it will pick up moisture when exposed to the atmosphere. Additives or other components added to formulations containing hygroscopic resins need to be moisture-free. If the additives cannot be dried with the resin, special handling procedures or individual feeders are required to mix the dry resins and other additives or components at the extruder feed throat.

In some instances, resins containing moisture can be processed in a vacuum vented extruder with the moisture removed in the vent section. This does not work with all resins because some degradation can occur before the moisture is removed.

Overdrying of resins must be avoided in order to prevent resin degradation, which may result in the loss of properties and/or the development of color bodies. Nylon 6,6 when overdried becomes yellow and is accompanied with a loss of some properties.

15.9.2 Hazards Associated with an Extruder

The three biggest potential safety hazards associated with extruders are burns, electrical shock, and falls [1]. Without proper protective equipment, burns can be common when working around extruders. If insulation is placed around the die make sure it is in good shape and properly installed. Touching exposed areas of a hot die or handling extrudate without gloves normally causes burns. Long sleeves with properly approved thermal gloves and face masks should be worn when working around the die, changing the die, tightening die bolts, or other functions performed on the die. Hot extrudate from the extruder will stick to the skin. Since polymeric materials are great insulators, after sticking to the skin they cool very slowly continuing to burn the affected area of the skin. Protective clothing should be made from nonmelting fabrics such as cotton and leather and never from a fabric made of thermoplastic fiber, which can melt and be hard to remove from affected skin. Polymer can also stick to protective clothing, where it holds heat for a long time, and can cause burns if it is not easily removed.

15.10 Never Stand in Front of a Die when an Extruder Is Starting up

Air in the extruder and possibly gas from degraded products (if the extruder has been present at temperature with material in the barrel for some time) is forced out of the extruder on start-up. If some polymer is left in the barrel, trapped air can be compressed, blowing the hot polymer out of the die, or blowing the die off the end of the extruder. Standing in front of the extruder creates an excellent opportunity for molten polymer to be blown out of the die, causing burns. If the die is blown from the extruder by the pressure, one can be seriously injured or killed by the impact of the die or broken bolts or from the die falling on the skin.

The potential for electrical shock exists when removing the extruder covers, thus exposing bare wires and electrical connections. Extruder heater bands are normally 220−440 V and can cause serious electrical shock. Check the wires to the heater bands on the die and adapters to assure that there are no frayed, bare, or exposed wires, or connections that can cause electrical shock. In some extrusion processes, water-cooling baths are very close to the die, which can create additional electrical hazard. Operators unless properly trained should never remove guards exposing electrical terminals on heaters or open electrical cabinets to solve electrical problems.

The third major potential safety hazard around extruders is falls. Pellets spilled on the floor are slippery and need to be cleaned up immediately. At start-up the extruder normally generates some scrap, which may be on the floor around the die of the extruder. This creates tripping hazards that must be removed immediately. Occasionally, processing issues arise at start-up leading to a large quantity of material on the floor around the extruder. In these situations, the extruder should be shut down, the area must be cleaned, and then the extruder should be restarted. Some extrusion processes use water for cooling. Water spills on the floor should be removed with a wet dry vacuum and/or swept to a drain. Wet floors are very slippery and can cause falls.

The most dangerous area around an extruder is the exposed screw turning in the feed throat. *Never, never stick one's hands or fingers into the feed throat of an extruder.* If the screw is turning, then there will be incredible power that can quickly remove a finger. If the feed throat is hot, one may also get burnt. Looking into the feed pocket is also dangerous and should only be attempted with a proper face shield. Aside from melt blowing from the die, it is also possible that molten polymer can be blown out from the feed pocket causing burns and other injuries.

The most dangerous time during extruder operation is start-up. An extruder is a pressure vessel. Material is being fed into one end with a positive conveying mechanism (screw) operating at high horsepower. If the die end of the extruder is blocked with solid plastic or contaminants, incredible pressure can build-up very rapidly in the extruder and blow the die off the front of the extruder. Always start the extruder screws slowly and monitor the die pressure closely until polymer is flowing continuously out of the die. Once die flow is established, the screw speed can be safely increased. As mentioned previously, never stand in front of an extruder during start-up in the event molten plastic is blown out of the die under high pressure.

Extruders are equipped with rupture disks and pressure gauges to eliminate the possibility of blowing the die off the end or the extruder and to monitor the pressure in and before the die. Make sure that the pressure gauges are functioning properly. If the extruder does not have a rupture disk (device at the end of the extruder barrel to relieve high pressure), it should be added. Alternatively, the extruder should have a pressure gauge with a feed-back loop that automatically shuts the extruder down in the event a certain preset pressure is reached. Most extruders are equipped with both a rupture disk and a high-pressure sensor that will shut the extruder down in the event of high-pressure situations.

Each extruder should be equipped with a fume hood at the die or vent port to remove any fumes generated by the extruder.

About the author Dr Mount is an independent consultant in the extrusion, coextrusion, film manufacturing, film metallization, and film converting industry.

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16 Blow Molding

S.L. Belcher
Deceased, formerly Sabel Plastechs, Inc., 2055 Weil Rd, Moscow, OH 45153, USA

16.1 Introduction

Blow molding covers three main thermoplastic processes: extrusion blow molding, stretch blow molding, and injection blow molding. Extrusion blow molding is the largest of the three, followed by stretch blow molding and injection blow molding. The total blow molding industry is growing approximately 3−5% annually and will continue to grow at this rate.

Extrusion blow molding is the largest process user of high-density polyethylene (HDPE). “Plastic News” reported through September 2008 that United States production of HDPE was 12.8 billion pounds. The extrusion blow molding markets for HDPE that are growing at a greater pace than the bottle market, in general, are for large holding tanks, 55 gallon drums, and automotive fuel tanks. Approximately 40% of the HDPE produced goes into the blow molding market, making it the workhorse process of the HDPE industry.

Blow molding is the forming of a hollow object by inflating or blowing a thermoplastic molten tube called a “parison” in the shape of a mold cavity. The process consists of extruding or “dropping” a parison on which female mold halves are closed. The female mold halves contain the shape of the product to be produced. The bottom opening of the parison is pinched shut by the closing female mold halves. A pressurized gas, normally air, is introduced into the parison blowing the heated parison out against the cavity walls to form the product. Figure 16.1 is a general schematic of the process.

The formed part cools as depicted in Figure 16.2, crystallizes, and is further cooled in the blow mold until it can be removed from the blow mold and retain the desired shape without warping.

16.2 The Process

Extrusion blow molding can be classified into two major categories: continuous extrusion and intermittent extrusion. Intermittent extrusion is further subdivided into reciprocating screw, ram, and accumulator parison extrusion.

Continuous extrusion has the heated parison being continuously extruded. A stationary extruder plasticizes and pushes the molten plastic through the head to form a continuous parison. A good example of the continuous extrusion process is the wheel machines used by major companies as Graham, Plastipak, Consolidated Container, Ball, Silgan, and the other large volume plastic bottle producers. Figure 16.3 is a schematic of the wheel process. In the wheel process the blow molds are continuously closing on the heated parison. Wheel machines may have up to 32 molds.

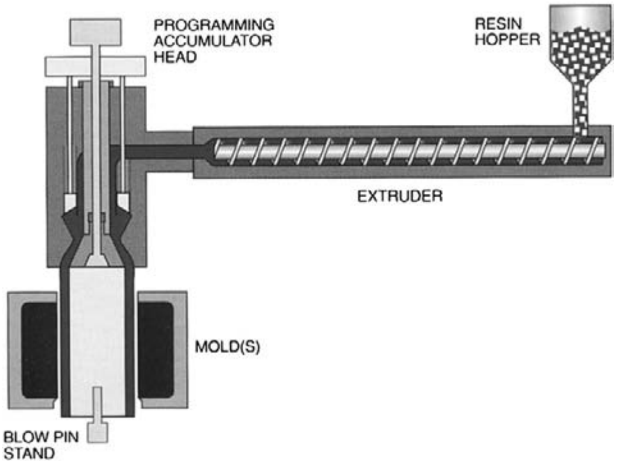


Figure 16.1 The extrusion blow molding process.

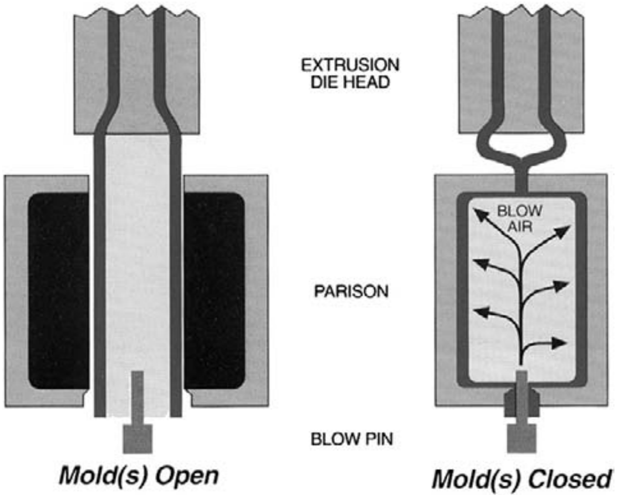


Figure 16.2 The blow molding cycle.

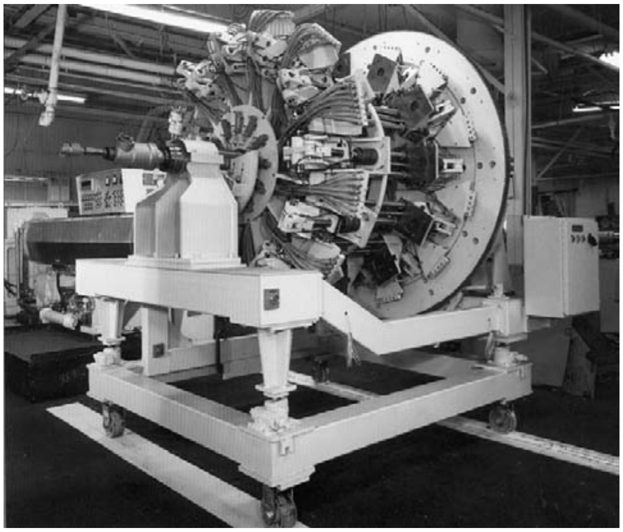


Figure 16.3 The wheel process.

The fact that the parison does not stop moving, it is necessary on other continuous extrusion machines to either move the parison to the blow mold or blow molds. This is labeled "parison transfer." Companies as Bekum, Kautex, Fisher, Milacron, and others move the molds to the parison or parisons. Figure 16.4 is a photo of a Bekum, where the blow molds move diagonally up to the parison being extruded. When the parisons are at the proper length, the blow mold halves close on the parison, a hot or cold knife, or heated nechrome wire cuts the parison between the top of the blow mold and the die head. The blow clamp and the molds then move back down to the blow molding station. Blow pins then enter at the top of the cut heated parison and compression molds the finish (the top of the container, whether it be threaded, snap cap design, or another neck configuration) and creates a seal so that blow air can enter through the blow pin and blow the heated parison out against the female mold halves to form the product. This style machine may be single sided, or double sided, and the blow molds and blow clamp can move horizontal, in an arc, or a straight downward movement to the parison.

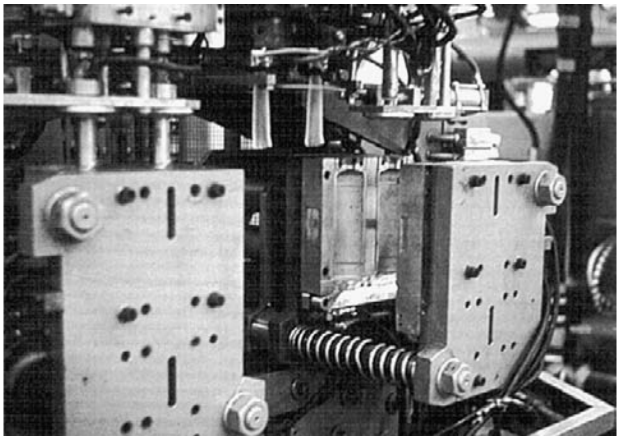


Figure 16.4 Beckum blow molding machine.

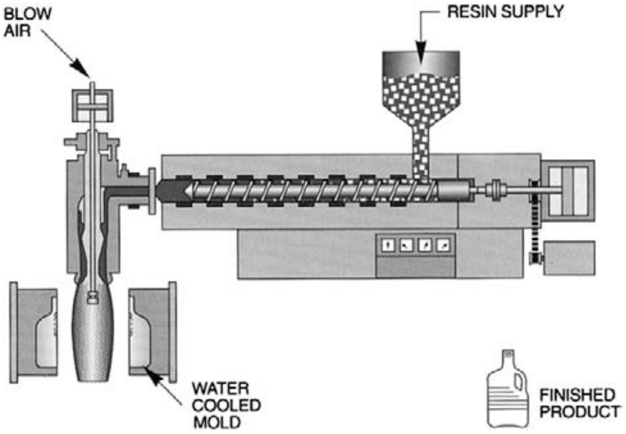


Figure 16.5 Intermittent parison extrusion blow molding machine using a reciprocating screw.

The intermittent parison extrusion blow molding machine using a reciprocating screw is often referred to as "shot" extrusion. The screw rotates and retracts, plasticizing or melting the resin as it moves back, then charging the shot in front of the screw. The screw then rams forward via hydraulic or electric means, pushing the heated plastic through the head and out of the die head tooling as a parison (Figure 16.5).

At this point, the blow molds close. Parison extrusion is rapid, compared to a continuous extrusion. For a typical blow molding machine producing gallon size HDPE milk containers the parison extrusion time is under 1½ seconds. Uniloy blow molding machines produced by Milacron can have from four up to eight heads for this application. These machines are used to produce approximately 80% of the HDPE milk containers in the United States and Canada. Figure 16.6 is a photo of a four-head Uniloy blow molding machine producing the 1-gallon HDPE milk container in actual production.

These bottles are automatically indexed into a downstream impact deflasher to remove the tail, moille, and handle excess material. The deflashed HDPE containers are then automatically leak tested in line prior to be conveyed to the rotary milk fillers and cappers.

Figure 16.7 depicts an intermittent extrusion blow molding machine with a ram (piston) accumulator remote from the die head.

The ram pushes the accumulated material through the die head to form the parison as a "shot." This type of machine is obsolete; however, there are machines of this type out in the industry still in use. The extruder or plasticizer is stationary and can continuously feed heated plastic into the accumulator. The extruder may be programmed to stop when the die is filled to a predetermined volume and then start again after the parison is extruded. The extruder speed is adjusted to fill the accumulator at the proper rate so the parison is extruded almost immediately after the blow mold has opened and the

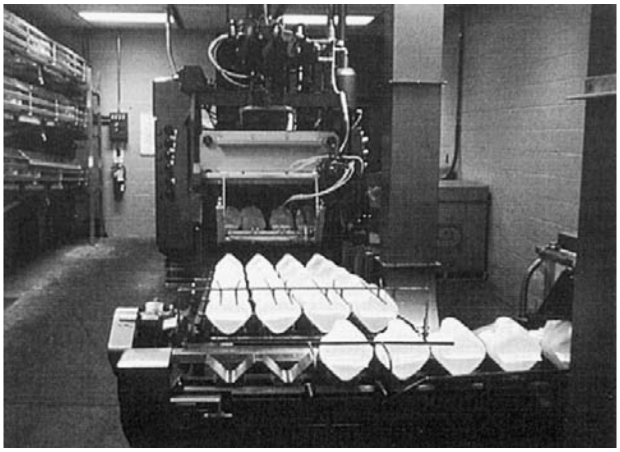


Figure 16.6 Four-head Uniloy blow molding machine producing 1-gallon HDPE milk containers.

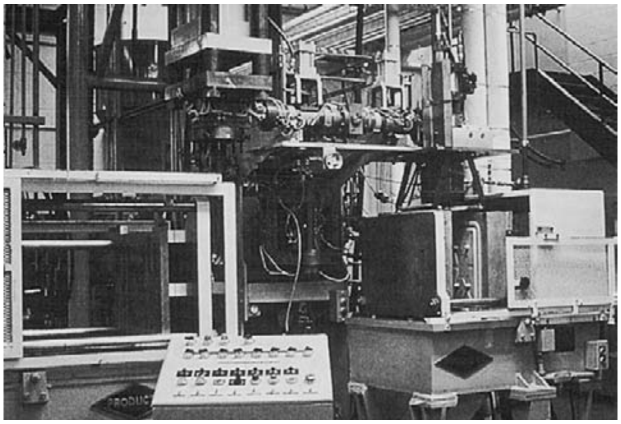


Figure 16.8 Blow molding machine in which parison is extruded almost immediately after blow mold has opened and product is ejected.

product ejected. Figure 16.8 is a photo of an original product blow molding machine of this style of equipment.

The ram extrusion process has been replaced by accumulator head machines as built by Kautex, Hartig, Graham, Milacron, Bekum, Automa, Battenfeld, and others. Figure 16.9 is a photo of a Hartig with a 50-lb accumulator head used to produce automotive fuel tanks.

In order to produce large volume holding tanks as 1500 gal, or greater, several extruders may be used to fill a large 300- or 500-lb accumulator. Machines of this type use the HLMI resins (high load melt index), so the parison will have adequate melt strength and allow the parison to hang on the die head during the mold closing. The accumulator head designed for first in first out (FIFO) allows for a complete parison shot to be pushed out. This results in a parison of improved circumferential wall thickness and an improved uniform melt temperature. The parison is extruded by moving the annular ring downward pushing the molten plastic through the die bushing and mandrel. Figure 16.10 is a Kautex In Line Head depiction.

Figure 16.11 is a photo of a large 1320-gal HDPE tank being produced on a Kautex accumulator machine.

In general, the continuous extrusion blow molding process will provide a more uniform temperature parison. The accumulator machines will allow for the parison to be dropped faster.

Recent developments as automotive fuel tanks and 55-gal drums have been produced using multilayer materials for barrier purposes and to use up the regrind. Thus, more use of the continuous extrusion process without the accumulator due to use of multilayer materials.

Probably, each of you has your preference for a specific brand of an extrusion blow molding machine. This may be due to having exposure to specific manufacturer's brand, or based on your broad exposure to many different manufacturers' equipment for your type of blow molding.

On any blow molding machine whether it be extrusion blow, injection blow, or injection stretch blow, you should determine if the machine will process the ounces, pounds, or grams per hour, that the specification sheet states. Remember,

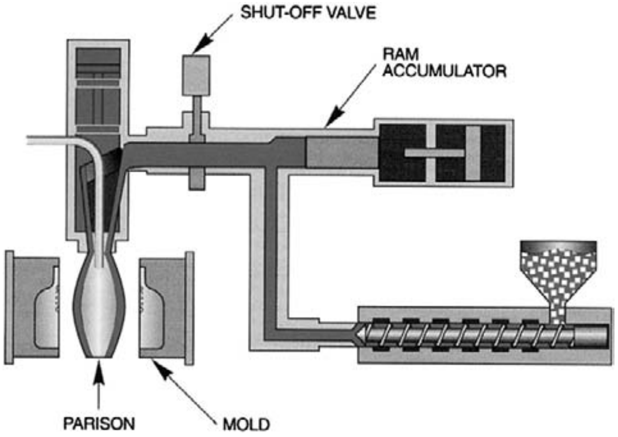


Figure 16.7 Ram accumulator blow molding machine.

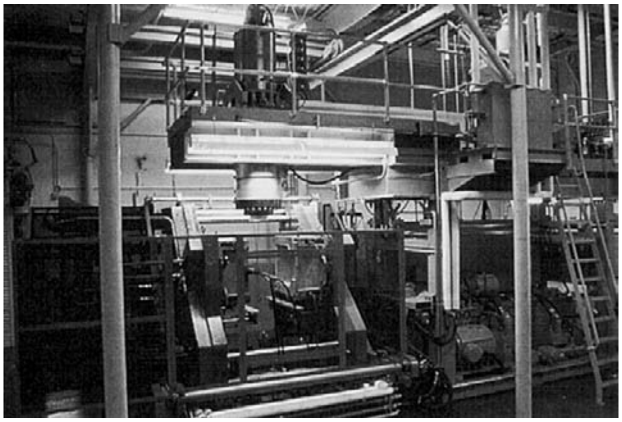


Figure 16.9 Hartig machine with 50-lb accumulator head used to produce automotive fuel tanks.

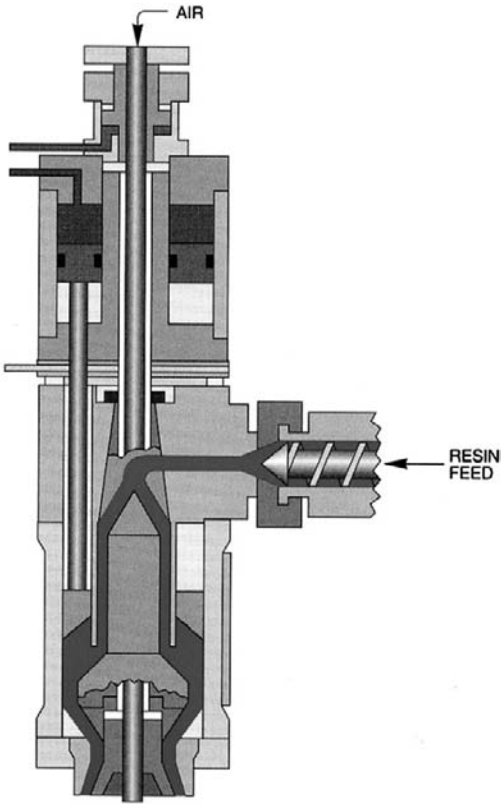


Figure 16.10 Kautex In Line Head

specifications are for styrene not for your specific resin. This goes back to the early days of injection molding.

You should know specifics as to the barrel, if it is lined type of lining, has a grooved feed throat, type of barrel heating and cooling, voltage of heater bands, number of zones on the barrel, location of thermocouples, and does it contain a melt transducer to read the extrudate actual temperature.

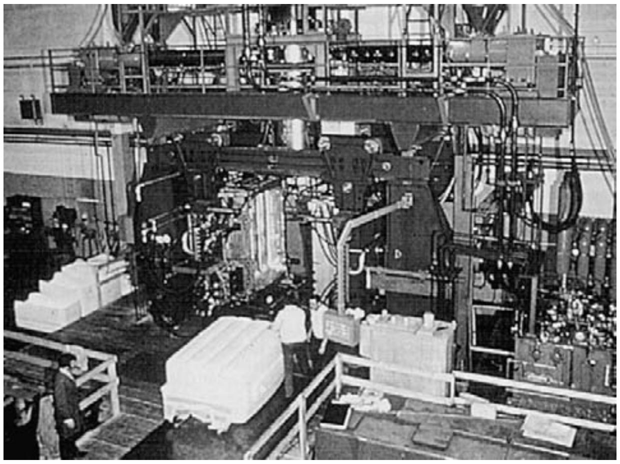


Figure 16.11 1320-gal HDPE tank being produced on a Kautex accumulator machine.

You should know all the specifics relative to the screw. You need to know is it specific to your resin or is it a general-purpose screw. The *L*/*D* of the barrel and screw plus the compression of the screw should be shown. Does the screw have the capability to be internally cooled or heated, and how many flights does it contain in the feed section, transition section, and the meter zone or is it of constant depth is the information you should know.

You should look at the heater bands on the barrel to ensure they are rotated and not lined up for all the electrical leads to be in line. If they are all aligned, this will be a cold line on the barrel, where all the heater bands clamp on the barrel. This is also true of the extrusion head and accumulator. The line up of all the heater bands may look nice on a new machine; however, you will have a line of no heat, except conductive heat within the steel in this location.

All melt transfer lines feeding the head or accumulator should be fully covered with a heating element.

Any area of exposed steel will be causing a cool spot that the heated homogeneous resin must pass through to the pin and bushing to produce a parison. Remember, you are purchasing or using an average machine to produce an average part.

If you are using an accumulator, you should know if it is designed for first in first out, or first in last out. Again, all the areas on the accumulator should be covered with heater bands and have thermocouple control points that are not at the top or bottom of the accumulator. You should check if you can produce the full range of the accumulator (i.e., 5 lb, 10 lb, etc.) and is the parison uniform in temperature along its length and circumference.

In the head, the maximum and minimum pin and bushing can be utilized. The centering of the pin and bushing are critical, and can the centering be easily reached, by your operators?

The head can be either center fed or side fed. Each equipment manufacturer has its own choice as well as you the user and producer.

You should know your head tooling as to type of steel, is it draw polished? Is it plated? What is the design? How are knit lines eliminated? and are all areas covered with heater bands? Is there a melt indicator in the head and where is it located and was it calibrated?

All the above are critical, so you should know where to troubleshoot problems if they occur in production.

Possibly, you design your own head tooling or you rely on an outside source.

If you are producing HDPE bottles, weight, wall thickness, handles, and neck dimensions all must be considered. The type of resin, as to swell, melt index, and hot melt strength, all have an effect on the pin and bushing design. The die land length and cross-sectional area must all be considered. When forcing a polymer through a die, the resin molecules will try to orient in the direction of flow. Naturally, as the extrudate leaves the die area, the resin wants to relax and the parison's own weight will exert force on the parison.

Shuttle machines and single station machines, other than the wheel type will normally use the core pin for entrance of the blow air. The mathematical formulas that can be used are:

$D_\mathrm{d} = 0.5\ N_\mathrm{d}$

$A_\mathrm{d} = 0.5\ A_\mathrm{b}$

where D_d is the die diameter and N_d is the minimum neck diameter, A_d is the cross-sectional area of the die and A_b is the cross-sectional area of the bottle wall.

Thus

$$A_\mathrm{d} = \frac{\pi}{4}(D_\mathrm{d}^2 - P_\mathrm{d}^2)$$

and

$$A_\mathrm{b} = \frac{\pi}{4}(B_\mathrm{d}^2 - (B_\mathrm{d} - 2t)^2)$$

and where P_d is the mandrel diameter and B_d and t are bottle diameter and thickness respectively.

As

$$A_\mathrm{d} = 0.5 \times A_\mathrm{b} = 0.5 \times \frac{\pi}{4}(B_\mathrm{d}^2 - B_\mathrm{d}^2 + 4B_\mathrm{d}t - 4t^2)$$

then

$$\frac{\pi}{4}(D_\mathrm{d}^2 - P_\mathrm{d}^2) = 0.5\frac{\pi}{4}(-4t^2 + 4B_\mathrm{d}t)$$

and

$$P_\mathrm{d}^2 = D_\mathrm{d}^2 - 2B_\mathrm{d}t + 2t^2$$

or

$$P_\mathrm{d} = \sqrt{D_\mathrm{d}^2 - 2B_\mathrm{d}t + 2t^2}$$

Given product weight W, length L and density ρ

$$A_\mathrm{L} = \frac{W}{L\rho}$$

then

$$A_\mathrm{d} = 0.5 \times A_\mathrm{b} = 0.5\frac{W}{L\rho}$$

or

$$\frac{\pi}{4}(D_\mathrm{d}^2 - P_\mathrm{d}^2) = 0.5\frac{W}{L\rho}$$

then

$$D_\mathrm{d}^2 - P_\mathrm{d}^2 = \frac{4 \times 0.5}{\pi}\frac{W}{L\rho}$$

or

$$P_\mathrm{d}^2 = D_\mathrm{d}^2 - \frac{2W}{\pi L\rho}$$

and

$$P_\mathrm{d} = \sqrt{D_\mathrm{d}^2 - \frac{2W}{\pi L\rho}}$$

in a situation as the wheel where the parison is controlled

$D_\mathrm{d} = 0.9\ N_\mathrm{d}$

$A_\mathrm{d} = 0.9\ A_\mathrm{b}$

Naturally, if the resin is prepuffed this will affect the formulas. Normally, the land length of the die will be eight times the gap distance between the pin and bushing. Land length should never be under one-fourth of an inch to ensure you achieve the desired parison flare out. Sharp corners and abrupt changes in the tooling should be avoided. In a normal setup the pin should be approximately 0.010 in. below the bushing (Figure 16.12).

The formulas presented here are for use with long land dies, those having a 20—30:1 ratio of mandrel land length to clearance between mandrel and bushing.

In their use, consideration must be given as to the anticipated blow ratio, the ratio of maximum product outside diameter to the parison diameter. Normally, ratios in the range of 2—3:1 are recommended. The practical upper limit is considered to be about 4:1.

For large bottles with small necks, this ratio has been extended as high as 7:1 so that the parison fits within the neck. In such a case, a heavier bottom and pinch-off results from the thicker parison. Also, less material is distributed in the bottle walls 90° from the parting line than in similar bottles with lower blow ratios. In this case, it is normal to ovalize the bushing.

When the neck size of a bottle or the smallest diameter of the item is the controlling feature (as when the parison must be contained within the smallest diameter), the following approximations may be used to calculate die dimensions:

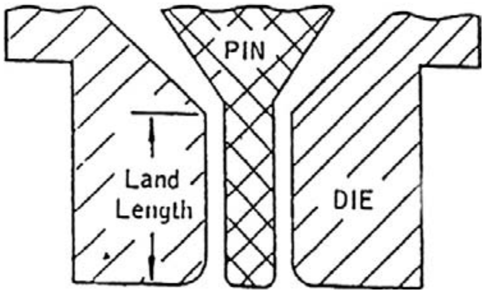


Figure 16.12 Pin position.

For a free falling parison:

$$D_\mathrm{d} \cong 0.5N_\mathrm{d}$$

$$P_\mathrm{d} = \sqrt{D_\mathrm{d}^2 - 2B_\mathrm{d}t + t^2}$$

Where:
D_d = Diameter of die bushing (in.)
N_d = Minimum neck diameter (in.)
P_d = Mandrel diameter (in.)
B_d = Bottle diameter (in.)
t = Bottle thickness at B_d (in.)

This relationship is useful with most polyethylene blow molding resins, and is employed when bottle dimensions are known, and a minimum wall thickness is specified. It is particularly useful for round cross-sections.

The 0.5 figure presented for selecting the diameter of the die bushing may change slightly, depending on processing conditions employed (stock temperature, extrusion rate, etc.), resin melt index, and die cross-sectional areas available for flow. It may be slightly lower for a very thin die opening (small cross-section) and higher for large openings.

If product weight is specified rather than wall thickness for a process employing "inside-the-neck" blowing, the following approximation may be employed:

$$P_\mathrm{d} = \sqrt{D_\mathrm{d}^2 - \frac{2W}{\pi L \rho}}$$

where:
W = Weight of object (g)
L = Length of object (in.)
D_d = Density of the resin (g/cc)
T = Wall thickness (in.)

This system is applicable to most shapes and is of particular advantage for irregularly shaped objects.

A controlled parison is one in which the dimensions are partially controlled through tension (i.e., the rotary wheel, the falling neck ring, etc.)

Because of this, the following relationships are employed:

$$D_\mathrm{d} \cong 0.9N_\mathrm{d}$$

$$P_\mathrm{d} = \sqrt{D_\mathrm{d}^2 - 3.6B_\mathrm{d}^\mathrm{t} + 3.6t^2}$$

$$P_\mathrm{d} = \sqrt{D_\mathrm{d}^2 - \frac{3.6W}{\pi L \rho}}$$

The pin and bushing or mandrel should be drawn polished for the initial trials. If no revisions are necessary then chrome the surfaces. In some instances, you may wish to coat the pin and bushing for easy flow and to prevent sticking and donuts being formed by the parison as it exits the die.

Blow air entrance and size of the blow air lines must always be checked. You must have adequate flow of the blow air and you should know where the main restriction for the volume of air required is in your blow air circuit. This is particularly true in large part blow molding.

It is a good practice to blow little barrels upon initial start-up so that you know when the part is fully formed, time wise with the air pressure you are using. Today's trend is to use two-stage air. The initial air entering is at 40—60 and then to use high pressure up to 250 lb to freeze the product in the mold and to achieve full details of the female mold.

When blow molding HDPE, the cooling time controls the cycle. This mold cooling is critical. Companies today are using two blow entrances to blow mold the product. In this situation, once the part is fully formed, one blow air entrance is used to exhaust at a specified pressure, while blow air at the full high pressure is constantly fed into the part. This allows for the blow air to act as inside cooling since it is flowing and not stagnant. When it is stagnant, the air in the product becomes heated from the heat of the product. By circulating the blow air, this heat is removed. The adiabatic expansion of the air entering provides cooled air to flow. Cycle times can be reduced up to 30% on small and large parts, plus warpage can be eliminated and paneling. You must have sufficient compressed air to use this air circulation inner cooling method. The blown product will exit the blow mold in a more uniform temperature since you have cooling of the outside skin of the product via mold cooling and you have the inside skin being cooled by the circulating air.

All so often we assume the mold opening time and mold closing time repeats. You should really know your clamp opening time and your total mold closing time. In closing, it is a good practice to close fast until you are approximately 0.5—0.1 in. of final close. Of course, this depends if your mold has moving cams or cylinders, stretch bars, movable blow pins, etc. All of these movements should be timed so you know if they repeat within a ≠ time.

The parison weight has always been a problem even with parison programmers. You should always produce a parison with the parison programmer and check the parison to determine if you are achieving the thickness in the heated parison at the desired location within the parison. If you use regrind, this will have a major effect on your parisons repeatedly, also color additives and lubricants.

So often a color match is made using virgin resin with the color additive, yet in production you use a percentage of regrind.

The screw of the plastifier is designed to pick up pellets, not chopped and screened chips of your resin. In grinding, you do not achieve uniform ground resin. You get strings, fines, and various sizes of chips from your grinders. Thus, you are feeding the hopper throat of your machine with a different bulk density of resin constantly. The plastifier is nothing but a pump and with different bulk density, your melt has differential pressures within its melt stream.

Fines are always in your system. Fines do not melt at the same melting temperature as your virgin resin or your regrind. Their molecular weights are different. Fines should always be eliminated. Fines can clog your dryers, cause streaks, star bursts, black specks, and tear drops in your blown product.

It is recommended that you use a separating type grinder anytime you use regrind in your daily production. It is wise to also pass your virgin material through a fine eliminator system while it is being fed to your machine hopper.

If you are feeding your blow molding machine through the use of a blender, it should be of the weigh blender type. However, you should conduct a test on the blender so you know it is feeding proper percentages of virgin resin, regrind, and colorant. You can save money if your color chip was produced using virgin resin and a color additive by having a true color chip produced using your percent of virgin resin, your percent of regrind (which already is colored), and your color additive. Colorants are expensive and this is one area where you can save significant costs over a year's production.

The style of parison cut off under your head tooling is one area in large part extrusion blow molding plants that can save thousands of dollars. So, often extra parison length is used, first of all because the mold maker left too great a distance in the blow mold for the tail and moille. Second, instead of a hot knife, or hot wire cut off or a scissors style parison pinch for the parison is not cut, or an arc pinch bar arrangement is used. These arrangements cost you extra resin, waste cycle time, cause more regrind, less efficiency of product parts, costs extra energy and extra labor.

Automatic part removal from your blow mold is nice, but have you figured what the extra parison length has cost you in extra drop time, extra resin, extra regrind, extra energy, and extra labor. More work needs to be accomplished in mold trimming, and with post-trimming using a computer coupled to a laser.

16.2.1 Parison Programming—Wall Distribution

Producing a quality parison with good wall distribution is the heart of extrusion blow molding. Controlling wall distribution consists of choosing the correct parison size for blowing a particular product, die shaping, and parison programming.

Parison size is very important—too small a parison can result in a thick pinch-off, which can cause rocker bottoms and warpage, and too high blow ratios to make the product without excessive thinning or blowouts. Too large a parison may result in a thicker wall than wanted at the ends of the pinch-off, excessive "flashing," trimming problems and excessive cooling requirements. The correct parison lies somewhere between these two scenarios.

"Programming" is defined as controlling the wall thickness of the parison from the moment the parison is exiting the die head. Figure 16.13 is a schematic of a programming die head.

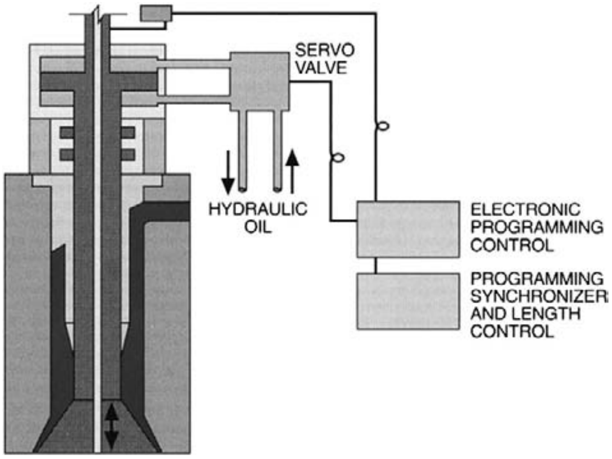


Figure 16.13 Programming die head.

Figure 16.14 below is a schematic depicting the movement of the pin in diverging tooling and in converging tooling.

Figure 16.15 is an example of parison programming to produce an irregular shaped detergent container.

Another method used in the blow molding industry to aid in wall distribution is die shaping. Die shaping is machining the die gap larger in specific areas to increase the parison thickness where desired in the product to be produced. Figures 16.16 and 16.17 are photos of a pin and bushing with die shaping. The depth, width, and land length of the die shaping is based on experience. Usually, the shaping for a gallon container will be 0.002—0.003 in. deep. Die shaping requires a precise set-up on the machine by the machinist.

16.2.2 Resin Characteristics

One of the most important items in blow mold design is for the designer to understand the plastic resin and its behavior in blow molding the required product. All the thermoplastic resins used except PET are like blowing bubble gum.

Once this statement is made, then it is important to note that probably the most uncontrollable variables in the blow molding process is the base resin chosen to be used.

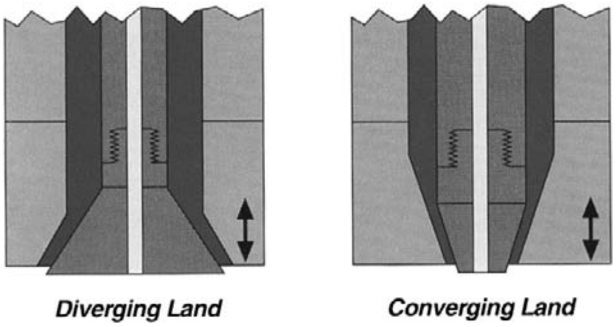


Figure 16.14 Pin movement in diverging tooling and in converging tooling.

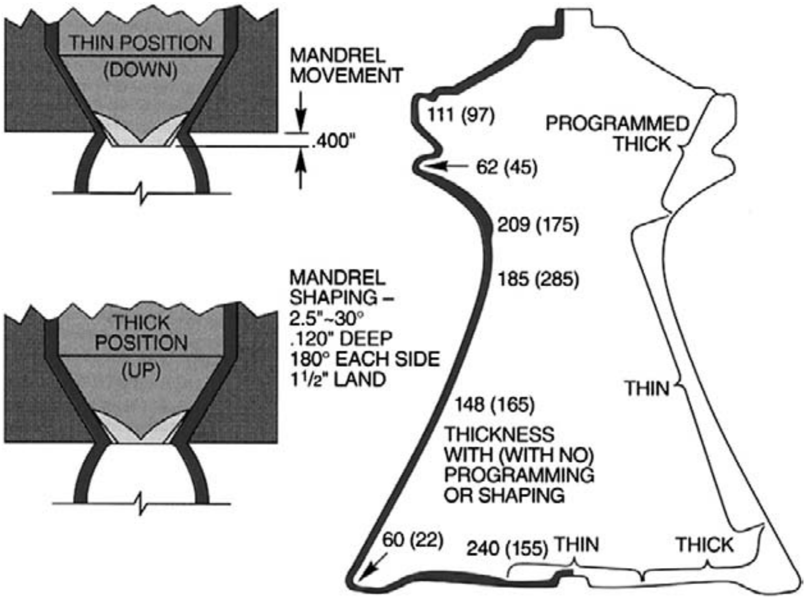


Figure 16.15 Parison programming produces an irregular-shaped detergent container.

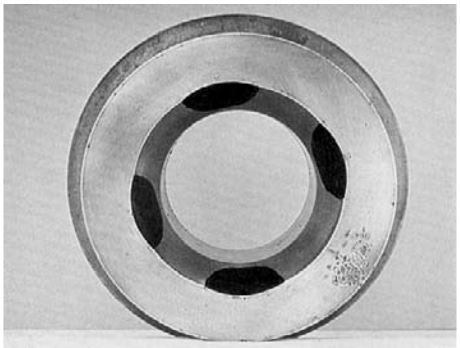


Figure 16.16 Pin and bushing with die shaping.

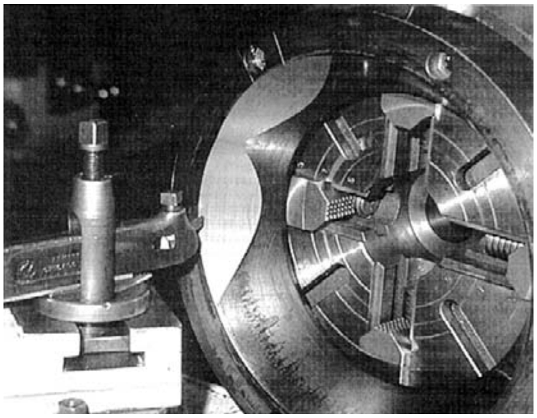


Figure 16.17 Pin and bushing with die shaping.

Variations from supplier to supplier of like resins, and even variations from lot to lot and box to box within a lot from one supplier, can cause havoc in the blow molding process. While the molder may not be able to control the base resin entering the process, he can do much to reduce the variations within the process.

Elimination of contamination of resin by dirt, trash, and/or other resins can be eliminated by common sense, control, and cleanliness, in the process. Proper, consistent proportioning and blending of new resin, color concentrate, additives, and regrind will reduce variations to a minimum.

Resin temperature affects viscosity and part quality by causing variations in the parison extrusion time, length, thickness, and cooling time. This temperature is a critical parameter that must be monitored carefully and the source of any variations must be accurately identified. Extruder factors that can cause resin temperature variations include:

- Extruder heat profile
- Screw speed
- Screw and barrel condition
- Barrel cooling conditions and setup
- Temperature settings for controls in manifolds
- Heads and tooling
- External factors (e.g., air currents caused by fans, open window, air leaks, etc.).

From a processing technology standpoint, all thermoplastic materials that have the following properties are suitable for blow molding applications:

- Sufficient thermal stability for the processing temperature range and, if necessary, for repeated processing
- Sufficient flowability of the homogeneous, plasticated melt

- Sufficient stretchability of the tube (parison) even at high stretching speeds
- Excellent repeatability of parison weight and length
- A smooth parison surface
- Compatibility with additives such as master batches, pigments, etc.
- A sufficiently wide processing range for the required finished part properties
- Excellent lot to lot consistency
- Good drop impact resistance at low temperatures

For technical parts, good mechanical properties are of prime importance. However, excellent surface quality must also be obtained if, for example, the part will subsequently be painted.

Depending on the size of the container, a resin may or may not be a good choice. The following list reflects many practical applications.

16.2.3 Small Parts, Under 5 L

Polyolefins (HDPE/LDPE/PP)
Polyvinylchloride (PVC)
Polyacrylonitrile (PAN)
Polystyrene (PS)
Styrene-based polymers (SAN)
Polyester (saturated; linear: PET)
Polyvinylidene fluoride (PVDF)
Thermoplastic Elastomers (TPE).

16.2.4 Large Parts, Over 5 L, Including Technical Parts

Polyolefins (HDPE/PP)
Polycarbonate (PC)
Polyacetal (POM)
Polyamide (PA)
Polyvinylidene fluoride (PVDF)
Thermoplastic olefins (TPO)

For large part blow molding, high molecular weight HDPE is normally used. The higher molecular weight helps provide the melt strength needed for the production of such heavy parts as 55-gal drums, which can weigh up to 22 lb. The high molecular weight also provides more toughness to meet the demanding performance requirements of such parts as automobile fuel tanks. These grades are usually supplied in a density range of 0.945−0.955 g/cc, and a melt flow range of 2.0−15.0 g/10 min (melt flow index, MFI, 190°C/21.6 kg). Applications include shipping drums, bulk shipping containers, 90-gal refuse carts, gasoline tanks, lawn and garden spray tanks, and a variety of other tanks.

16.3 Formulas for Blow Molding

16.3.1 Blow Ratio

The blow-up ratio used in blow molding is expressed by the formula below:

$$\text{Blow ratio} = \frac{\text{largest diameter in blow mold}}{\text{parison inside diameter}}$$

Generally, the value is between 1.5 and 3; however, it can be up to 7 in unusual products.

It can also be stated that the root diameter of the neck of the product in relation to the maximum diameter of the body of the product to be produced.

16.3.2 Part Thickness

The blow-molded product should be designed in such a manner to minimize any areas of extreme stretching or of too deep a draw, due to the thinning out of the parison as it is being blown to the cavity walls of the blow mold. All corners should have generous radii and the product should have smooth transitions from one section to another as the panel to the shoulder, or the label panel to the support segment joining the base of the product.

The amount of stretch out of the parison is a function of the part size and configuration in relation to the parison size and its wall thickness.

A practical guide for designing a rectangular container is to allow a minimum corner or edge radius of at least one-third the depth of the blow mold half. For cylindrical containers, the radius should be at least one-tenth the diameter of the container.

In general, the formula for average part thickness can be expressed as follows:

$$\text{Average part thickness} = \frac{\text{parison surface area}}{\text{product surface area}} \times \text{parison thickness}$$

16.3.3 Clamp Force (tonnage)

Clamp tonnage is determined by the addition of the air blow pressure in pounds per square inch times the product's projected area in square inches, plus the pinch-off area in pounds per square inch. A safety factor of 25% is used.

The specific pinch-off force for various plastic resins are listed below:

PVC—400−500 lbs/inch.
HDPE—600−700 lbs/inch.

PP—700—800 lbs/inch.

PC—1000 lbs/inch.

Thus, the required clamp tonnage is the addition of the above two forces.

Required clamp tonnage = $A + B$

$$\text{(A)}\ \frac{\text{Part projected area }(\text{in}^2)\times\text{ blow pressure }(\text{psi})\times 1.25}{2000\ (\text{lbs/ton})}\ (\text{tons})$$

$$\text{(B)}\ \frac{\text{Pinch-off length (in)}\times\text{ specific pinch-off force (lbs/in)}}{2000\ (\text{lbs/ton})}\ (\text{tons})$$

This calculation will indicate if your blow molding clamp tonnage is sufficient to blow the product with a specific air pressure and not have the clamp blow open during the process.

16.3.4 Die Swell

The extrudate will swell as it exits the die head (see Figure 16.18). This swelling behavior is a result of the elastic component of the resin's flow. It is very possible to measure the resin's swell as it exits the die and to use this to ascertain the tooling sizes, and to determine if the resin can be used in producing the product.

There is also a weight swell of the resin and this is a result of the temperature, length of parison, speed of parison drop, hang time of the parison, and the hot melt strength of the resin to be used.

Swell ratios are defined below in Fig. 16.18.

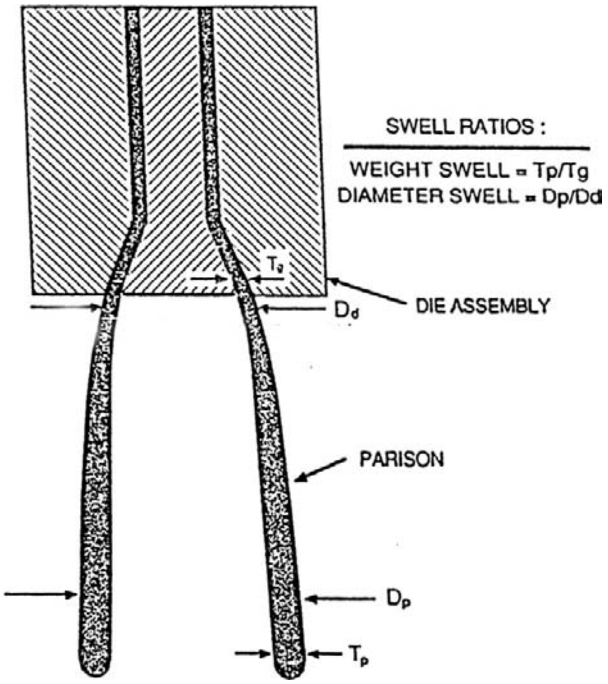


Figure 16.18 Extrudate will swell as it exits die head.

16.3.5 Reynolds Number

To determine the proper flow for each blow mold, the Reynolds Number should be determined. The Reynolds Number is a nondimensional parameter used to determine the nature of flow along surfaces. Numbers below 3000 represent laminar flow, numbers from 2500 to 3000 are transitional flow, and numbers above 3000 represent turbulent flow.

To determine the Reynolds number, the following formula is used.

$$Re = \frac{\rho \nu D}{\mu}$$

where:

D = channel dia. (ft) (1 in = 0.08333 ft)

ν = fluid velocity (ft/sec)

ρ = fluid density (lb/cu ft)

μ = fluid viscosity (lb/ft.sec) (1 poise = 0.0672 lb/ft.sec)

16.3.6 Heat Extraction Load

The heat extraction load or the amount of heat to be removed from the product must be determined. This is important, as the amount of heat taken out by the blow mold must be known if the process is to be economically predictable. The amount of heat to be removed, Q, is determined by the material's temperature and the amount of plastic being delivered to the mold. It is calculated as follows:

$$Q = C_\rho m \Delta t (0.003968)$$

where:

Q = total change desired during molding, BTU

C = specific heat of the plastic material being processed (cal/g°C)

m = amount of plastic per hour to be cooled expressed,

Δt = initial plastic (parison temperature into the mold minus final (demolding) temperature of the plastic, °C (0.003968 BTU = 1 calorie)

16.3.7 Other Factors

16.3.7.1 Pinch-offs

When blow molding whether it be a container, or an industrial part, particular attention should be made to ascertain the best pinch-off design is used in the tooling. The pinch-off areas pinch the ends of the plastic parison and seal the edges together when the blow mold closes. These surfaces are subject to more wear than any other part of the blow mold. The high heat conductive metals are preferred for blow molds, such as aluminum, beryllium copper, or ampcoloy in the pinch-off areas. Steel inserts are often used if mold repair is a problem due to the softer metals shorter wear life.

A neck pinch-off insert is shown below in Figure 16.19.

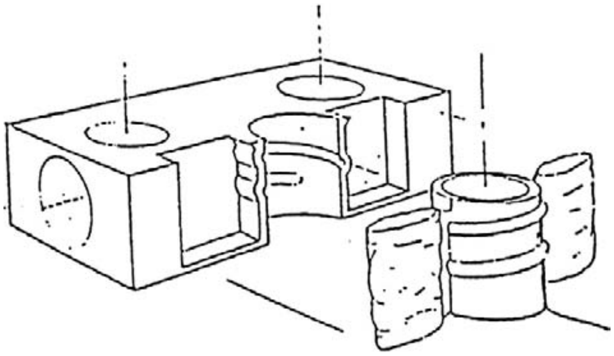


Figure 16.19 Neck pinch-off insert.

Generally, in large volume production, pinch-off inserts are made of steel (P-20 or S-7) with the other portions of the blow mold produced from a nonferrous metal. The pinch-off edge should not be similar to a knife edge, or it will tend to act as a cutter and will yield a "V" groove where the tail or pinch-off area of the parison is forced to bond. Figure 16.20 depicts a poor weld line due to the pinch-off having a knife edge.

Poor pinch-off; relief angle was either too large or too small.

A quality pinch-off is shown in Figure 16.21.

In container blow molds used in extrusion, there will be a hardened steel insert with a land of 0.003/0.005 in., then a relief angle of 20° with a total depth of 0.030 in. measured from the inside bottom of the blow mold and then a 45° cut to the bottom of the relief section in the pinch-off area. Normally, the total of this relief will be 90% of the parison wall thickness to be pinched (Figure 16.22). This design will also minimize residual flash. It is best to design the pinch land at 0.010/0.015 in. and have metal to remove if the pinch is not adequate.

Figure 16.20 Pinch-off with knife edge produces poor weld line.

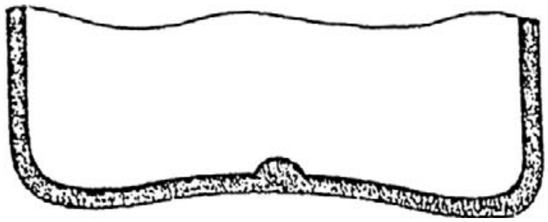


Figure 16.21 Quality pinch-off.

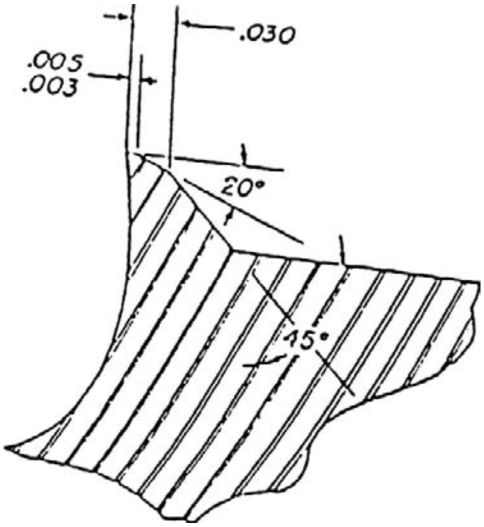


Figure 16.22 Design often used to minimize residual flash.

Anyone that does extrusion blow molding will state, "The best pinch-off design is the one that works in your tooling."

16.3.7.2 Venting

All blow molds have to be vented. The air that first occupied the product area must escape more rapidly than the hot plastic is being blown to fill the product area within the closed blow mold. This is known as venting.

Improper venting in some cases is very hard to ascertain as the production problem that is keeping from consistent quality parts being produced each cycle. Olefins will show burn signs and in some cases, carbon residue on the blown product if the venting is really insufficient. There may be no burning of the plastic evident, however, the part produced just does not totally reproduce the blow molding surface. In blow molding styrene and particularly PET, the resin will cool and just quit stretching since the compressed air due to it being trapped is higher pressure than what is inside the heated parison or preform.

Well-designed molds are vented, as entrapped air in the mold prevents good contact between the parison and the mold cavity surface. When air entrapment occurs, the surface of the blown part is rough and pitted in appearance. A rough surface on a shampoo bottle, for example, is undesirable because it can interfere with the quality of decoloration and can detract from the overall appearance. Molds are easily vented by means of their parting line, with core vents and with small holes. A typical mold parting line venting system is shown in Figure 16.23.

When certain areas of the mold cavity are prone to trap air, core vents as shown in Figure 16.24 can be used.

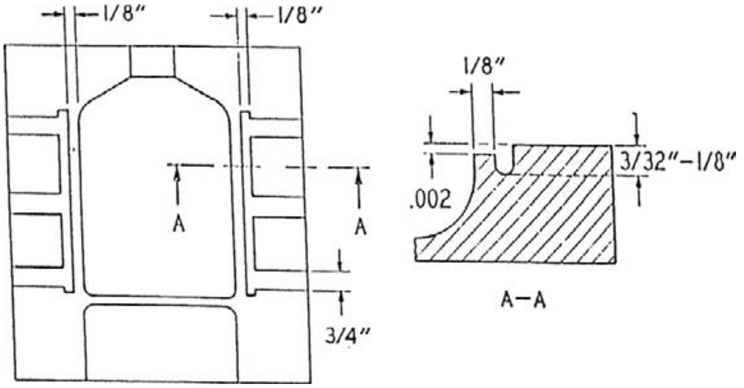


Figure 16.23 Typical mold parting line venting system.

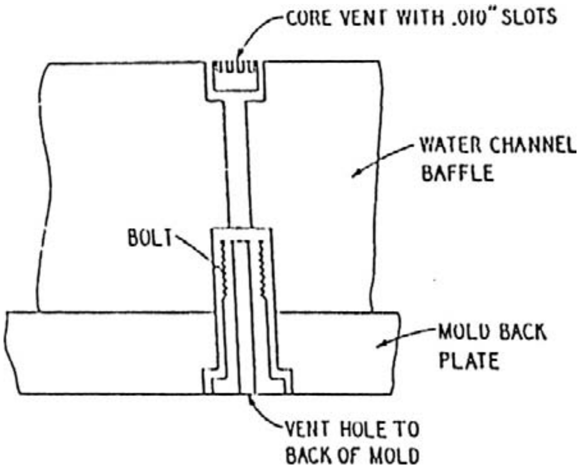


Figure 16.24 Use of core vents to release air in mold cavity.

Venting in the mold cavity should be anticipated in the mold design and layout of the cooling channels so that provisions can be made for their locations. For cast mold the cooling channel baffles can be located over areas to be vented, as shown in Figure 16.25.

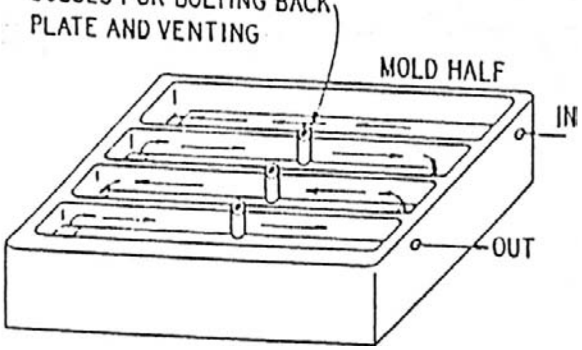


Figure 16.25 Colling channel locations in cast mold.

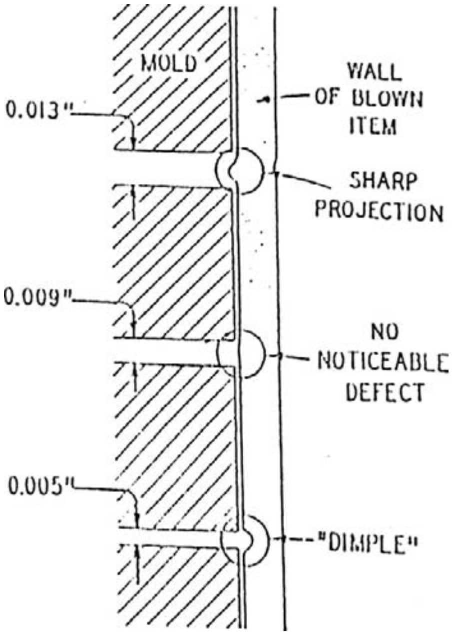


Figure 16.26 Effect of hole size on part surface.

The vent opening will pass through a boss in the baffle to the back or outside of the mold. In machined molds, care must be taken so that vents miss the drilled cooling channels. When core vents cannot be used because the slots mark off on the blown part and show, small drilled holes can be used. The effect of the size of hole on the surface of the part is shown in Figure 16.26.

If the hole is too large, a protrusion will be formed; if it is too small, a dimple will be formed on the part. Venting also can be incorporated in molds that are made in sections. A 3- to 10-mil gap between the two sections with venting to the outside of the mold is a very effective vent. For small containers a 2- to 3-mil opening is used, and up to a 10-mil opening has been used on large parts such as a 20-gal garbage container.

Table 16.1 Shrinkage and other properties of some common blow molding materials

Polymer	Shrinkage* (%)	Linear Coefficient of Thermal Expansion ($K^{-1}\ 10^{-4}$)	Specific Volume (V) at 20 °C (cm^3/g)
LDPE	1.2–2	2–3 (20 °C)	1.09
HDPE	1.5–3	2.0 (20 °C)	1.05
Polyacetal	1–3	1.3	0.7–0.71
Polypropylene	1.2–2.2	1.6	1.10
Polystyrene	0.5–0.7	0.7–0.8	0.89–0.95
Polyvinylchloride	0.5–0.7	0.8	0.81

** Measured on an axially symmetrical test bottle with an average wall thickness of 0.7–1 mm, by method of R. Holzmann, Kautex-Werke, and Hangelar.*

The mold cavity surface has an important bearing on mold venting and on the surface of the molded part. With polyethylenes and polypropylenes, a roughened mold cavity surface is necessary for the smoothest surface. Grit blasting with 60–80 mesh grit for bottle molds and 30–40 mesh grit for larger molds is a common practice. The clear plastics such as PVC and styrene required a polished mold cavity for the best surface. A grit-blasted surface will reproduce on some clear plastics, an effect that is not normally desirable.

16.3.7.3 Shrinkage

Because molding is executed with a melt that is then solidified, shrinkage and warpage are experienced with most materials. Higher crystallinity polymers have higher shrinkage values (Table 16.1). Shrinkage is dependent upon the wall thickness, due to the different cooling rates, the cycle time to cure the product will be what it takes to cool the thickest wall section.

Cooling of a plastic part consists of three separate transfer mechanisms:

1. Conduction of heat in wall of part
2. Conduction of heat in mold wall
3. Convective transfer of heat in cooling fluid

Step 1 is dependent upon resin type, temperature, and wall thickness. Step 2 depends upon the mold material's thermal properties, porosity, and mold/cooling layout geometry. Step 3 can be optimized with regard to temperature, fluid flow rate, and prevention of scale formation on the liquid side. The cooling rate of most processes is limited more by the rate of conduction within the plastic than by the rate of conduction in the mold. The cyclic time of a part is usually strongly dependent on its wall thickness.

16.4 Troubleshooting

The common blow molding difficulties are listed below with their suggested solutions:

Problem	Suggested Solution
1. Low gloss	1. Increase material temperature 2. Increase mold temperature 3. Improve mold venting 4. Increase air pressure 5. Increase air blowing rate
2. Excessive cycle	1. Decrease material temperature 2. Decrease mold temperature 3. Decrease part wall thickness 4. Improve mold coring 5. Increase material density 6. Increase air pressure 7. Increase melt index (with decreased stock temperature)
3. Die lines	1. Clean the die 2. Smooth and polish the die 3. Increase mold temperature 4. Increase air pressure 5. Increase air blowing rate 6. Increase purge time when changing materials 7. Improve die streamlining

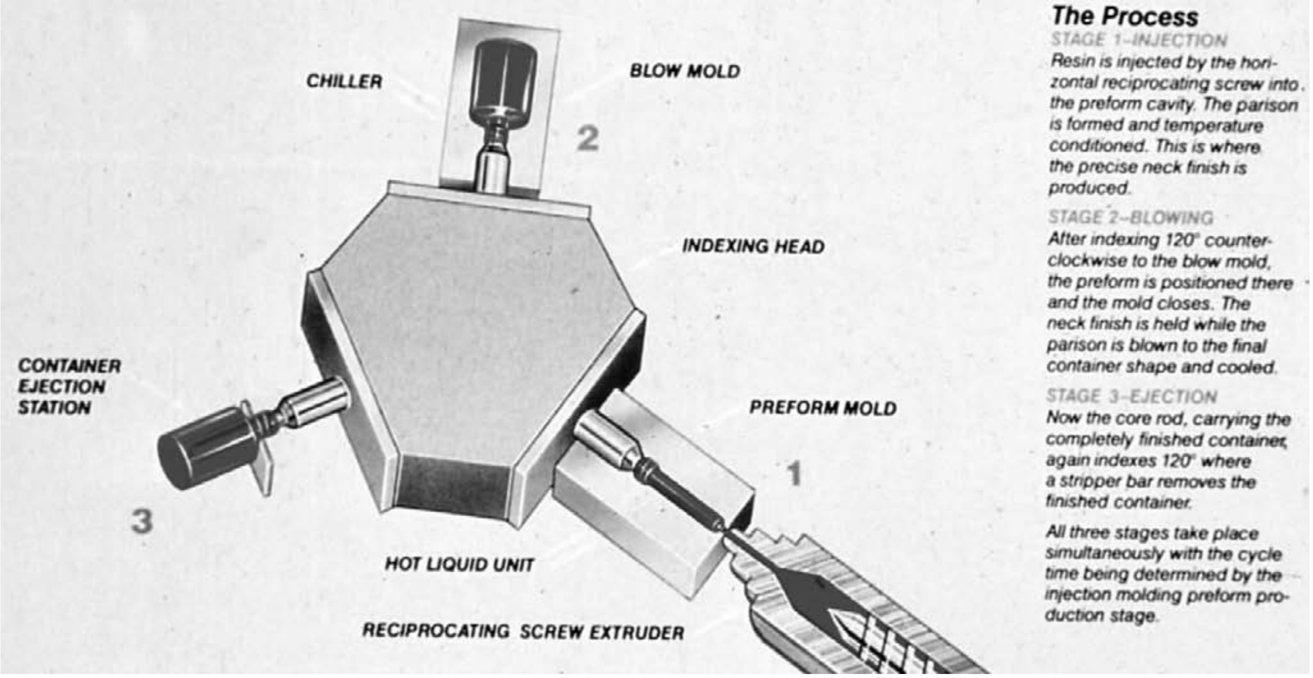
(*Continued*)

Problem	Suggested Solution
4. Low bottle weight	1. Increase due to mandrel clearance 2. Decrease material temperature 3. Increase extrusion speed 4. Decrease extrusion die temperature
5. Surface roughness	1. Increase stock temperature 2. Decrease extrusion speed 3. Increase die temperature 4. Improve die streamlining
6. Weak pinch	1. Adjust material temperature 2. Increase pinch blade land width 3. Decrease rate of mold closing
7. Parison curl	1. Adjust and center die-parison curls toward thin area 2. Improve die and head heat uniformity 3. Dirty die head
8. Wall thickness non uniform	
(a) Vertically sag	1. Decrease material temperature 2. Increase extrusion speed or accumulator ram pressure 3. Lower melt index 4. Increase material density
(b) Circumferentially	1. Decrease blow-up ratio 2. Improve head and die heat uniformity 3. Adjust and center the die
9. Excessive thinning at parting line	1. Decrease stock temperature 2. Increase mold temperature 3. Increase air pressure 4. Increase air blowing rate 5. Improve mold venting 6. Improve mold temperature
10. Excessive shrinkage	1. Decrease wall thickness, or make more uniform 2. Decrease mold temperature 3. Increase air pressure 4. Decrease material temperature 5. Decrease density 6. Improve mold coring
11. Excessive parison swell	1. Increase material temperature 2. Increase die temperature 3. Decrease extrusion speed 4. Increase melt index 5. Reduce die size
12. Donut formation	1. Wait for mandrel temperature to reach die temperature 2. Clean the lower surface of the die
13. Warped top and bottom	1. Slow the cycle 2. Decrease mold temperature 3. Decrease stock temperature 4. Decrease part weight 5. Improve mold coring
14. Variable bottle weight	1. Finer extruder screen pack 2. Increase screw cooling 3. Raise rear extruder heats 4. Decrease extrusion rate

16.4.1 Injection Blow

Extrusion blow molding is normally used to produce plastic containers of the size 8 oz and above. Under 8 oz, it is normally more economical to use the process described as injection blow molding.

Injection blow molding is the process whereby the plastic preform is injection molded and the preform travels on the core rod to the blow mold station, where blow air enters through the core rod and lifts the hot preform material off the core rod and forms it by air pressure to the design of the female blow mold. Upon cooling to the desired shape, the blow molds open and the core rod containing the blown plastic bottle indexes to the stripper station where the blown bottle is stripped from the core rod. The process then repeats. Figure 16.27 depicts the total process.



The Process

STAGE 1–INJECTION

Resin is injected by the horizontal reciprocating screw into the preform cavity. The parison is formed and temperature conditioned. This is where the precise neck finish is produced.

STAGE 2–BLOWING

After indexing 120° counterclockwise to the blow mold, the preform is positioned there and the mold closes. The neck finish is held while the parison is blown to the final container shape and cooled.

STAGE 3–EJECTION

Now the core rod, carrying the completely finished container, again indexes 120° where a stripper bar removes the finished container.

All three stages take place simultaneously with the cycle time being determined by the injection molding preform production stage.

Figure 16.27 The injection blow molding process. *(Courtesy of Johnson Controls, Inc.)*

The advantages and disadvantages of injection blow molding versus extrusion blow molding can be summed up as listed below:

IBM vs. EBM

Extrusion Blow	**Injection Blow**
Scrap	
From 5% to 30% scrap must be ground, mixed with virgin and recycled—increasing equipment investment and maintenance cost to 15%, also causes a variation in bulk factor in raw material resulting in instability of process.	No scrap normally with proper tool and controlled shop efficiency. *All bottles are completely finished in mold.* Scrap comes from start-up and errors in color mix. Re-run scrap does not affect process materially.
Orientation of plastic	
Except in special Bekum two-stage extrusion blow molder, all extrusion parisons are blown at too high a temperature to orient the plastic.	Injection blow inherently gets some orientation from the injection stage during cavity filling. Also, since plastic temperature drops about 150 ° styrene orients into a strong container. No effect on P.E.
Tool cost	
Blow mold and extrusion tooling required only—cost is 30–40% of injection tooling cost. Superior for very low volume requirements under 500,000 per year.	Must have three core rods for each cavity and an injection mold. Tooling is precise and expensive. However, high price is justified by higher efficiency and is some times indicated by preference for this method.
Clarity	
Extrusion die lines appear with some materials, or if tooling is improperly finished.	Containers are always clear when using transparent materials. Polypropylene is clearer because some orientation occurs during blow-up in the hoop direction
Bottom pinch-off scar	
Often creates objectionable appearance or weak point where seal is not adequate.	No pinch-off.

(*Continued*)

IBM vs. EBM

Extrusion Blow	Injection Blow
Bottom push-off	
Is difficult because need to pinch-off and seal parison.	Great design leeway for bottom shapes with retractable bottom plugs in blow mold.
Machine cost	
For medium-size bottles cost is similar for same production.	Cost per 1000 bottles per hour improves greatly for higher number of cavities. Such as 10–14 cavities on a 10-s cycle.
Widemouth containers	
Must be postfinished, inspected, and trimmings removed. Neck is poor in quality and generally flimsy. Very thin neck possible, if desired. Tolerances are very limited.	Injection-molded neck, any thickness except must be minimum of approximately 0.040 in. Finish and tolerance excellent.
Inside neck tolerances	
Good on some equipment, but moving tool parts wear. Accurate under cut difficult.	Accuracy excellent for plug inserts for squeeze bottle or cap seal for flexible materials (nose or deodorant spray).
Special shapes for safety caps.	
Postforming limited in shape and tolerances.	Offers wide range of any form than can be injected and molded.
Rigid containers	
Neck finish poor because of difficulty with pinch-off and postfinishing. Very large parts can be blown. Handle ware can be produced.	Excellent results with many molds in use and more being readied for production.

There are both three- and four-station injection blow molding machines in the industry today. Wheaton Industries, which is one of the largest injection blow molders in the world, pioneered the four-station design, primarily for safety. However, with the movement to PET on the injection blow molding machines the fourth station has become a necessity to allow for the core rods to be conditioned through the use of an air chamber. The core rods are not temperature controlled, but are allowed to have their bodies or shanks, to cycle within a specified temperature window as depicted below.

Many companies have tried to use the three-station machines utilizing water to temperature control the core rods, however, the process is not stable and the producer cannot produce at the necessary production efficiency. The temperature-controlled core rod just cannot maintain the proper temperature at the right time to produce acceptable PET bottles.

Basic credit is given to Piotrowsky for developing the first true injection blow molding process. Others followed as Farkus, Moslo, and Gussoni, with the industry once having Piotrowksy's principle adopted the Gussoni method as the simplest method to use in a production machine (Figure 16.28).

Normally, the injection blow molding machines use the horizontal rotary transfer table (Gussoni Method) as Wheaton, Jomar, Bekum, Fischer, and Johnson Controls. Battenfeld Fischer also produced a vertical rotary table type machine known as the FIB 15 but is now obsolete. Companies producing IBM machines are now Wheaton (Alcan), Milacron (Rainville), and Jomar.

Most of the thermoplastics used for extrusion and injection molding are used in the IBM process. Some of the resins are especially formulated for use on IBM machines. Easy flow, metal release, heat stability, and melt strength are some of the properties, which are specifically designed into materials for IBM processing. Resins currently processed on IBM equipment include HDPE, LDPE, PS, ABS, PP, PVC, Barex, PET, TPR, polysulfones, polycarbonate, Amidel, acetal, and polyarylate.

Tooling for injection blow molding consists of injection molding die set, injection molding manifold, parison injection molds, blow mold die set, blow molds, neck rings, core rods, face bars, end plates for the parison injection molds, secondary nozzles for the injection manifold, stripper bar, and retractable bottom plugs for the blow molds if the bottle push up exceeds 0.045 in. in depth.

Tooling can cost anywhere from $30,000 to $160,000 depending on cavitation. If PET is processed the conditioning chamber is added tooling required.

All the injection blow molding machines sold today use a horizontal recriposcrew plastifier for injection molding the preform except Jomar, though Jomar has now offered a horizontal recriposcrew, a deviation from their vertical screw design.

Most injection blow molding machines are designed to accept tooling from others as Rainville's tooling will fit into a Wheaton machine and vice versa. The modifications are relatively easy and inexpensive to fit tooling from one make machine to another if no additional cavities are required.

Three main factors are involved when choosing an injection blow molding machine. First, is the capacity of the plastifier in its ability to plasticize enough plastic material for maximum cavitation. Since the cycles can be relatively fast on the IBM machine, the recovery time of the plastifier can be a limiting factor as to how many cavities can be produced

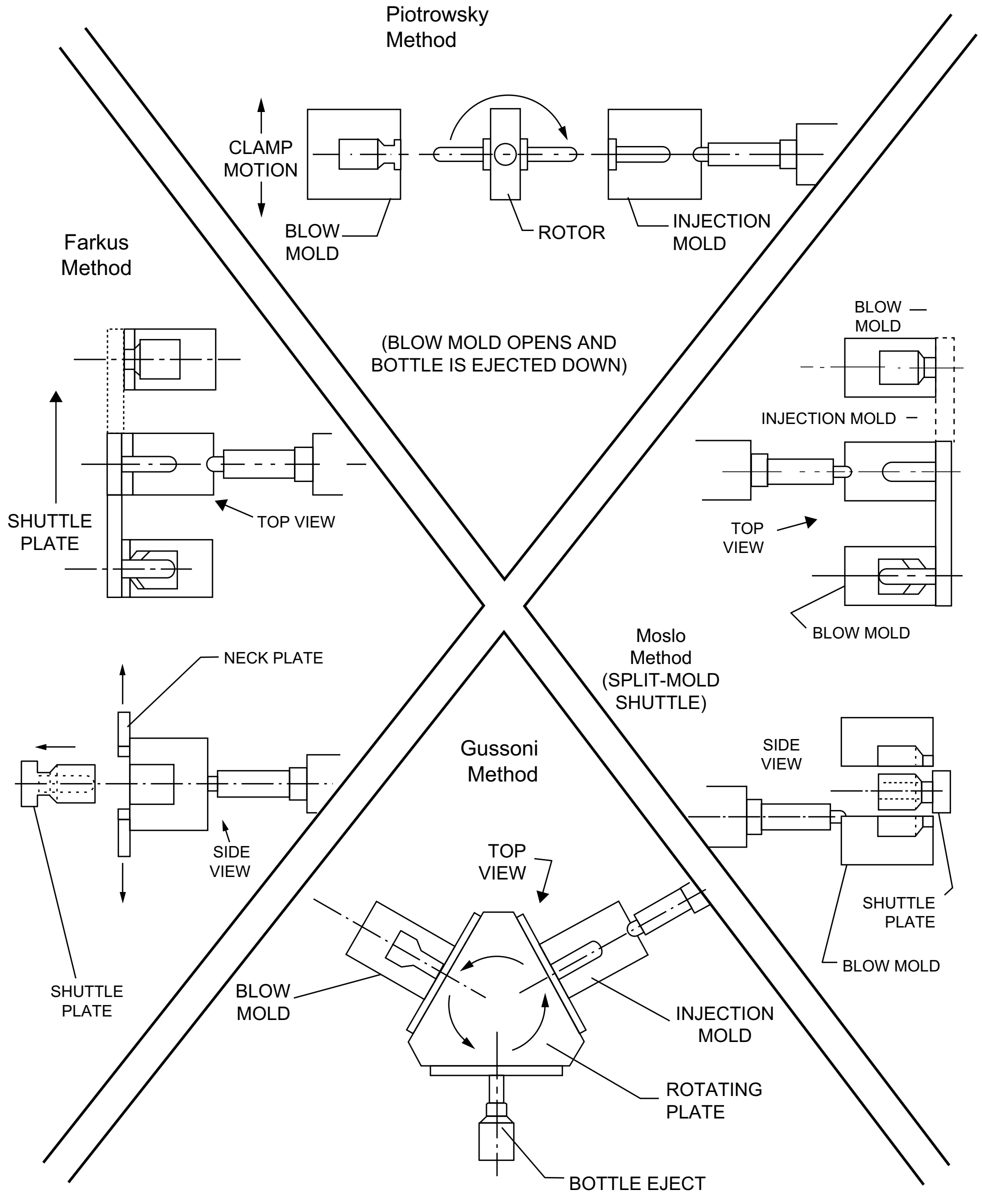


Figure 16.28 Injection blow molding methods.

or as to how fast a cycle can be used in production. Second, is the injection station clamp tonnage capacity. Clamp tonnage is calculated by using the projected area of the preform as it is cut on the horizontal plane, multiplied times the number of cavities, multiplied times the injection pressure required to have the thermoplastic material fill the parison injection mold. Normally, injection pressure for LDPE, HDPE, and PP will be 3000−5000 psi while for PVC, polycarbonate, and PET this could be as high as 8000−10,000 psi. Injection blow molding machines are available with the injection clamp ranging from 5 up to 180 tons utilizing a hydraulically operated clamp.

The third important factor when selecting an IBM machine is the dry cycle or the time required for the mold to open, index the table, and then for the molds to close. This is really dead time for the user and this time should be held to a minimum. Machines are available with the open, index, and close time at 1.5 seconds while others require 2.7 seconds. The smart buyer will monitor all three of these factors before selecting a production machine.

There is no rule of thumb for cycle times due to different machines recovery time and dry cycle, nor is there a rule of thumb for calculating tooling costs. The injection blow molding industry has been hampered in its growth due to the tooling knowledge and preform designs being closely guarded secrets by actual producers of injection blow-molded containers. Tooling costs for items such as baby bottles, mascara, vaseline jars, pill bottles, deodorants, etc. can run from a low of $12,000 for a single cavity to well over $140,000 for 16 cavities of the 50 mL distilled spirits PET container that weighs 12.5 g and runs on a 9 second total cycle.

The design of the preform in injection blow molding is critical. The preform should be designed to have a wall thickness in the body of the preform anywhere from approximately 0.035 in. (~1 mm) to approximately 0.200 in. (5 mm). The preform length is designed to clear the inside length of the bottle in the blow mold by approximately 0.005 in. (0.125 mm). Thus there is minimum stretch in the axial direction of the preform when the bottle is blown. The diameter of the core rod is in all practicality determined by the maximum inside dimension (I-dimension) of the finish of the desired container. In determining the wall thickness of the preform in the main body, it is necessary to know what wall thickness is desired in the final blown article plus the maximum inside diameter of the desired blown article. The ratio of the inside diameter of the blown bottle (D_1) to the inside diameter of the preform (D_2) is known as the hoop ratio.

$$\text{Hoop ratio} = D_1/D_2$$

If the wall thickness in the blown article is to be 0.022 in. (~0.56 mm) and the hoop ratio is 3, then the preform should have approximately 0.066 in. (1.67 mm) wall thickness in the main body. The tip of the preform should be designed for good plastic flow, yet not bullet shaped to permit easy deflection due to the injection pressure. It is best to have at least 0.0455 in. (1.1 mm) flat on the tip of the preform design. This can be greater depending on the gate diameter or orifice size of the gate. The outside radius of the core rod should be designed to approximately 20% extra material at this area, as this is the material that expands the greatest and the further distance since it makes the heel area of the blow container. Injection blow mold tooling is a subject by itself as is most injection molding, blow molding or any other plastic process tooling. Injection blow molding is an art and a science and with the new process controls, it is becoming more a science. All electric machines are now being offered by Milacron. Wheaton (Alcan) builds their own for their own use.

16.4.2 Stretch Blow Molding

The most important development since the introduction of the two-piece can has been the stretch blow molding of polyethylene terephthalate (PET) for the soft drink beverage industry.

From a zero number in 1977, in just over 28 years, the number of (PET) soft drink containers produced in the US has made it the largest single item produced per year. In 2008, the number of PET soft drink stretch blow-molded containers passed over 30 billion.

In the late 1960s and early 1970s several companies were working to produce a thermoplastic soft drink container. Coca-Cola was working with Monsanto and Monsanto actually was the first in the commercial market in 1974 with a “LOPAC” 32 oz soft drink bottle. The material was low oxygen polyacrylonitrile. Meanwhile, DuPont was working with Cincinnati Milacron and Pepsi to produce a PET stretch blow-molded base cup design 64 oz container. In 1976, the “LOPAC” bottle came under scrutiny by the FDA, thus opening the door for PET’s dominance.

Stretch blow molding is possible for thermoplastic material as PET, AN, PVC, PP, nylon, polycarbonate, polysulfone, acetal, and polyarylate. The amphorous materials as PET, PVC, and AN with their wide range of thermoplasticity are easier to stretch blow than the partially crystalline polymer, polypropylene.

Stretch blow molding is the stretching of the preform in both the axial direction and the hoop direction when producing a container from a preform, thus the molecules become aligned in two directions yielding a biaxially oriented container.

As stated, stretch blow molding is stretching the parison or preform in both the axial direction and the hoop direction with the material in the parisons or preforms temperature in the orientation temperatures for the specific material to orient, and to blow it into a container shape at this temperature.

The approximate temperature to achieve the maximum materials properties during stretch blow molding are as listed below:

Polypropylene—160 °C
Polystyrene—125 °C
Polyethylene terephthalate—105 °C
Polyacetal—160 °C
Polyvinyl chloride—120 °C

Each of the above materials also has its own stretch ratios. In order to understand stretch blow molding it is necessary to understand the terms orientation temperature, blow pressure, blow-up ratio, axial ratio, hoop ratio, and stretch ratios.

The orientation temperature is defined as the temperature window whereby the parisons or preforms materials must be within in order for the molecules to become aligned or biaxially oriented.

Normally in any material that has been biaxially oriented the properties of the beginning raw material will be enhanced. These properties that usually show improvement are tensile, oxygen barrier, moisture barrier, carbon dioxide barrier, drop impact, clarity, top load, and burst strength. Table 16.2 provides some insight to a few of the orientable materials and a few of the properties that are possible.

The hoop ratio is defined as the ratio of the largest inside diameter (D_1) of the blown article to the inside diameter (D_2) of the parison or preform.

Table 16.2 Typical barrier properties of plastics

	CO_2*	O_2*	Water Vapor Transmission†
Polyester	12–20	5–10	2–4
Nitrile (LOPAC)	3	1	5
PVC	20–40	8–15	2–3
HDPE	300	110	0.5
Polypropylene	450	150	0.5
Polycarbonate	550	225	75

** cm^3—mil/100 in.^{2}—day—1 atm at 73 °F, 0% RH. † g—mil/100 in.^{2}—day at 100 °F, 100% RH.*

$$\text{Hoop ratio } (H) = D_1/D_2$$

The axial ratio is defined as the axial length (A_1) where the actual axial stretch is initiated in the preform measured to the inside bottom of the bottle to be produced divided by the axial length (A_2) of the preform as it is measured from the point where stretching is initiated to the inside bottom of the preform.

$$\text{Axial ratio } (A) = A_1/A_2$$

The total blow-up ratio (BUR) is equal to the hoop ratio times the axial ratio.

$$\text{BUR} = H \times A$$

It is easy to understand that this orientation and ratios can be different throughout the blown article.

The natural stretch ratios are the limits that each material has before it will burst or just quit and not stretch any further. For instance, PET has a natural stretch ratio of 16; polypropylene, 6; PVC, 9; polycarbonate, 6; polystyrene, 10; and AN can be stretched to 12.

Polyester, which is PET, is sold as Mylar (DuPont), and is totally biaxially oriented. It is stretched four times in each direction when it is produced as a film.

It was not known that PET could be injection molded until early 1972. Until then PET preforms were made by extruding pipe and cutting the approximately 1 in. in diameter pipe into approximately 6 in. lengths and then through secondary operations, swedging the heated top to produce threads and the heated bottom to close the end to resemble a test tube.

The first injection-molded preform was done by Mr. William Gaiser at Broadway Mold in Dayton, Ohio working with DuPont and Cincinnati Milacron in early 1972. Figure 16.29 shows the original mold as it is on display at Broadway Companies.

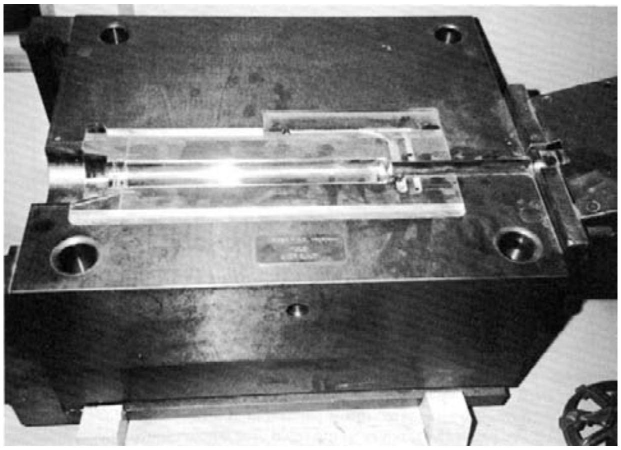


Figure 16.29 First injection-molded perform. *(Courtesy of Broadway Companies, Dayton, Ohio)*

The single-stage process consists of the following: (a) a plaster plastifier, (b) an injection mold, (c) a conditioning station, (d) a stretch blow molding station, and (e) an eject station and neck rings or thread splits to carry the preforms or bottles in the process. The single-stage process allows for the total process to take place in one machine.

It is the lowest cost investment for a producer wishing to enter into the market. The bottles produced via this process have fewer scuff marks and have the best pristine appearance. Normally, if the annual volumes required per year do not exceed approximately 16–20 million bottles/year, the single-stage process is the process of choice.

The disadvantage of single-stage PET stretch blow molding are the following:

1. Relatively slow since the injection cycle controls the machine's output.
2. More material is required as preform design cannot be optimized.
3. Barrier properties will be lower than a two-stage produced container as the single-stage stretch blown bottle is blown at a higher temperature. Thus, top load and tensile properties are lower.

4. Cannot handle seasonal demands as easy as two stage since the bottle must be blown as the preforms are produced. This causes the producer to have a large building to inventory blown bottles versus a two-stage system that basically stores preforms until bottles are required.
5. Since all the technologies are in one machine, there is a higher scrap rate and it takes a better qualified technician to run a single-stage machine than the two stage. In the two-stage machine, the technician is either concerned with blowing or injection molding performs, not both processes at once.

Many people are confused between injection blow molding and injection stretch blow molding. In reality, the latter method or single-stage blow molding method can be used in production to do no axial stretch and vice versa.

The difference between the two systems that totally differentiate injection blow molding from the single-stage blow molding system primarily used for PET is that in injection blow molding the preform is transferred on the core rod. In the single-stage process, the preform travels from the inject station to the conditioning station, to the blow molding station to the eject station via neck rings. The core rods are removed from the preform at the injection station, after the injection-molded preform has exited the injection mold cavity.

Single-stage blow molding machines are predominately used to produce PET bottles. There are installations, however, that are using crystal polystyrene, and coinjected materials as PET/nylon/PET, and PET/EVOH/PET.

The coinjected type bottles are produced on Nissei single-stage machines utilizing two plastifiers (Figure 16.30). There is no adhesive or tie layer utilized in the process. The question of delamination due to dissimilar materials being utilized in the preform and bottle, also the mismatch of polymer viscosities when in the melt stream and this effect on adhesion can only be answered by the machine user and company that purchases the multilayer bottle to package their product.

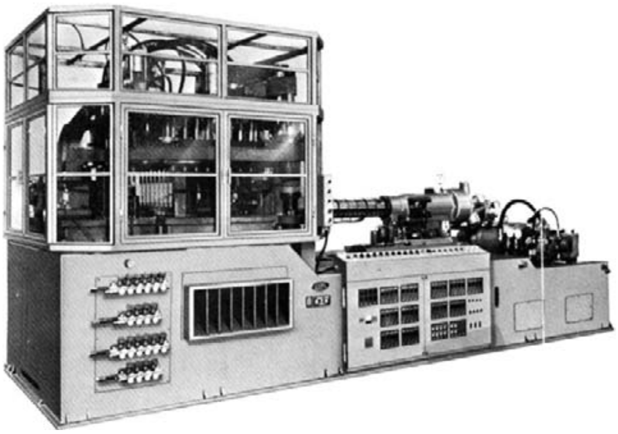


Figure 16.30 Single-stage blow-molding machine. *(Courtesy of Nissei ASB Machine Co., Ltd.)*

Many companies are using Husky injection machines to produce coinjected preforms. This is expensive, thus companies as Constar, Ball, Plastipak, Amcor, and others are also using coatings. Sidel offers machines to add a coating to the PET container.

The two-stage PET stretch blow molding system is usually referred to as the reheat blow molding system. The abbreviation RHB® is a registered trademark of Cincinnati Milacron. They were the first company to offer a machine that used injection-molded PET preforms and reheated them in a four-lane oven, heated by metal sheath heaters (Calrods™). The preforms were held in a collet and rotated at approximately 60 rpm. Upon exiting the oven, the preforms equilibrated to allow the inside skin of the preform to rise to approximately the same temperature of the outside skin, and then the preforms were placed in a shuttling type pallet, transferred to the stretch blow clamp, blown with a two-stage air system (200 psi low blow pressure—500−600 psi high blow pressure) and then exhausted. The molds would open, the pallet shuttled to the eject station and were ejected. This machine was named the Cincinnati Milacron RHB-V and could produce 2-L base cup design carbonated beverage bottles at 2800 per hour. Krupp Corpoplast entered the market shortly thereafter through Owens-Illinois with a rotary machine, whereby the preform was heated via quartz lamps as they revolved in front of the lamps on a wheel via chucks, each chuck holding a preform and transferring from the heat stations through equilibration into the eight-station blow molding rotary horizontal wheel. Corpoplast used only one blow pressure. The machine was designated the B-40 and could produce 2-L base cup design carbonated beverage bottles at 2800 bottles per hour. Cincinnati Milacron's RHB-V® has had many improvements since 1976 and was now sold in the market as the RHB-W and could produce 5500 2-L base cup design carbonated beverage bottles. Corpoplast (Krupp) is now offered to the open market without Owens-Illinois and the earliest B-40 was rated at 4800 2-L carbonated beverage bottles per hour. Krupp's latest machine can produce up to 42,000 2-L PET containers per hour.

Reheat stretch blow machines are now offered by Bekum, Sidel, MAAG, Krupp, Sipa, Krones, plus others.

Injection machines used to produce PET preforms were initially offered by Cincinnati Milacron and Husky. Injection machine builders supplying machines to the PET injection-molded industry are Nestal, Mechi, Formpast, and Nissei. Husky has approximately 60% of the market.

Injection molding machines that were used in injection molding, the HDPE base cups were Cincinnati Milacron, Husky, Nestal, Mechi, Nissei, and IMPCO. The base cup PET container is now obsolete.

In the two-state PET stretch blow molding system, the preform design and manufacture is critical. The saying in the industry is "if you make a good preform, the blow molding machine will make a good bottle," and is the key to quality and efficiency.

PET injection-molded preforms were originally molded in 8 cavity hot runner injection molds, as the industry lacked good PET knowledge not only on the material, but also on injection mold design and injection machine design. This was quickly forced to change when the 2-L carbonated beverage bottle became an overnight success. The injection-molded preform industry moved to 16 cavity molds, to 24 cavity, and today the latest technology of 144 cavities. Husky of Canada and Cincinnati Milacron did offer complete 48 cavity injection molding PET preform systems. The system consisted of the injection machine, the 48 cavity hot runner injection mold, a take-out robot with soft drop of the preforms, mold chillers, PET high temperature hopper drier with automatic loading and a unit to keep the mold area from condensation due to the cold water and the amount needed to circulate in the mold to allow for cycles in the high teens.

The original 2-L injection-molded PET preform weighed 67 g and injection cycle was 32 seconds. Today, the latest 2-L injection-molded PET preform for the beverage bottle weights 47.9 g and is produced on 144 cavity hot runner injection molds at cycles as low as 16 seconds utilizing a robot or other means for secondary cooling.

The two-stage system offers many advantages to the industry. They are as follows:

1. Lowest total cost bottle produced
2. Lowest gram weight bottle produced
3. Optimization of preform design for optimum bottle properties
4. Allows for preforms to be produced in one central location and shipped to outlying areas to blow molding machines in other locations
5. Produces the strongest and best barrier bottle
6. Allows for high volume production of both the injection-molded preform and the stretch blow-molded bottles
7. Allows for the producers to better handle the peaks and valleys of consumer demands.

The main disadvantage of the two-stage PET stretch blow molding system is the cost of investment to enter into the PET stretch blow molding market. A total line can cost from US $3 million to over US $12 million depending on the annual volume of bottles required. This has to be compared to the single-stage PET stretch blow molding process which allows for a user to enter the market for approximately US $1 million to produce 8 million to 16 million PET stretch blown bottles per year based on 7 days, 24 hours a day, or 8000 hours of production.

There are several differences between the major stretch blow molding machines in the industry. Cincinnati Milacron offered an indexing type machine. It had the advantages as being very rugged and versatile. It was also a relatively simple machine to operate and provided the user a machine that produced the lowest cost bottle per machine cost. The ovens could be moved to allow for equilibration time to be adjusted for each different style preform.

The rotary machines built by Krupp Corpoplast, Sidel, Krones, and Sipa have the advantage that the blown bottle has more in mold time and if center rods and mold bottom are used, there is no sacrifice in overall production cycle.

The two-stage process consists of the injection-molded preform being heated via metal sheath heat or quartz lamps to the orientation stretch blow molding temperature for the material being processed (PET—195—240 °F). The preform exits the heating area and passes to the equilibration area. From this area it is then transported to the blow mold area where air or other gases enters heated preform at pressures from 200 to 600 psi. The blow air is exhausted and the blow mold opens and the stretch blown bottle is transported to the eject station. The bottles are ejected, then sent downstream for case packing or labeled and then palletized.

There are many companies today that use Krones or Sidel stretch blow molding machines to produce the bottles and they are then fed to an in-line filler, capper, labeler, and then packed for shipment. This is the future for large volume products.

The design of the preform is an art and a science. Today, through the use of computers, it is becoming more of a science.

In stretch blow molding, a major problem is to achieve the orientation temperature throughout the parison or preform uniformly. On all machines used for stretch blow molding there is a conditioning station or a zone where there is an attempt to stabilize the temperature of the hot plastic material so it can be effectively and efficiently stretch blown into a final container shape.

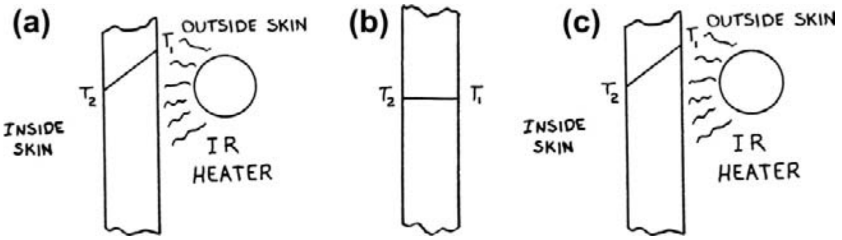
Figure 16.31a depicts the wall of a preform as it exits a reheat oven. Figure 16.31b depicts the wall of a preform as it leaves the single-stage process second station. Figure 16.31c depicts the ideal that is sought on both processes. A single-stage process will produce a more optically clean container. The two-stage machine will produce the best barrier bottle plus better wall distribution.

Stretch blow molding is so diverse and offers so many advantages it is the method of the future. New polymers plus alloy polymers will be developed tailored to this process.

Blow air pressure has an effect on the quality of the container. PET should be blown with a minimum of 300 psi. Due to container design it may be necessary to use 550—600 psi blow air. The air must be oil free.

In spite of all the advances in resin and equipment, blow molding is still an art.

Figure 16.31 Temperature profiles of preform wall.



Choosing the right type of equipment is only part of the solution, as well as the best resin. Good tooling is a prerequisite to producing a good container as well as good equipment. It is a common saying among blow molders—"if you produce a good preform—you produce a good bottle or product."

Acknowledgments

Special thanks to Don Peters (Chevron Phillips) for his guidance and mentoring these many years.

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17 Compression Molding

Robert A. Tatara
Department of Technology, Northern Illinois University, DeKalb, IL 60115, USA

17.1 Basics of Processing by Compression Molding

Compression molding is among the oldest materials processing techniques. For plastics, it was one of the first industrial methods, with equipment dating back 100 years, and is also known as *matched die molding*. The basic process consists of heating a thermoset resin, under severe pressure, within a closed mold cavity until the resin cures through a chemical reaction of crosslinking polymeric chains. Under pressure, the resin liquefies and flows, taking the shape of the mold cavity, and then hardens into the desired part or product. Once sufficiently cooled and strong, the part is removed from the mold and the cycle is complete although the curing reaction continues while cooling to ambient (room) conditions. Common resins include phenolic (phenol-formaldehyde), urea-formaldehyde, melamine-formaldehyde, epoxy, polyester, vinyl ester, silicone, alkyds, diallyl phthalate (allyls), and various rubbers and elastomers.

This process is suitable for a wide range of industrial, commercial, and consumer parts and products ranging from very small to large automobile body panels. Plastics product areas are lighting and electrical devices, closures, transportation, and appliances. Specific items are electrical wall switch plates and receptacles, circuit breakers, bottle caps, buttons, packaging, containers, covers, protective helmets, pump components, gears, brake parts, frames, pulleys, vehicle panels, dishware, and appliance housings, bases, handles, and knobs. It is especially useful for a wide variety of fiber-reinforced products. Possibilities range from simple geometries to complex three-dimensional shapes; Figure 17.1 shows an automobile electronic-throttle-control housing made from a polyester bulk molding compound with glass reinforcement.

Fundamentally, a compression molding device is a vice-like press with heat; hence, it is also known as a *heated press*, and a schematic view of the basic machine is found in Figure 17.2. The apparatus is compact but heavy and often has its own support structure; or it may be placed on a sturdy table or platform. The heavy-duty metal base plate of the press supports a lower platen and four guide (slide) rods which enables the up and down motion of the hydraulics. The lower platen is heated in a variety of ways; common are electric cartridge heaters, hot oil, or with steam. Electric heaters are easily controlled in the common molding range of 300–400 °F (150–200 °C), but hot oil is the preferred mode when higher temperatures are called for. In addition to providing a platform for any mold, this platen directly heats the lower half of the mold. Set directly above the lower platen is the upper platen, similarly heated to transfer thermal energy to the top surface of an upper mold half. A part ejector system consisting of ejector (knockout) pins connected to an ejector (knockout) plate may be integral to the platen system or part of the mold. The upper portion of the machine of Figure 17.2 houses the hydraulic unit which basically consists of a hydraulic-powered piston, or ram. Operation of the ram may be manual (pumped by hand), semiautomatic (opening a valve that supplies pressure), or automatic (timer-controlled). The hydraulic ram forces the upper platen down on the upper half of any mold placed within the machine, and this type of compression press is termed a *downstroke machine*. If the hydraulic force is upward, it is an upstroke machine. Press forces may also be mechanical, as in a toggle arrangement, or pneumatic that utilize facility-compressed-air for lower-force moldings. The daylight opening is the distance between the main plates and represents the available space for the platens, mold halves, and handling of the mold. If the platens are integral to the machine, then the daylight opening would be the space between the platens and limits the thickness of the mold. At a minimum, the daylight must accommodate a stroke of twice the part's depth. Molds may be bolted to the platens or simply placed upon the lower one. In the configuration of Figure 17.2, the platens transfer heat only through the flat surfaces in direct contact with the mold halves. To improve thermal transfer, an option is to recess the platens for mold insertion; this provides excellent mold body support as well as more uniform heating, due to the fact that the mold body is surrounded by heated surface area.

Once the compression stage is completed, the part is ready to be removed from the mold cavity. A small mold is simply taken from the daylight opening and cooled by dripping water until sufficiently cool for safe handling. Or it is cooled by circulating water through the upper and lower platens while still contacting the closed mold. Thermosets are nearly fully cured and can be taken out even when still somewhat hot and require minimal cooling. For larger and more complex molds, cooling channels are machined into the mold itself and water is pumped through them. Thermoplastic parts

Figure 17.1 Complex automobile electronic-throttle-control housing compression molded with a glass-reinforced polyester bulk molding compound. *(Bulk Molding Compounds, Inc., West Chicago, IL)*

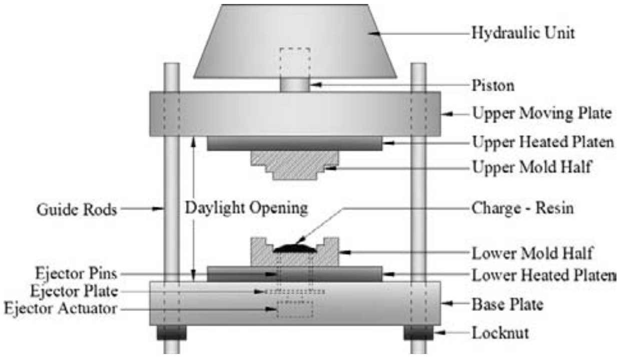


Figure 17.2 Schematic view of the major components of a typical compression press.

must be completely cooled so they are not deformed when ejected from the mold.

17.2 Molding Force and Pressure

A compression press is rated by its capacity or maximum force. The force is determined by the hydraulic fluid-pressure and ram area:

$$\text{Press capacity (tons)} = \frac{\text{ram area } \left(\text{in}^2\right) \cdot \text{hydraulic pressure (psi)}}{2000 \text{ lb}_\text{f}/\text{ton}}$$

or

$$\text{Press capacity (kN)} = \frac{\text{ram area } \left(\text{cm}^2\right) \cdot \text{hydraulic pressure (MPa)}}{10}$$

Selecting a machine's capacity is a function of the force necessary to mold parts; a proper machine selection should include excess capacity and a 25% safety factor beyond the force needed is reasonable:

$$\text{Press capacity} = 1.25 \cdot F$$

where F = force needed to mold the part(s). The required mold force is dependent on many factors including the specific resin, resin form (granules or preforms), resin viscosity, fillers, additives, reinforcements, molding temperature, part thickness, and complexity of part design. Due to the fact that the reaction kinetics and polymer rheology are complex in plastics processing, the actual molding force is best set through experience or experimentation. However, there is some guidance for this force expressed as compression molding pressure, P, computed from F/A. Here A is the part's projected area. The projected area is based on overall maximum width and length dimensions of the cavity. For regular, simple shapes this equals the actual surface area. In most cases the part is irregular and the projected area exceeds the actual surface area which results in a conservative pressure requirement (more pressure than necessary). The required molding force is computed by:

$$F(\text{tons}) = \frac{P(\text{psi}) \cdot A(\text{in}^2)}{2000\ \text{lb}_f/\text{ton}}$$

or

$$F(\text{kN}) = \frac{P(\text{MPa}) \cdot A(\text{cm}^2)}{10}$$

The molding force is also directly related to the hydraulic fluid-pressure. If this pressure is available, then the molding requirement can be expressed in terms of the hydraulic pressure as:

$$\text{Hydraulic pressure (psi)} = \frac{P(\text{psi}) \cdot A(\text{in}^2)}{\text{ram area } (\text{in}^2)}$$

or

$$\text{Hydraulic pressure (MPa)} = \frac{P(\text{MPa}) \cdot A(\text{cm}^2)}{\text{ram area } (\text{cm}^2)}$$

Various general recommendations are available for the molding pressure. Most span 2000–10,000 psi (14–69 MPa) with 2000–6000 psi (14–41 MPa) suitable for most applications and molding granules and powders; 3000 psi (21 MPa) constitutes a reasonable first approach.

To improve upon the accuracy of predicting molding force when accounting for very thick parts, a better model is called for. Strong [1] defines an excess depth factor, ρ, that adds to molding force on parts exceeding some base thickness, d, and has recommended values for parts of thickness, t:

$$F(\text{tons}) = A(\text{in}^2) \cdot \frac{P(\text{psi}) + \rho(\text{psi/in}) \cdot (t - d(\text{in}))}{2000\ \text{lb}_f/\text{ton}}$$

The usual base thickness is 1″ (2.5 cm) so that this equation becomes:

$$F(\text{tons}) = A(\text{in}^2) \cdot \frac{P(\text{psi}) + \rho(\text{psi/in}) \cdot (t - 1.0'')}{2000\ \text{lb}_f/\text{ton}}$$

or

$$F(\text{kN}) = A(\text{cm}^2) \cdot \frac{P(\text{MPa}) + \rho(\text{MPa/cm}) \cdot (t - 2.5\ \text{cm})}{10}$$

where

- $P = 1500–8000$ psi (10–55 MPa) and $\rho = 500–750$ psi/in (1.4–2.0 MPa/cm) for $t > 1''$ (2.5 cm), or
- $P = 1500–8000$ psi (10–55 MPa) and $\rho = 0$ for $t \leq 1''$ (2.5 cm).

Specifically, Berins [2] recommends for phenolic molding resins:

- $P = 3000$ psi (21 MPa) and $\rho = 700$ psi/in (1.9 MPa/cm) for $t > 1''$ (2.5 cm), or
- $P = 3000$ psi (21 MPa) and $\rho = 0$ for t $\leq 1''$ (2.5 cm);

or, when the charge is preheated the required pressure may drop to 60 by 70%. In any case, all force equations may under-predict when molding extra thick sections or complex parts requiring excellent part definition.

17.3 Typical Presses

Compression press capacities range to 100 tons (890 kN) for smaller parts or parts with a short production run; larger and more automated machines extend to 5000 tons (44,500 kN). As a minimum, a 250-ton (2200 kN) press is needed to process some reasonable range of products. Figure 17.3 presents a photographic view of a 25-ton (220 kN) manual-hydraulic compression press. The press sits on its own large

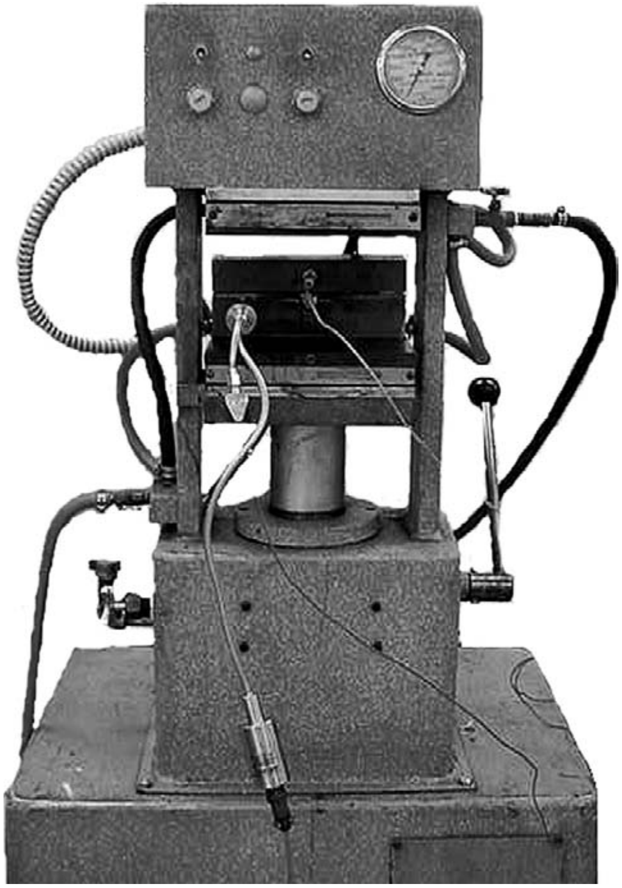


Figure 17.3 Photographic view of a 25-ton (220 kN) manual-hydraulic compression press. (*Plastics Technology Laboratory, Northern Illinois University, DeKalb, IL*)

Figure 17.4 Photographic view of a 30-ton (270 kN) electric-hydraulic compression press. (*Plastics Technology Laboratory, Northern Illinois University, DeKalb, IL*)

Figure 17.5 Photographic view of a 500-ton (4450 kN) hydraulic press to process desk parts. (*Lawton Machinery Group, De Pere, WI*)

metal base. The hand lever to pump and pressurize is on the machine's left-hand side while the pressure release valve is on the opposite side. It is an upstroke unit and is shown nearly fully closed, with a mold. In this position, visible is the extended hydraulic piston underneath the lower platen. At the top of the machine is the control panel with a force gauge, toggle switches for the lower and upper platen heaters, and light indicators that display when the heaters are cycling on. The controls to set each platen temperature are on the backside of the unit. The cooling water-control valve is on the machine's left-hand side just below the control panel; the water lines are also visible in the figure. Slots are in the platens that house bulb-type temperature readouts. For the mold shown, sensors for mold cavity pressure and temperature readings exit the front side of the rectangular mold. Figure 17.4 is a 30-ton (270 kN) electric-hydraulic upstroke unit where an electric-driven pump moves the hydraulic piston. This figure also includes the main control box with a power switch, heater switch, two press closing switches, press opening stroke, and upper and lower platen temperature readouts. To close this press, two buttons must be depressed simultaneously; this ensures that the operator does not have a hand inside the machine's clamping region. Figures 17.2−17.4 are examples of small units. Presses larger than about 150 tons (1330 MPa) become quite heavy and large necessitating solid, stable ground support. Figure 17.5 presents a 500-ton (4450 kN) upstroke press. It was used to mold school desk parts from a melamine compound; note the heavy-duty hydraulic features. A 2000-ton (17,800 kN) downstroke machine is available in Figure 17.6; this press is capable of high closing speeds and utilized for compressing thermoplastic sheets of fiber-reinforced mats. The high force is generated with three pistons. Rather than standard guide rods, this unit has 45° gib-guided columns for better positioning.

Electric molders, where an electric motor closes and opens the press and replaces the hydraulic pump, offer advantages. In addition to eliminating the need to maintain a clean hydraulic system, an electric motor allows for smoother, quieter, and more accurate platen movement and part ejection. There are fewer energy demands as once clamped, further energy is not expended in holding the mold closed, and hydraulic fluid cooling is not needed. But although becoming popular for injection molding applications, all-electric compression presses are not yet plentiful. Generally, their electric components are more costly than equivalent hydraulic ones but the cost differential is expected to decrease in the future, especially for smaller presses.

The basic mechanics of the compression molding process have not changed much and at the present time modifications tend to be driven by the need to accommodate new molding

Figure 17.6 Photographic view of a 2000-ton (17,800 kN) hydraulic press to process thermoplastic fiber-reinforced sheets. (*Lawton Machinery Group, De Pere, WI*)

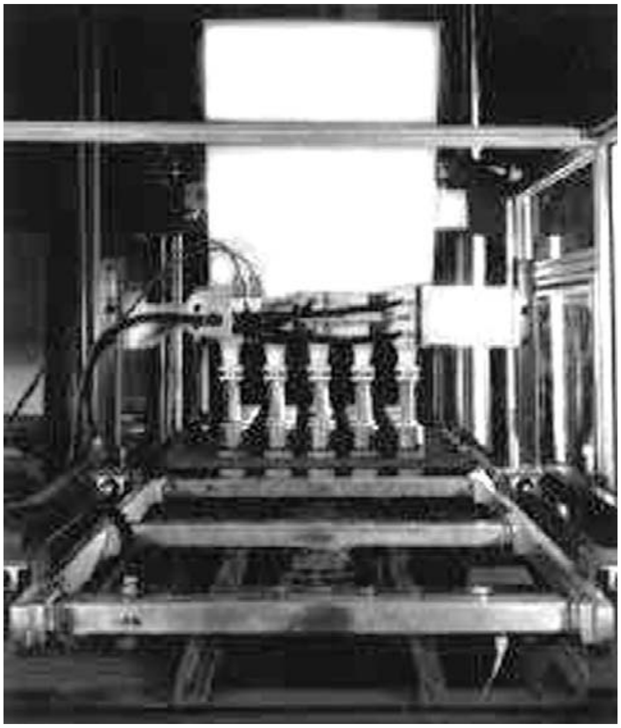


Figure 17.7 Automated resin charge delivery system. *(Hull Industries, Inc., New Britain, PA)*

materials. Typically, the molding sequence involves a loader placing the charge into the open mold; the closing and opening strokes are completed; and the ejector pins push out the finished part which is picked or stripped from the cavity. A mold can have multiple cavities in order to manufacture several like, or different, items in the same cycle. Of course, as with all industrial processes, there is a preference to minimize cycle time and production costs. This is accomplished by introducing automation and controls, keeping in mind that not all parts lend themselves to automation. The most automated machine will provide a metered resin charge into the mold cavity, mold the part(s), eject the part(s), and trim flash. A series of metering cups and resin delivery tubes is shown in Figure 17.7; a measured amount of resin is automatically loaded into the cups and dispensed into the mold cavities. A new set of charges is supplied to the cups while the part cures. Another automated machine type is the rotary press. Here multiple molds move in a circular pattern but the unit is limited to smaller molding forces. Newer presses have faster closing speeds, both to charge contact and the compression stage. Structurally, large fiber-reinforced, molded parts require a very level molding platform and excellent parallelism. Improved controllers allow for complicated molding recipes, multiple degassings, and better monitoring of the curing. For instance, rather than measuring only time, the mold cavity is instrumented with sensors monitoring a specific resin property that correlates with curing; the mold opens when an electrical or thermal property criterion is reached. Platen heaters may be subdivided into several zones, each with an independent set-point and temperature controller; this will smooth out the mold temperature profile.

Here, for illustrative purposes, is a sample procedure with manual manipulation of a small mold. This procedure is hot molding of thermosetting granules, where both the mold and the press platens are preheated before the resin is charged into the cavity of the mold. Of course, precautions must be observed when molding, including wearing safety glasses, goggles, or a face shield; using heat-resistant gloves when handling the hot mold, molded products, and in the vicinity of the hot platens; and ensuring that operators be familiar with the features and operation of the compression molding press prior to its use.

17.3.1 Sample Compression Molding Procedure

1. Power on the machine by engaging the switch.
2. Choose either manual or automatic running mode.
3. Set desired process parameters including platen heating temperatures, molding force, mold closure speeds, and cycle times.

4. Close the mold without resin.
5. Open the safety door on the compression press and position the mold in the middle of the lower platen; then close the safety door.
6. Turn on the upper and lower platen heaters at the temperature set-point(s).
7. Close the press, contacting the lower and upper surfaces of the mold with the corresponding platens, and hold until the mold is heated to the molding temperature.
8. Release the press and remove the heated mold.
9. Open the mold and separate its halves.
10. Apply a mold-release wax to the inside cavity surfaces of both mold halves.
11. Pour a measured amount of resin (charge) into the lower half cavity, tilting it from side-to-side to spread the charge evenly.
12. Match the upper mold half with the lower and once again place the closed mold centered on the lower platen of the compression press.
13. With the safety door shut, stroke the press to pressurize the mold cavity to an intermediate level for a specified amount of time, and then release this clamping force to degas the mold cavity.
14. Pressurize to the desired maximum level and hold for the required compression time to complete the curing.
15. Open the press, remove the mold, and turn off the platen heaters.
16. Cool the mold, open it, remove the part, and deflash.
17. Reduce the lower and upper platen temperatures by engaging the platen cooling circuit to move water through internal cooling channels.
18. Once the platens are cooled to near room temperature, stop the flow of water.
19. To force out residual water in the cooling system, gradually open the air valve for several seconds of flushing.
20. Power down the machine.

All process control parameters must be set before a molding operation. Figure 17.8 is an example of an input keypad. The keypad is used in conjunction with an LCD display showing set-points and processing messages. It is used to establish any process parameter such as molding temperature, molding pressure, molding time, manual versus automatic control, and closing and opening speeds. Additionally, other parameters such as machine alarms, mold degassing, heating rates, and complex processing schedules may be set, and saved for future repetition, by scrolling through the various menu options. Once the operator becomes familiar with the operation of the press and the molding conditions are entered with the keypad, the machine is ready to produce a part. Of course, any procedure is dependent on equipment, tooling, charge, and part complexity.

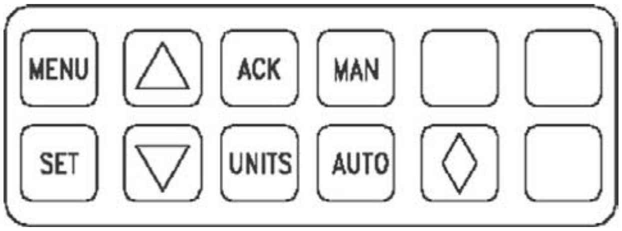


Figure 17.8 Sample digital programming keypad of a compression molding machine. (*Plastics Technology Laboratory, Northern Illinois University, DeKalb, IL*)

17.4 Compression Molds and Associated Tooling

Compression molds must withstand large shear and compressive forces. Common materials for these molds are stainless and tool steels such as P20 mold steel. Steel molds may be chrome plated for extended life, improved wear, and surface hardness. H13, alloyed with 0.35% carbon, 5% chromium, 1.5% molybdenum, and 1% vanadium, is a desirable tool steel having good hardness at elevated temperature, wear resistance, and impact resistance. Beryllium copper offers hardness, high strength, and good heat transfer to accelerate mold heating and cooling. Polishing of interior mold cavity surfaces ensures part quality; due to the high compressive forces, any cavity imperfections will be mirrored in the part itself. Other possible materials for shorter runs and lighter duties are 6061 and 7075 aluminums. Molds are made by hobbing, EDM, or machining.

For smaller parts and limited production runs, molds are manually manipulated; they are charged, placed between the platens, and removed for cooling and part ejection. When this is no longer practical, mold halves are bolted directly to the platens and the ejector system is integral to the movement of the press. The charging of resin and taking the ejected part from the press is still a manual procedure. A fully automated system does not require manual charging or part removal.

There are three main types of mold closures. But these types may always be redesigned, modified, and altered to better serve the process. The flash type is the simplest and least expensive and suitable for relatively thin, shallow parts. The cavity is slightly overcharged with resin so that excess flash material, a few thousandths of an inch (hundredths of a millimeter) thick, must be trimmed off in a post-processing operation. This design relies on flash formation to ensure that the part is fully formed. If extensive flash removal is required, the initial advantage of inexpensive mold construction is offset by post-processing costs. Since there is an outlet for

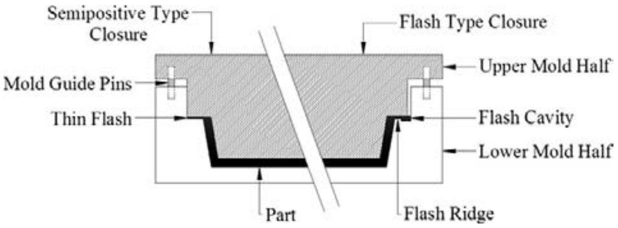


Figure 17.9 Schematic view of semipositive and flash mold closure designs.

excess material, higher compression forces produce more flow ending as flash, rather than maximizing the cavity pressure. Thus, products having only medium part definition are produced; such parts may have inconsistent density and correspondingly mediocre physical and mechanical properties. The semipositive type of mold closure allows for a small amount of excess resin that is easily pinched off and separated from the part; separation may occur in conjunction with the mold opening and part removal steps. With no flash or a very thin layer of attached flash, the part requires little post-processing. With this closure type, resulting parts have a high degree of compaction yielding very good performance properties. Figure 17.9 illustrates the key differences between the flash and semipositive designs. For the flash type, a flash ridge creates an overflow path to a flash cavity or pocket, where excess material accumulates. (Rather than a contained, internal pocket, an alternate design can direct the flashing to outside the mold's boundary, where it may expand without limitation.) The material freezing at the flash ridge is thinner than the part and processed to separate it from the part. This figure also highlights the use of mold guide pins to ensure more accurate clamping alignment. Figure 17.10 is a photographic view of a sample part with the associated flash when molded with each type of mold closure. Figure 17.10.a illustrates the thin, uneven flash layer that is typical with the semipositive closure. Here the flash thickness is approximately 0.0025″ (0.06 mm) and easily stripped off. In Figure 17.10.b, a portion of the heavier flash is broken off to show the boundary between the part and the waste material from the flash ridge and pocket in the flash design.

Lastly, the positive type utilizes an exact metering of charge, and the two mold halves form a complete seal; of course, the amount of charge must be carefully controlled as any excess or deficiency of resin will affect part dimensions. But severe overcharging will prevent complete closure of the mold halves while a significant deficiency in charge will produce an incomplete product. Small clearances for flash can still be provided for, especially if there is a chance of excess charge, even though very little or no flashing occurs during the molding. This form of tool is well-suited when processing fiber-reinforced molding compounds since fiber-rich layers do not extrude easily into flash. Figure 17.11 displays a thin, 3″ (76 mm) square plate with its tooling. The plate is made without any flash as the mold is of the positive closure type.

In any case, due to the high molding pressures, as with injection-molded products, it is difficult to remove a finished part from the mold cavity, despite the fact that the part shrinks upon cooling. Even with a mold taper and coating a release agent on the inside surfaces of the cavity, great surface tension forces and mechanical compression can adhere the part to either mold half. The force to remove a part depends on the resin as well as the cavity construction, and a well-designed ejector system is needed. Since at this point the part is not fully hardened, small-diameter ejector pins may penetrate or scar the part's surface as the pins push it out. Using additional pins or larger-diameter pins better distributes the ejection force. When the part tends to stick to the lower mold half, a solution is to fabricate a thin metallic plate in the shape of the bottom surface of the part and put it at the bottom of the mold half; the

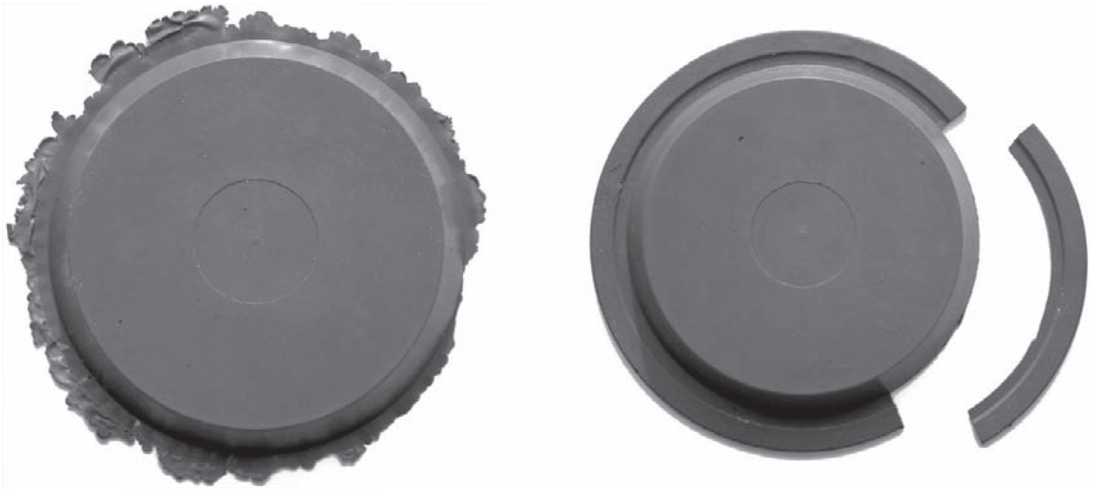

(a) Excess flash from semipositive mold closure **(b)** Excess material from flash mold closure

Figure 17.10 Pictures of a sample part with flash made from two different mold closures.

Figure 17.11 Square plate with its positive closure compression mold.

charge is placed on this plate and the part is molded as usual. Now the ejector pins force out the plate with the part, evenly, without pin-to-part contact. Figure 17.12 is a photographic view of such a design. Once removed successfully, any part may be supported in a fixture until completely cooled; this will minimize dimensional distortion and warpage from thermal contraction and stress relief.

17.4.1 Mold Instrumentation

It must be remembered that any specified molding temperature is that of the mold body, not the platens. But, since presses have programmable platen temperatures, in many cases it's the platen temperatures that are tracked. Therefore, it is imperative to minimize the difference between platen and tool (mold) values. This difference exists due to two factors. Firstly, because the tool material has a thermal capacity, there is a time lag between the platen setpoint value and the actual mold temperature. Secondly, unless the mold is well-insulated, radiative and convective heat losses from the exposed surfaces of the closed mold to its environment occur.

Figure 17.13 shows an illustrative temperature profile. Here, a thermosetting resin is compressed while still at room temperature (cold formed), and then the platen heaters are activated until the mold is brought up to a curing temperature of 340−350 °F (171−177 °C). The mold's mass (empty) was 30.5 $\mathrm{lb_m}$ (13.8 kg) and it was fabricated from 4140 steel; its rectangular dimensions when closed were 8.875″ (225 mm) long, 2.313″ (59 mm) wide, and 3.500″ (89 mm) high. Throughout the cycle, there is relatively close agreement between the upper and lower mold sections' temperatures, within 10 °F (6 °C). But note that each platen is 20−40 °F (11−22 °C) warmer than its corresponding mold half. Thus,

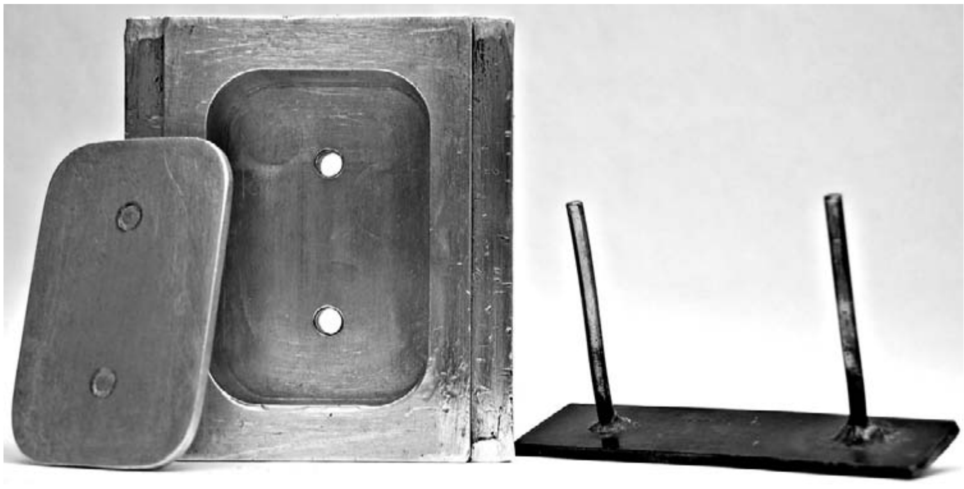


Figure 17.12 Sample bottom mold half with part cavity plate and ejector pins.

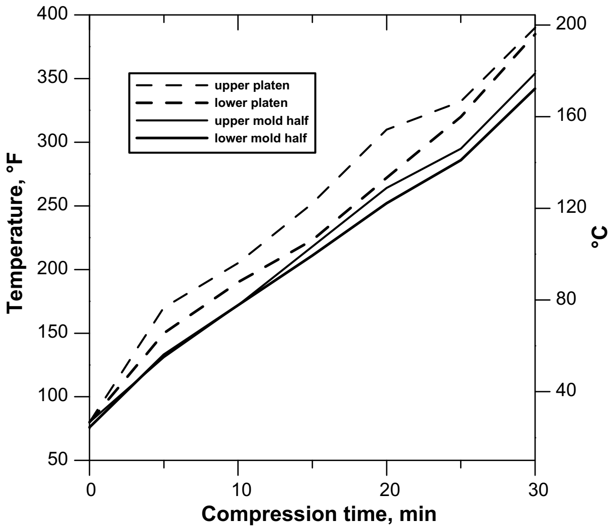


Figure 17.13 Temperature profile for upper and lower platens and steel mold halves during a compression molding cycle, starting with the mold at room temperature.

any platen set-point would not accurately represent the tool temperature, and it is beneficial to be able to directly monitor mold temperatures in addition to platen values.

The heat transfer path from the surface of each platen into the mold is conduction while heat is lost simultaneously from the sides of the closed mold to the surrounding air (ambient). Kuczmarski and Johnston [3] have demonstrated that the convective losses constitute a more significant factor than mold body conduction when minimizing the platen and tool temperature differential. Their numerical simulation indicated that reducing the exposed surface area by redesigning the mold is a reasonable way to decrease the temperature variation, and more practical than using a mold material having a higher thermal conductivity.

A mold is easily instrumented with thermocouples, at least one in each half of the mold. For the expected temperatures, type J (iron-constantan) probes are suitable and have a standard measurement uncertainty of ±4.0 °F (2.2 °C), while a corresponding digital monitor or readout will add another ±0.7 °F (0.4 °C). Additionally, a measure of the cavity pressure can be obtained with a force transducer. Although the cavity is not pressurized as in the case of a true fluid, cavity pressure readings may be used to verify that the molding force is completely transmitted to the resin charge. In some mold designs, there is the potential of metal-to-metal contact between the upper and lower mold halves prior to complete closure; in such a case, the machine's force would not be equal to the force on the resin. A typical surface, diaphragm-tipped transducer is quite accurate and has a range to 10,000 psi (69 MPa); it is also available with a thermocouple at its tip. However, the pressure must be sensed by contacting the part's surface and will create a small blemish. Thus, such a probe must be located where a high surface finish is not a requirement. Figure 17.14 shows a thermocouple probe with a threaded pipe fitting that is screwed into a mold body. Also seen is a pressure and temperature combination probe, whose tip is fitted flush with the cavity wall of a mold to monitor the melting charge.

17.5 Commonly Used Resins

Phenolic resins are produced by chemically combining phenol and formaldehyde through a condensation reaction

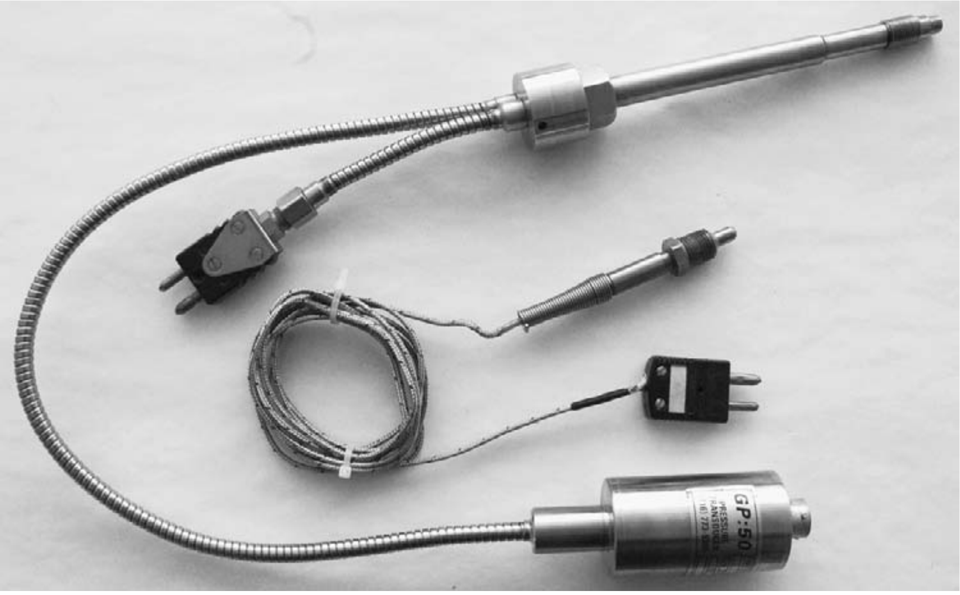


Figure 17.14 Common probes for monitoring mold body and mold cavity temperatures and pressure. (*Plastics Technology Laboratory, Northern Illinois University, DeKalb, IL*)

under alkaline conditions. Depending on the specific reaction mechanism employed, either a resole resin or a novolak is formed. Resoles are referred to as single-stage polymers since they do not require any curing agent. Novolaks, on the other hand, are designed to incorporate a curing agent, such as hexamethylene tetramine (usually called hexa), and are referred to as two-stage; fillers and additives are then added to produce standard phenolic molding compounds. Applications include castings from molding powders, coatings, adhesives, and binders. Phenolic resins can tolerate high temperatures and bear large mechanical loads with minimal creep and are also bonding agents, since they mix well with both inorganic as well as organic fillers and reinforcements. They have very good solvent resistance and product life. Additionally, the phenolic molecules crosslink through the filler and reinforcement, which helps to provide excellent final properties.

Closely related to phenolics, amino plastics are the result of aldehydes reacting with amines. Examples include urea-formaldehyde and melamine-formaldehyde. Urea-formaldehyde crosslinks with water as a byproduct that is vented out the mold. Its molding compounds, similar to those of phenolics, contain filler, catalyst, colorant, plasticizer, and lubricant. A stabilizer can be included to increase the storage life by retarding chemical activity. Parts made from urea-formaldehyde have very good electrical properties along with resistance to various chemicals, including solvents and weak acids and bases. For better property performance, melamine-formaldehyde is harder and even more resistant to chemicals, moisture, and heat. Melamines offer many molding compounds in a wide range of colors. Melamine-phenolic resins are mixed compounds known for brighter coloring and less part shrinkage than melamine-only molding compounds.

Another popular resin is unsaturated polyester, especially common in fiber-reinforced parts. Unsaturated polyesters are cured through heating and styrene monomers crosslink the polymer chains. Polyesters have strength and resilience while vinyl esters offer better chemical and moisture resistance. Chemically within the polyester family are alkyds. Their molding compounds are standard formulations of filler, catalyst, colorant, and lubricant and quickly cure at relatively low pressure and temperature. Molded products are dimensionally stable, especially when glass fibers are present, and have very good electrical properties.

For higher temperature applications, epoxies can be cast into thick sections and easily reinforced becoming dimensionally stable; molded parts resist attack by moisture and chemicals. Epoxies polymerize when rings of epoxy group atoms open and link other monomers. Diallyl phthalate (DAP) is a common allyl molding dough consisting of filler and short fibers, and its curing does not create corrosive byproducts. Parts are easily compression molded and tend to have good strength and excellent electrical, thermal, moisture, and chemical resistance. Silicones are primarily elastomeric materials but also are filled or glass-reinforced and molded into stiffer, solid, structural parts. These lightweight products exhibit excellent electrical and thermal performance.

Less used are various thermoplastics including nylons, polypropylene, and polyethylene terephthalate. Although not as strong, these have more impact resistance than thermosets and also may be reinforced.

17.6 Resin Charge Characteristics

Unlike many conventional thermoplastic processing methods which utilize resin as pellets, in compression molding the resin charge is available in several forms. Common are granules, a coarse powder, that when heated and pressurized liquefy and cure to harden. Figure 17.15 is a photographic view of a charge of melamine-phenolic molding compound in standard granular form. Pastes are combinations of a liquid thermoset with its filler. Dough molding compounds are viscous pastes that are mixes of the resin, filler, and reinforcement as in a BMC (bulk molding compound). Other engineered compounds, SMCs (sheet molding compounds) and GMTs (glass mat-reinforced compounds), are manufactured in sheets. Preforms are granules that have been already compacted into a simple shape, such as a disk, for easy handling and loading into the mold cavity and overall convenience. Preforms introduce a degree of automation to the charging step and they may be made at the molder's facility or at a remote site; preform-use greatly reduces cycle time and increases part production rates.

17.6.1 Thermoset Resin Pricing

Thermosetting resins are the primary materials for the compression molding process. As with all resins, pricing can change rapidly and significantly, trending with petro-chemical feedstocks. Pricing can also vary greatly from molding compound to compound even for the same base resin; the presence and type of reinforcement as well as certain

Figure 17.15 Granules of a melamine-phenolic molding compound.

Table 17.1 Relative pricing of common thermosetting resins [4]

Thermoset Resin	Relative Price*
Alkyds	0.9
Phenolic molding compounds	1.0
Melamine-phenolic compounds	1.1
Melamines	1.2
Epoxies	1.6
Polyester	2.1
Phenolics, reinforced grades	1.4–3.6
Vinyl ester	3.1
Silicone epoxy	4.5
Diallyl phthalate (DAP)	3.3–6.6
Silicone molding compounds	8.1

Price of the resin divided by price of standard phenolic molding compound

additives will substantially alter the molding compound cost. Table 17.1 lists common resins with relative costing, based on standard phenolic molding compound. The phenolics and melamines are common, inexpensive molding resins as are ureas. Alkyds also are priced attractively. Epoxies and polyesters are slightly higher in price but still cost-effective for a wide range of products. The high cost of allylics, such as DAP, is an obstacle and somewhat restricts their use. Likewise, silicones are limited to applications where their property performance is needed to justify the higher cost.

Common thermoplastic molding pellets are derived from fossil fuels and suffer the price fluctuations present in this market. However, thermoset molding compounds contain a high percentage of filler; the fillers are usually inorganic and made of inexpensive, plentiful materials. Thus, the thermoset molding compounds are not as sensitive to market crude oil and natural gas pricing. Currently, in response to sustainability issues, molding compounders are looking toward recycled materials for fillers, including waste streams from fiberglass manufacturers. Also there are molding compounds where bio-based, renewable polymers have replaced some portion of the standard, active polymer; "Green BMC" incorporates a soy-based resin and has properties comparable to standard formulations.

17.7 Processing Parameters for Granules, Powders, and Preforms

Processing by compression molding ranges from completely manual to a high degree of automation. The charge can be automatically weighed and poured into the mold cavity where the press cycles through heating, compression, degassing, and cooling. Programmable robotic arms can open, close, and move a mold and handle the finished part(s). As with other plastics processing techniques, there are several important parameters that call for close control.

17.7.1 Curing and Solidification Reaction

Most thermosetting resins are heat-activated and their polymerization reaction ultimately crosslinks the chains as the molecular weight of the material approaches infinity. Any polymerization via condensation reaction produces small amounts of gas or vapor (such as water), that must be vented out of the mold cavity. Venting ports may be provided within the mold or the mold may be slightly opened during the compression molding cycle to release any gas; such a step is known as *bumping, breathing,* or *degassing the mold cavity.* A minimum 1/16" (1.6 mm) opening of the mold cavity, held for a few seconds, would provide sufficient venting. Venting is especially important for thick phenolics and any other formaldehyde-based resins.

Polymerization, by addition or condensation, is usually exothermic adding to the external heat from the platens. Due to the fact that the resin in its raw state, and also when finished, is a thermal insulator, excess heat can be generated and trapped within thick parts. (Only the layers near the surface of the curing part will have high heat transfer rates to the conductive mold surface.) The excess heat generation will accelerate the crosslinking and can be great enough so that a thicker part can cure faster than a thinner one that relies mainly on the heat transferred from the mold cavity surfaces. In the extreme, thick parts or part sections may suffer thermal degradation of the polymer chains, reducing part appearance and performance properties.

In the case of thermoplastics which are already fully polymerized, the curing of a heated liquid or semi-solid to a complete solid is a phase change accompanied with heat removal. The heat sink consists of the upper and lower mold surfaces, so that the resin layers in the vicinity of these surfaces freeze first. The process is complete when the core solidifies.

17.7.2 Resin Charge Control

Compression molding is charge-dependent; so overcharging prevents the mold halves from seating properly and creates added flash. For optimal physical and mechanical performance, any preform or resin granules should be distributed to match the part's shape; this promotes uniform cured density which yields maximum toughness and compressive strength. Thus, a circular preform would not be appropriate for a rectangular cavity. Any flash removal imparts additional cost in preparing the part. In some cases, especially with tougher resins, the flash may be difficult to remove. Methods such as cryogenic flash removal involve cooling the part and the additional brittleness allows the flash to be broken off. If the charged mass is deficient, the part will be dimensionally incorrect. Or the plastic will have voids from gases evolved and trapped where not enough resin was available to displace the gas as the mold was pressurized.

When starting with a room-temperature charge, the thermal energy is transmitted by conductive heat transfer from the platen surface, through the mold body, and into the charge layer in contact with the mold cavity. For very thick parts and/or when utilizing preforms, preheating the charge offers substantial molding benefits primarily in shortening cycle time, since the preheating is done external to the molding machine. A 70 or 100 MHz high-frequency electronic heater can bring a preform's temperature up to 212 °F (100 °C) in 10 s and because the heating is internal, similar to that from microwaves, the preform temperature is more uniform than would be from platen-generated heat [5]. After preheating, the preform is transferred to the mold cavity and less time is required for the platen heaters to bring the charge up to the standard 300−400 °F (150−200 °C) molding temperature. Furthermore, the softened charge will flow easier upon initial contact by the mold halves. But preheating a thermoset will initiate the curing so that transfer time must be kept to a minimum.

17.7.3 Mold Closure Control

As with most non-Newtonian fluids, liquid polymeric materials are sensitive to shear and temperature. The application of the molding clamping force must be smooth and even. If the application is too rapid, the resin will shear, overheating the molecular chains. On the other hand, if the molding pressure is ramped up too slowly, the resin will cure and harden before maximum compaction occurs. One useful feature of many molding machines is two-stage clamping which allows for a relatively rapid mold closure up to the point at which the resin begins to compress; then the clamping rate is reduced as the closure continues to maximum cavity pressure. Hull [5] recommends 200−800 in/min (85−339 mm/s) and up to a maximum of 80 in/min (34 mm/s) for the first and second closing stages, respectively. Alkyds and polyesters polymerize rapidly, thus the compression speed must be quicker than usual. Although the rate to open the mold and reset the compression stroke should be as rapid as possible, the initial release of the closed mold should be gradual to prevent part damage. This is especially critical for thin parts which may have sections pulled out along with the opening mold half, while the rest of the part remains inside the other mold cavity. Along with speed considerations, the platens and guide rods must ensure that the compression force is applied exactly perpendicular to the mold body for uniform pressure upon the charge.

17.7.4 Temperature Control

Although thermosets tolerate a range of temperatures, excessive heat degrades the resin resulting in brittleness, other reduced mechanical strength properties, and poor part surface quality. A liquefying resin's viscosity is inversely related to and strongly dependent on temperature. Therefore, if the mold temperature is set too low, the resin's viscosity is greatly increased and the material may not flow enough, especially to constricted-volume regions, for optimal part definition. As in the case of molding pressure, the optimal temperature will be a function of the specific resin, resin form (granules or preforms), resin viscosity, fillers, additives, reinforcements, molding pressure, part thickness, and complexity of part design. This temperature is best determined by experience and testing, although the consensus is 300−400 °F (150−200 °C) for most resins, including phenolics. Slightly lower molding temperatures are recommended for amino-based resins [6]: 260−340 °F (127−171 °C) for urea-formaldehyde and 260−360 °F (127−182 °C) for melamine-formaldehyde, and likewise 275−350 °F (135−177 °C) for allyls [7]. Of course, preheating the charge prior to insertion into the mold cavity may lead to better part quality and shorter cycle time.

17.7.5 Cycle and Molding Times

For economic efficiency, overall cycle time must be minimized. Note that the molding time is the time under full pressure and does not include other steps such as loading, mold closure, degassing, and part ejection, all of which contribute to the overall cycle time. Compression molding time must be adequate for complete curing, but maintaining the resin too long at compression temperature and pressure will degrade the material. Clearly, part thickness is a crucial factor as a thin part will harden in seconds while a relatively thick one requires many minutes to complete the curing process. Recommended compression (curing) times are ½ to 5 min, with 1½ min at 340 °F (171 °C) as typical [2]. Although the part can be removed from the mold once minimal stiffness is achieved (hot rigidity), the polymerization reaction continues and may require hours for complete cure. Thus, there exists the potential for part deformation in the form of warping if the part is unsupported after removal from its mold. Increasing molding temperature at least 9 °F (5 °C) and/or the compression time 5−10 s will accelerate molecular chain crosslinking and reduce warpage [5].

17.8 Resin Matrix Modifiers

A modifier may be classified as an additive, filler, or reinforcement. Additives are blended into a resin at low concentration, a few percent by weight. An additive is employed to significantly affect a physical, chemical, thermal, optical, electrical, environmental, or processing property and can be relatively costly. On the other hand, up to 60−70% filler may be mixed into the resin. Loadings of even 90% are possible, but in that case the resin serves as an adhesive or binder and the part made is not a true plastic. Fillers are inert and are used to add bulk volume or to replace the more costly resin. Reinforcing agents are longish fibers molded with the resin matrix to improve mechanical strength. Tensile, compressive, impact, and bending strengths are all greatly increased. Reinforcing materials range from common and inexpensive glass or paper mats to exotic polymer or carbon ones.

17.8.1 Additives

To improve mechanical, physical, chemical, electrical, optical, thermal, or molding performance, additives may be combined with the resin matrix. Reaction catalysts include hexamethylene tetramine for phenolics. Mica, alumina, and silica provide electrical arcing resistance. Halogenated compounds are a fire retardant, while zinc stearate and wax-like materials improve part release from the mold cavity. The molding process is improved through solvent-like additives that reduce the charge's viscosity. Wetting and adhesion promoters improve bonding between a resin matrix and any reinforcement fibers. Viscosity thickeners minimize the separation of fiber from the resin matrix. Reaction inhibitors provide longer storage life for bulk and sheet molding compounds by delaying the onset of crosslinking. For SMCs, low profile additives reduce the shrinkage, important for optimal surface finish. Examples of physical property modifiers are colorants such as dyes and inorganic or organic pigments. Antioxidants, heat stabilizers, impact modifiers, and ultraviolet stabilizers are needed for thermoplastics, which lack the durability of thermosetting materials.

Any additive may be mixed into a resin charge or is already present as with standard molding compounds. If physically mixing the additive, care must be taken to thoroughly combine it with the resin granules. Unlike extrusion and injection molding, where extensive mixing takes place automatically via the action of the screw or auger, little flow occurs in compression molding and uneven additive distribution in the charge will display itself in the finished part. Additives, typically, are added in concentrations under 5%; at levels above this they could be considered fillers.

17.8.2 Fillers

Currently, many plastic products utilize low-cost materials as fillers. Ideally, the filler is added in a concentration that allows the product to retain sufficient mechanical strength, physical properties, and final quality. Certain fillers may improve a plastic's shrinkage, thermal stability, color, and opacity. If the filler is added in a reasonable quantity, any degradation in strength from that of unfilled resin can be offset by the cost savings. Common fillers include clay, talc, ground limestone, carbon black, marble dust, glass, paper, wood flour, and metals, and are added in concentrations ranging from 10 to 50% (by weight). To enhance biodegradability, bio-based fillers are receiving increased attention. Examples include wood flour, sugar cane, lignin, flax, grasses, bamboo, starch, chicken feathers, soy protein, and cellulose. This trend is consistent with recent United States governmental policies that prioritize the procurement of materials having significant bio-based content; this program is targeted to increase to a 50% bio-based level over the next several decades. Natural and bio-based materials are suitable only for low to moderate operating conditions as they have low thermal resistance and tend to absorb moisture; the principle advantage is low cost.

For phenolics, biofillers are added in two ways: chemical reaction and simple mechanical mixing. Chemically, combining a biofiller with phenolic and using sodium hydroxide as a catalyst, then molding, is a more complex activity but imparts added strength to molded specimens [8]. But any such pretreatments (including any drying) make the filler more costly. Simple mechanical mixing can lead to satisfactory parts. A study on compression molding corn-based DDGS (distillers dried grains with solubles) with phenolic, generated specimens that were tested for tensile yield strength, Young's modulus, and percent elongation at yield [9]. Results demonstrated that at 25% DDGS, by weight, the tensile yield strength is still approximately half that of the pure phenolic case. Higher levels of biofiller further reduce the strength to nearly one-quarter (at 50% DDGS), and under one-sixth (at 75% DDGS) the baseline. Young's modulus is also reduced from that of 100% resin, but less severely. At 25% DDGS, a 10−15% stiffness reduction is noted, while 50% and 75% filler levels cause 50% and 70% decreases in Young's modulus, respectively. The ductility of the blends, as measured through percent elongation, is restricted about 50% by inclusion of biofiller, although a clear trend is not seen. In this study, bio-based filler content was also trended with hardness (Figure 17.16); data included the DDGS as well as Alpha grass lignin and wood flour from other researchers. Figure 17.16 indicates a general softening as filler level increases. The Shore D values are about 10−30% lower for 30−90% filler; data all correlate reasonably well which indicates that performance is mostly dependent on filler concentration rather than the actual biomaterial.

17.8.3 Reinforcements

To directly improve tensile strength, stiffness, compressive strength, and impact resistance, fibers are added to a thermoset or thermoplastic. Often, the fibers are glass but carbon, metallic, inorganic, and other polymeric ones are possible. Of course, these are the key component in a BMC, SMC, GMT, or a long fiber thermoplastic (LFT). Although compression molding is well-suited to making parts and products with high strength-to-weight ratios, in some

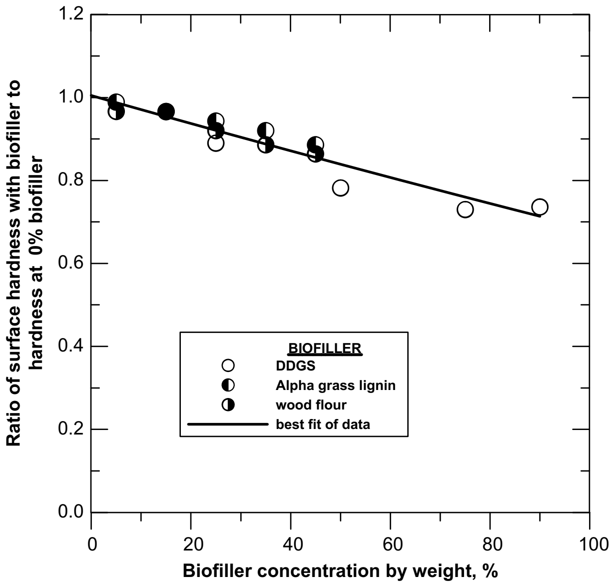


Figure 17.16 Relative Shore *D* surface hardness response for phenolic resin with varying percentages of bio-based fillers.

instances their mechanical properties are affected by the processing. Additionally, part surface quality, mold design, and cycle efficiency are issues.

17.9 Engineered Fiber-Reinforced Molding Compounds

Commonly used to make strong, stiff, and lightweight products are bulk molding compounds (BMCs) and sheet molding compounds (SMCs), often unsaturated polyester resin with glass fiber reinforcement. Non-thermosetting alternatives, introduced around 1980, are the GMT (glass mat thermoplastic) and LFT (long fiber thermoplastic). The automotive and truck industries make great use of these four resin forms for bumpers, panels, lids, hoods, and pump impellers and housing. Other products are boat hulls, doors, roofing, satellite dishes, snowmobile panels, appliance housings and control panels, lighting fixtures, sinks, and furniture. Compression processing of these compounds has special requirements and outcomes.

A typical BMC, also termed DMC (dough molding compound) or premix, is composed of a resin, filler, reinforcement, and catalyst. The filler loading may be quite high. The components are simply mixed together, forming a viscous paste; mixing intensity is limited to avoid shear heating the thermosetting resin and preventing damage to any glass fibers. Figure 17.17 presents a stack of BMCs; these may be cut and used directly in a mold or pressed into preformed shapes. Fibers can be up to 1″ (25 mm) long, but 1/8″ to 1/2″ (3–13 mm) is more typical. A standard formulation is unsaturated polyester resin, calcium carbonate filler, mold release, colorant, inhibitor, other additives, and 10–25%, by volume, glass fibers [10]. Due to the fact that the material is partially polymerized, it is tacky with a consistency similar to dough. In the compression process, the resin charge is centered in the lower mold half and the material will flow to fill the cavity. But there may be separation of the BMC components if the flow length is too great; this would result in parts having non-uniform mechanical performance. This is the restrictive factor so other combinations of resin and reinforcement are sought. Additionally, if more concentrated and/or longer fibers could be utilized, many parts would exhibit better mechanical strength.

Figure 17.17 Stack of bulk molding compounds. *(Bulk Molding Compounds, Inc., West Chicago, IL)*

One option is the sheet molding compound which is very suited to larger parts. Here, the reinforcement fibers are chopped, randomly oriented, and commonly 0.75″–2″ (19–51 mm). A reasonable mix, by weight, of resin/inorganic filler/1″ (25 mm) chopped glass reinforcement is 25/45/30 [11]. The fibers are securely encased between polyethylene films that have been coated with resin (polyester, vinyl ester, or epoxy) and filler. Rather than mixing of components as in BMCs, fibers are carefully placed by processing equipment and contained by resin layers. This also allows for the placement of longish glass fibers in adjustable concentration and direction, thus increasing the strength, compared to the randomly directed material, of any finished part. Like a BMC, a sheet molding compound is tacky and the polyethylene films separate individual resin/fiber layers. SMCs are available as large rolls, and individual sheets matching the desired product's size are cut from the roll. (The thermoplastic cover layers are discarded.) Recently, attention is being devoted to reduce the weight of SMC composites. Calcium carbonate, the common inorganic filler, contributes to the total material's specific gravity of 1.9; substitution by glass beads reduces this by 1/3 with only minor property loss, and nanocomposite fillers and carbon fibers have even greater potential [12].

Glass mat-reinforced sheets are composed of thermoplastic polypropylene (polyamides, polycarbonate, and PVC are occasional options) with glass fibers 1″ (25 mm) or more in length. A variety of fiber layer types are available such as directional, random, shorter, longer, mats, or weaves. When a natural fiber such as flax is used, the composite is termed an NMT (natural fiber mat-reinforced thermoplastic). Using a polypropylene matrix, along with typical glass reinforcement, provides stiffness and superior low-temperature impact strength. Since with thermoplastics polymerization is complete, GMTs must be preheated before compression molding. Although not as mechanically strong, stiff, and heat-resistant as an SMC, a GMT panel is tougher and more lightweight.

Having a fiber length of at least 0.4″ (10 mm) is the long fiber thermoplastic, LFT. Here, polypropylene is combined with fibers, typically glass but aramid, carbon, and stainless steel are also available, and often molded into automotive parts and panels. Other resins are polyamides, polycarbonate, and thermoplastic polyesters. Fiber content ranges from 20 to 60% by weight with 40% standard. There are two resin delivery methods to a compression press. One way is to melt pre-compounded pellets that contain fibers spanning the length of the pellet, and then place the charge within the mold; pellets up to 1½″ (38 mm) are available from compounders. The melting is done with some type of plasticizer, such as an extruder. An alternative is to compound fibers with plain pellets in an extruder on site, and direct the formulation to the mold. Here, the fibers are introduced in the extruder as late as possible to minimize fiber damage. Due to simpler processing, LFT material is less expensive than GMT while capable of lightweight, impact resistant, and strong parts.

17.9.1 BMC, SMC, GMT, and LFT Processing

A BMC resin is centered in the lower mold cavity; upon pressurization, it will flow. The flow will be predominately directed in-plane and radially from the center point of the charge.

For SMCs, material can be centered or distributed throughout the entire mold, and part thickness is built up within the mold cavity by adding more sheets. Thus, this compression produces far less flow, compared to the BMC process, and the integrity of the reinforcement is maintained. Generally, 1 to 4 sheet(s), each about 1/8″ (3 mm) thick, are used and occupy about half the mold's surface [13]; of course, extra sheets can be added where additional mechanical strength in a part is sought. The compression process creates some flow, orientating the fibers; the charge layers contacting the hot mold cavity surfaces will flow and harden before the center layers. Thus, properties have directional dependency in the completed parts. The placement and shape of the charge are even more significant than the molding conditions, in spite of the fact that the resin flows a rather short distance in the mold's cavity. Due to fiber orientation in the direction of flow, tensile strength and tensile modulus can be over 2½ and 1½ times, respectively, the value perpendicular to flow for a sample part with a charge initially covering 38% of the mold [14]. The degree of anisotropy also affects residual stresses, shrinkage, and warping and diminishes as the mold coverage area is increased. A reasonable area is 60–80% and fiber orientation is always considered while placing the charge.

A glass mat thermoplastic charge spans about 80% of the part's surface, but layers ought not to be placed side by side [15]. Here, two separate flow fronts will fuse together at the junction between the layers. This creates a classical weld (knit) line and produces a latent, or obvious, part defect. The defect may be in part appearance or mechanical strength. Part thickness control is through stacking of individual sheets. Molding problems include part blistering, shrinkage, and warpage.

Although not too different from processing powders or granules, the compression molding conditions for BMC and SMC resins include a wide range in pressure due to variations in the shape, size, and molding compound formulation. Forces tend to be less while molding temperature and curing time also vary depending on catalyst, part thickness, and mold closing speed. The curing reaction is temperature-sensitive and, approximately, each 18 °F (10 °C) decrease in temperature increases curing time by 50% for SMC parts thinner than 1/4″ (6 mm) [16]. Representative conditions are presented in Table 17.2. Davis et al. [10] propose somewhat higher pressures, 2000–6000 psi (14–41 MPa) with a cycle time of 55–95 s for SMCs, and 3000 psi (21 MPa) along with 120–140 °F (50–60 °C) for GMTs and LFTs with at least 60–90 s just to preheat a glass mat thermoplastic prior to transfer to its mold. Note that Table 17.2 lists cycle time

Table 17.2 General processing conditions for engineered fiber-reinforced molding compounds

Fiber-Reinforced Molding Compound	Molding Pressure, psi (MPa)	Molding Temperature, °F (°C)	Cycle Time (Exclusive of Any Preheating)
BMC [15]	350–2500 (2.4–17)	250–350 (121–177)	30 s to many minutes
SMC [15]	500–2500 (3.4–17)	250–350 (121–177)	30 s to many minutes
GMT [17]	1500–2000 (10–14)	77–160 (25–70)	30–60 s

minus any preheating, but it does include platen travel, unloading, loading, and curing. The reaction curing time may be half of the cycle time for an SMC. But care must be exercised when attempting to minimize the overall cycle time, especially in the mold closure rate. Closing too rapidly may prevent adequate venting of air, water vapor, or other volatile gases that will be trapped within the resin matrix. (Using a vacuum to increase the venting potential is one processing option.) This detracts from product appearance, creating surface blisters and internal voidage, and diminishes performance properties. Of course, if the rate is too slow when molding thermosets, the material will become overly viscous as it solidifies.

In any case, a uniform mold cavity temperature is important when manufacturing SMC parts. For instance, Barone and Caulk [18] have shown that a 45 °F (25 °C) temperature variation in the surface temperature of the mold exists in larger SMC-molded parts and is proportional to (part's length)^2/(thickness • cycle time). This temperature inconsistency is magnified when trending to thinner parts made with shorter cycle times. Such variance leads to inconsistent surface quality and is mitigated through improved design of platen heating. A non-uniform molding temperature may also lead to blistering. When molding SMCs, the required pressure of Table 17.2 is also a function of charge viscosity, preheating, and composition; fillers as well as denser and longer fibers require more force. Press speeds, to first close the mold and then to apply pressure on the charge, have greatly increased as equipment technology has progressed. For thermoset-based reinforced material (BMC and SMC), speeds to fully pressurize the cavity's charge have accelerated from about 12−35 in/min (5−15 mm/s) up to 80 in/min (34 mm/s).

Generally, for thermoplastic sheets, closing and compression speeds are much faster than for thermoset charges. For GMTs, the material must be quickly transferred from the preheating stage into the mold and processed. Recommended speeds are 1000 in/min (425 mm/s) and 24−70 in/min (10−30 mm/s) for the closing and compressing stages, respectively [17]. GMT and LFT parts are often quite thin and cool rapidly, and 2100 in/min (900 mm/s) to contact and then 70−165 in/min (30−70 mm/s) for compression [15] are better. The preheating time is the largest contributor to the processing rate, and this heating can add one to several minutes to an overall cycle. Molding pressure is dependent on other conditions such as preheating, mold temperature, and fiber loading that factor into the cycle time. For instance, a higher processing temperature reduces the molding pressure requirement but also will add more cooling time to the overall part cycle. Likewise, higher fiber content in the GMT charge requires significantly more pressure. For LFTs, the charge is already heated from the plasticizing delivery system. Generally, molding conditions for LFTs are similar to GMT processing, and certainly dependent on fiber type, size, and content.

Viscosity-control additives can improve the flow characteristics of the fiber-reinforced resin matrix during the pressurization stage. Specifically, thickeners minimize fiber separation from the resin itself. If the viscosity of the charge is too low, the resin tends to flow farther and faster, and it easily fills tight cavities and sections compared to the flow of the fibers. The result is that the part can have regions of nearly pure resin along with other regions having highly-concentrated fiber. To minimize separation between the compound components, improved coupling agents promote stronger bonding between fibers and resin.

17.10 Comparisons with Transfer Molding and Injection Molding

The choice of optimal plastics processing method is based on many engineering and economic factors. Any reasonable comparison must be made with other processes that also utilize high pressure with heat to mold a part within a closed cavity. Two such common methods are *transfer molding and injection molding*. Compression and transfer molding routinely use thermosetting resins. Injection molding of thermosets is challenging and requires close control. Any premature polymerization will freeze the injection screw and require a costly overhaul of the injection molder; raising the barrel heaters will not re-melt the material. However, injection molding allows for much more mold and part complexity, including undercuts and hollow parts, than compression. Transfer molding falls in between, closer to injection molding as undercuts and hollow features are possible in the mold design.

Large parts are sometimes cost-prohibitive in injection or transfer molding. And low mold construction costs, in conjunction with the simple operation of a heated press, give a great advantage to the compression molding process as part size increases to several pounds and up. Likewise, operation of a compression molding machine is simple with fewer temperature zones, and less movement of machine and mold components; this leads to lower maintenance and operating costs. Of course injection molding provides the shortest cycle time, usually measured in seconds, with transfer molding measured in minutes to allow sufficient time for curing. Compression molding cycle times are on the order of minutes also, generally even longer than transfer molding. Flash removal is exclusive to compression molding but this represents the least amount of scrap material among these competing processes.

Due to the fact that in compression molding the resin liquefies and flows a very short distance, there is insufficient time for much molecular orientation of the polymer chains. This generally provides for uniform part properties and density in all three dimensions as well as fewer residual stresses. In injection and transfer molding processes, the molecular chains will tend to elongate along the flow streamlines and this orientation bias will freeze in place upon part cooling, increasing tensile strength in that direction. This orientation control is useful in many products. On the other hand, a part's mold shrinkage is less and more uniform with compression molding, and many times better than with injection-molded parts.

Another important advantage of compression molding is with the use of reinforcements in longish fiber form. Although the resin does flow, the distances are quite short so that fibers are not stressed and retain their integrity. Thus, bio-based and natural fibers are mostly processed by compression presses. Transfer and injection molders are limited to short fibers, since long ones would be damaged, especially from passing through narrow runners and gates as well as from the churning action of an injection molding screw. Thus, longish-fiber cloths or mats are successfully employed, even in high concentration, with compression molding resulting in composites having superior mechanical properties. Additionally, with compression molding, fiber orientation is controllable with careful positioning of the reinforcements within the mold so that part dimensional strength is adjustable.

17.11 Similar Processes

There are a few variations on the conventional compression molding process. These include cold forming (cold molding) and sintering, and are useful when processing certain resin formulations, including thermoplastics, but may need post-processing actions such as additional pressurization, annealing, and/or machining to finalize the shape and properties. Items for the electrical industry are often made by these methods.

For molding common thermoplastics such as ABS, PVC, and polycarbonate, cold forming compacts by a factor of 3—6 a granular charge at 3000—5000 psi (21—34 MPa), but without heat into a preform [1]. This preform is not mechanically strong with inferior dimensional control and surface quality, but any air has been forced out and it is ready to be further processed. Phenolic thermosetting material is cold molded, and then cured in an oven.

Preforms may be strengthened by sintering. This may take place outside or within the compression mold and the heat is controlled just below the melting temperature, so the final part is fused, as is the case with rotomolded products. The fusing does harden the part but not to the degree achieved by any process where melting occurs. Plastics in the fluoropolymer family are difficult to process by traditional means but are successfully molded through sintering.

17.12 Modeling the Fluid Dynamics and Heat Transfer of Mold Filling

The closing of the mold creates a perpendicular (normal) force upon the charge, compacting it. Once enough compaction is obtained, the charge resists further normal deformation and will be squeezed to move tangentially to the molding force. As the resin charge liquefies under pressure, a flow front is formed that eventually extends to fill the entire mold cavity. This length of travel may be relatively long, especially when using mats of SMCs and GMTs which may occupy only a portion of the mold surface. It is advantageous to be able to predict this mold-filling process, but to do so an appropriate mathematical treatment is needed. Physically, the flow is quite complex. The polymer melt is a viscous fluid described in one, two, or three dimensions. Furthermore, the fluid is not isothermal and experiences heat transfer between the melt and inside mold surfaces. Additionally, there is an internal heat generation with thermoset curing. Finally, the fluid undergoes a transient phase change when solidifying, and physical properties must be adjusted with changing temperatures. Thus, to properly account for the hydraulic and thermal effects, differential continuity and momentum equations must be solved in conjunction with the differential energy equation. The non-Newtonian nature of polymer melts requires viscosity to be a function of the temperature and flow conditions. Any reinforcing fibers are reoriented, or even damaged during flow.

Since it is unlikely that a simple, overall analytical solution would be obtained for any part, the approach must be to analyze the flow on a differential and local basis with finite element techniques. Such an effort relies on extensive computational power for adequate detail and resolution. Finite element techniques require subdividing, or meshing, the part geometry into minute, individual volume elements where the mathematical relationships are applied. Two sample parts subdivided into individual finite elements are present in Figure 17.18; meshing can be made more detailed (or coarser) depending on desired solution accuracy. More detailed meshing implies more elements and increases required computational capacity and program running time; so its selection is a compromise between numerical accuracy and computer hardware and software limitations. Proper volume connectivity ensures that the equations propagate throughout all the interior volumes of the part and to the mold surface interface, where boundary conditions are stated. The most accurate solution requires thousands of elements. Finite element methods are commonly applied to a variety of fluid flows but the complex rheology of compression molding requires significant simplifications in the modeling or can only be utilized for very simple part shapes.

For thermosets, the velocity profile of the flow front has been established to be relatively flat and plug-shaped. A thin melt region exists between the charge core and mold surfaces, which ensures that core fluid layers move together in the direction of flow. In the case of thermoplastics, the flow front assumes a more parabolic shape, characteristic of laminar flow. However, due to the fact that solidification initiates in the material in contact with the cooler mold, resin at the core migrates toward the cavity surfaces creating a secondary flow pattern that is known as the *fountain flow effect*.

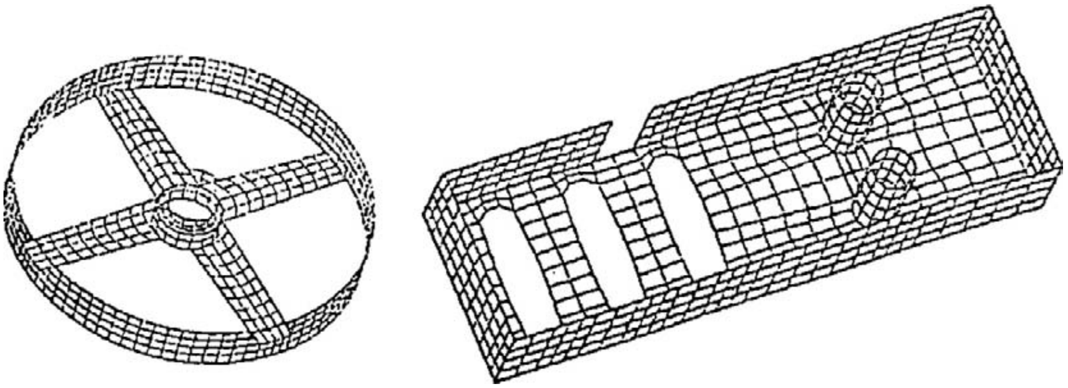


Figure 17.18 Geometrical meshing of some sample parts prior to finite element analysis. *(TECHNALYSIS, INC., Indianapolis, IN)*

Because many SMC parts have a thickness much less than the length in the direction of flow, an adequate model may be constructed based on classical Hele-Shaw flow; the flow field is essentially a flat sheet of a constant thickness. Tucker and Folgar [19] proposed such an approach, using further simplifications of an isothermal and Newtonian melt. Their model allowed for variable mold closure speed leading to flow in a two-dimensional plane with the thickness specified in the third coordinate. The energy equation neglected conduction within the plane but included viscous heating and a heat generation term to simulate the exothermic curing reaction. This methodology was further refined where, among other improvements, a frictional boundary condition replaced the conventional no-slip at the inside mold surface [20]. In a sheet molding compound, the fibers will reorient themselves with flow. A computerized predictive technique for this event is available [21]. Addressing the fountain flow effect characteristic of thermoplastic rheology, the methodology of Mavridis, Hrymak, and Vlachopoulos [22] clearly predicts streamlines originating from the flow's core and radiating in semi-circular patterns backward and to the upper and lower mold surfaces. Although this study focused on injection molding, its findings can be extended to other flows in narrow channels such as during compression molding.

Commercial software is available to simulate the compression molding process. One such product is PASSAGE/COMPRESSION. Its capabilities include Newtonian and non-Newtonian fluids, non-isothermal flow, fiber orientation prediction, shrinkage and warpage analysis, and stress analysis under external static and dynamic loads for thin-walled BMC and SMC parts. The first stage of the simulation represents the pressurization of the charge by the molder's force accounting for the speed of mold closure. Next, the flow front is established as the charge flows outward within the thin gap formed by the upper and lower mold surfaces. Once the mold cavity fills, the problem is a transient heat transfer analysis. Figure 17.19 displays these stages of molding. In the top view, the press begins, at time equals zero ($t = t_0$), exerting force on the resin charge; $h(t)$ is the thickness of the charge and is a function of time. Next, the flow front velocity profile takes shape. Lastly, the part is formed, flow is zero, and heat transfer takes place at the interface between the part and mold cavity surfaces. The software package relies on the Barone and Caulk and Hele-Shaw methodologies. Figure 17.20 is a sample analysis of the filling of a truck hood. Taking advantage of symmetry, only half of the hood needs to be modeled, reducing the computational demand and improving accuracy. The finite element grid is shown and the moving flow front is represented by the darker shading. The charge moves from the centerline of the hood in two separate flows which merge near 1/4 s (Figures 17.20.b and c), establishing a weld line. The remaining cavity volume fills toward one corner (Figure 17.20.e), identifying a region potentially needing venting. The simulation shows the progression of the melt front until it fills the part after 0.60 s.

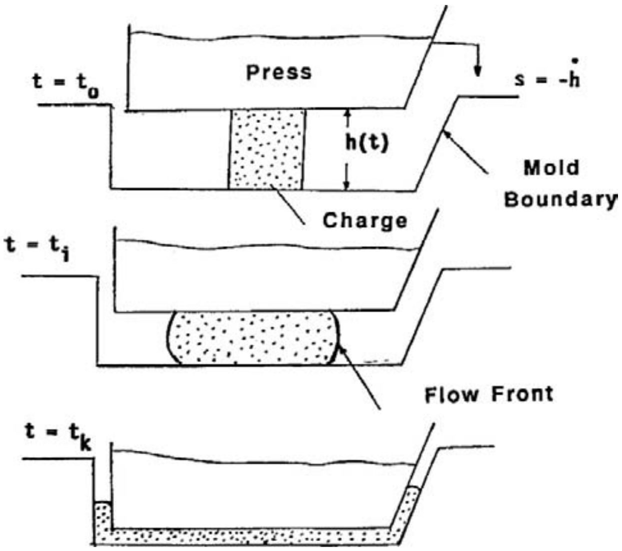
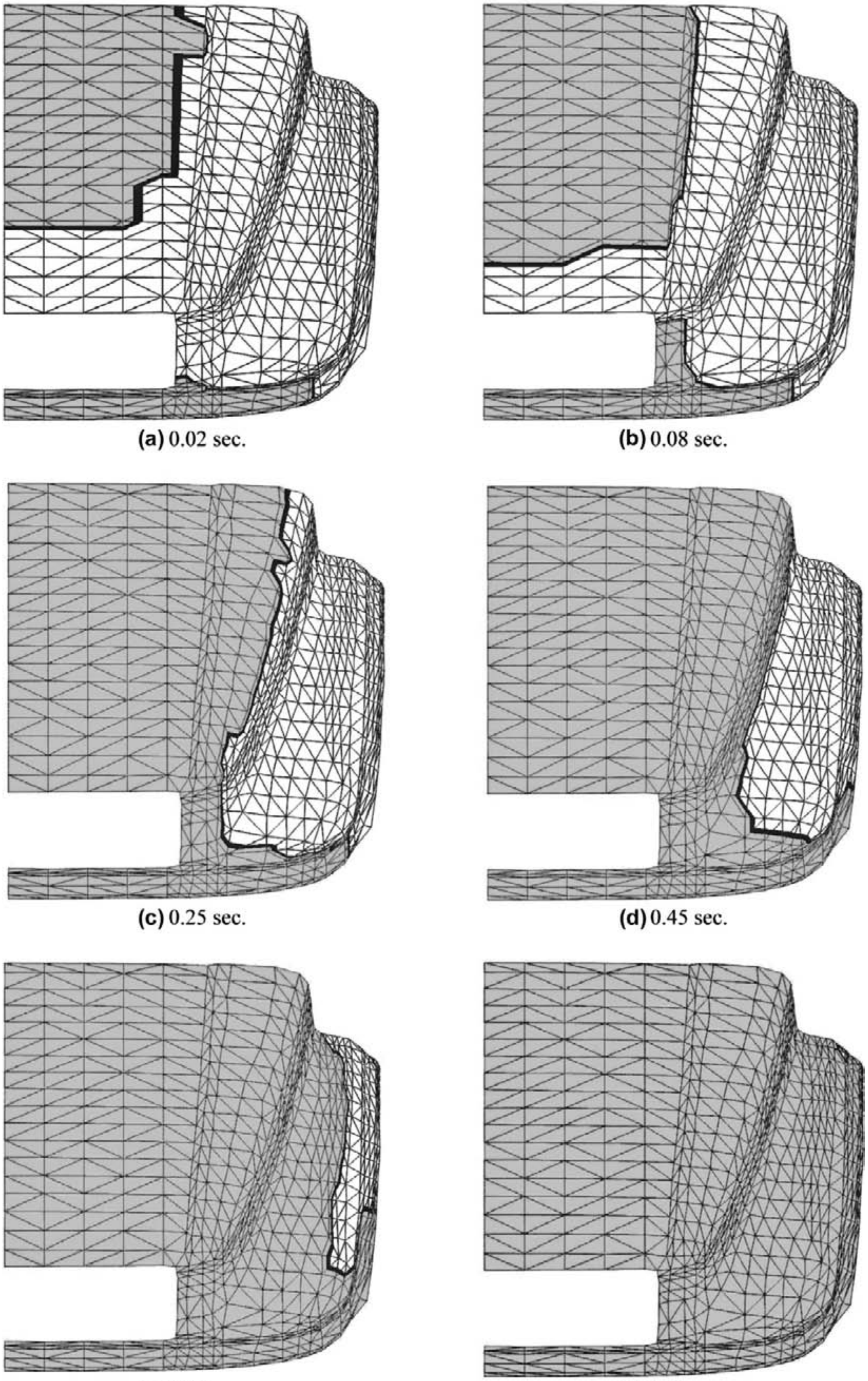


Figure 17.19 Theoretical representation of the behavior of the charge during the compression molding process. *(TECHNALYSIS, INC., Indianapolis, IN)*



(a) 0.02 sec.

(b) 0.08 sec.

(c) 0.25 sec.

(d) 0.45 sec.

(e) 0.57 sec.

(f) 0.60 sec.

Figure 17.20 Computerized simulation of the compression molding of a truck hood. *(TECHNALYSIS, INC., Indianapolis, IN)*

Table 17.3 Generalized part defect categories

Strength	Dimensional	Surface	Material
Cracking	Chipped edge	Dieseling	Contamination
Weld line	Excessive flash	Blister	Porosity
Fiber separation	Sink mark	Drag marks	Under-cure
	Shrinkage	Dull finish	Voids
	Warpage	Ripple	

Although predictive methods — computerized or not — are useful, it should be remembered that the actual compression molding process is quite complex. Large uncertainty arises from modeling assumptions and property data. Optimally, once a mathematical model is formulated, it ought to be benchmarked and verified using a known, simpler solution or case. Only then should other trials be attempted. Theoretical models are best used to eliminate competing designs and for useful relative comparisons. For instance, for a specific part, the difference in filling times under two different molding conditions may be calculated as 20%; this may be more accurate than the absolute filling time (calculated in seconds) for either run. Thus, for absolute data, prior experience and prototyping are better. In all cases, it is vital to experimentally verify the final design.

17.13 Ensuring Part Quality

Of course, there are many factors affecting the quality of a part or product. Quality problems may be readily apparent from visual inspection. Other defects may be internal and not ascertained until mechanical or other property testing. Processing conditions, mold design, and the resin itself can be the source of imperfections. Direct effects between production parameters and quality issues are impossible to exactly quantify and are best solved through experience and trial-and-error testing. However, compression molding defects have been characterized and guidelines for minimizing problems are available [10]; Table 17.3 lists some of these defects arranged in general categories.

Figure 17.21 Rectangular block with severe edge chipping.

Figure 17.21 presents a rectangular block measuring 3″ by 2″ (76 by 51 mm) and displays severe chipping; the damage is especially pronounced at the block's right-hand side and lower left corner. Also, the entire lower edge shows chipping. An example of porosity is in Figure 17.22, where voidage defects extend to the part's surface; the part is a 5″ (127 mm) remnant of a tensile bar. Extensive pitting is seen along the bar's surface. The porosity was caused by incomplete drying of the filler used in the molding compound; during the heated compression, the water evaporated leaving voids. This is an instance where an internal, material defect also negatively affects the surface of the item. Both figures are examples of quality problems that must be addressed through molding conditions, part ejection, or tool construction.

In a more general sense, for over a 100 years the basic concepts behind the compression molding technique have gone unchanged. But with the world looking for products that are more flexible, durable, aesthetically pleasing, and at low cost and weight, lately there have been technological advances to the equipment and resins used. Additionally, maintaining the highest part quality must coincide with faster processing and more efficient power consumption and material usage. Resins have been improved in terms of recyclability, cost, and property performance. Progress with

Figure 17.22 Tensile bar with voidage defects extending to the part's surface.

computers has allowed for simulations to make improvements in the equipment such as more uniform platen heat distribution. Molds are produced to a higher degree of precision. Computers have integrated touch screen interfaces and menus with measurement, imaging, and statistical analysis. In this type of control, sensor data are relayed back to microprocessors and various types of actuators throughout the system. Compression molding automation allows for small, but important changes in pressure, temperature, speed, time, and material handling. To maintain the highest quality, consistency is vital and automation includes the use of robotics which increases reliability of loading charges into the mold, part ejection, and post-processing steps. Thus, machine operators are free to focus on process and quality monitoring. Overall, recent technological advances have led to more reliable and cost-effective parts and products with the same basic hot press.

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18 Rotational Molding

Paul Nugent
www.paulnugent.com

18.1 Introduction

Rotational molding, also known as rotomolding or rotocasting, is a relatively small part of the plastics industry practiced by around 2500 companies around the world and it consumes approximately 0.7% of the total volume of the world production of plastics. It began with polyvinylchloride (PVC) plastisol molding in the late 1950s and progressed into polyethylene where it has largely remained. It is a small but exciting niche within the plastics world that reaches almost every conceivable market. Yet, it typically enjoys growth rates above industry average. It offers much in the way of design flexibility and scale of products with products ranging from simple bulk storage containers to sophisticated automotive, medical, and aerospace applications. Regularly used to produce parts of great complexity with a constantly growing range of applications, rotational molding lends itself to hollow, complex forms like no other process. Small parts such as medical pipette bulbs can be made in essentially the same manner as large 23 ft (7 m) boats. Intricate parts such as fuel tanks and components for aircraft ducting are becoming more common as rotational molding is recognized by a broader group of designers and engineers.

The apparent simplicity of the process and the "low-tech" markets such as simple storage tanks that are commonly molded have caused it to be somewhat overlooked as a technical process. However, current market trends to consolidate part components and shorter product life cycles with lower total volumes have brought an increased level of interest. Importantly, this market interest has attracted the interest and development efforts of major material suppliers—a key factor in the future development of the industry.

This chapter takes a look at the basic process of rotational molding, the markets that it serves, the materials, molds and machinery that are used, and finally takes a look at some of the design basics that can help make molding easier. For those who seek a deeper and broader treatment of the subject, *Rotational Molding: A Practical Guide*, also by the author, is the most comprehensive book available on the process, details of which can be found at www.paulnugent.com.

18.1.1 Typical Applications

The versatility of rotational molding is constantly demonstrated by a wide range of products in an equally wide range of markets. Some typical market sectors and the applications within them include the following:

- Agriculture (storage tanks, spraying equipment tanks)
- Automotive (interior panels, fuel tanks, duct work, air intake systems)
- Building construction (water tanks, septic tanks, highway barriers)
- Electrical-electronic (above-ground pedestals, below-ground chambers)
- Floor care (vacuum cleaner parts, floor cleaner tanks)
- Industrial (chemical tanks, cases, shrouds and housings, corrosion and pollution control equipment parts)
- Lawn/garden (mower shrouds, fuel tanks, duct work)
- Marine products (dock floats, hulls, fuel tanks, seating, fenders, live wells)
- Materials handling (tanks, drums, barrels, hoppers, IBCs, pallets)
- Medical equipment (spine boards, anatomical figures, inflatable masks, implants)
- Playground equipment (slides, climbing frames)
- Signs and displays (point-of-purchase displays)
- Sports/recreation (toys, play-balls, kayaks, canoes, helmet linings, pet products)
- Transportation (road traffic barriers, cones, signage, aircraft duct work)

Ideal non-tank applications for rotational molding are typically complex hollow forms in relatively low quantities (up to approximately 10,000 parts). There are obvious exceptions to this, children's toys for example. But for the most part, rotomolding offers benefits to end-users with low upfront costs in tooling and equipment and the ability to render almost any design that the molder can conceive.

The process is inherently a low pressure one and is closely tied in many respects to the processing attributes of polyethylene. Material choices outside the polyethylene palette are limited in comparison to other processes and thus rotomolding does not always suit applications that have more demanding performance criteria. Tolerance control, surface finish, and part stiffness are among the most common challenges.

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18.2 Rotational Molding Process

18.2.1 Four Basic Steps

At first glance, rotational molding is a relatively simple process. It utilizes high molding temperatures, thin-walled metal or composite molds, biaxial rotation in two perpendicular axes, finely divided powder or liquid polymers, and cooling using air and/or water to produce hollow, seamless parts with relatively low levels of molded-in stress.

Rotational molding has four basic steps as shown schematically in Figure 18.1.

1. Loading

A pre-weighed amount of powdered or liquid plastic is placed in one half of a thin-walled hollow metal mold that is mounted on the arm of a molding machine. The mold is then closed using clamps or bolts at parting lines between the mold sections.

2. Heating

The mold is then rotated biaxially about two perpendicular axes and moved into an oven where heat is applied. The metal or composite mold becomes hot and transfers heat to the powder or liquid material tumbling inside. As the temperature of the mold and material rises, a hollow part is formed as the material is deposited on the inner surface of the mold. In the case of powdered materials, they melt in successive layers to form the part while liquid materials typically chemically react as they form the part shape.

3. Cooling

When the material has melted or reacted and has been consolidated to produce the correct material properties, the mold is moved to a cooling station where forced air, water mist, or a combination of both is used to cool the mold to bring the part temperature down to a point below the crystallization or solidification point of the material. Uniaxial or biaxial rotation continues during cooling to prevent the molten material on the mold surface from sagging.

4. Unloading

Once the part has been cooled, the mold is moved to the unloading station where the part is removed. The mold is then ready to begin the process again.

Stages 1 and 4 are often combined into a single operating station (mold servicing) in machine design so that the most basic of machine configurations typically consist of three workstations: heating, cooling, and mold servicing.

However, the apparent simplicity of the process belies the complex interaction of heat transfer and material distribution that occurs within the mold during the process. Rotational molding is unique among plastics processes in that heating,

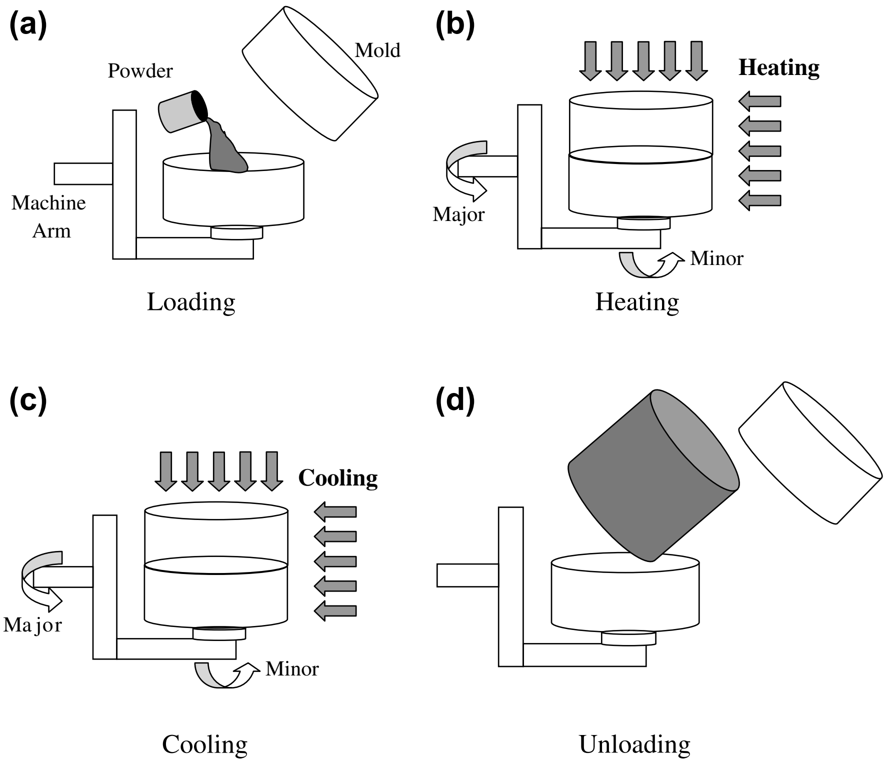

Figure 18.1 The four basic steps of rotational molding.

forming, and cooling of the material all occur inside the mold without the use of pressure; until recently, once a mold entered the oven, nothing more was known other than that the powder melted (or liquid reacted) and was then cooled to form the final part. Nowadays, sophisticated control systems, which can measure temperatures inside the mold during the cycle, scan the surface of the mold continuously for temperature readings, or even place a video camera inside to view the formation of the part, are available.

During the process, a number of key factors must be considered to ensure that the process is effective and economic: venting is used to ensure that pressure inside the mold is in equilibrium with the external environment; release agents must be used for most materials to ensure that they do not stick to the mold surface; rotation settings must be carefully selected as the relationship between the primary and secondary axes affects the way in which the material is distributed in the final part; and only the external surface of the part is in contact with the mold, particularly in the case of semi-crystalline materials such as polyethylene, which means that cooling rates must be controlled to minimize distortion while accelerating the process.

18.2.2 Advantages and Limitations of Rotational Molding

The main advantages of rotational molding can be summarized as follows:

1. It is ideally suited to the manufacture of hollow, complex shapes ranging in size from hearing aid components to industrial tanks of over 20,000 gallons (75,700 l) capacity and boats up to 23 ft (7 m) long.
2. Both molds and machines are simple and relatively low-cost. It is a low-pressure process that allows thin wall, low strength molds to be used. Small production runs can be cost effective.
3. Low pressure and low-shear rates during molding produce parts that have low levels of molded-in stress.
4. Parts have relatively good wall thickness distribution compared to processes such as blow-molding and thermoforming. External corners tend to thicken, which can be an advantage in applications where wear is critical.
5. Parts can have thin walls relative to their size and volume, i.e., large storage tanks.
6. Part wall thickness can be adjusted by modification of mold by simply adjusting the amount of material used.
7. Different sizes of parts can be produced simultaneously on the same machine at the same time.
8. Parts made of different materials can be molded simultaneously on the same machine and even on the same machine arm at the same time.
9. Large metal inserts and graphics can be molded directly into parts. A wide range of surface textures and details can be reproduced.
10. Color changes can be made quickly and easily. There is no purging process such as that found in injection molding or extrusion processes; parts can be molded in a new color without loss of material or parts.
11. Multiple-layer parts can be formed using the same low-cost molds. Multi-colors and parts with foamed layers can be produced using simple techniques.
12. All material placed in the mold is used to form the part. Scrap is limited to those areas that are removed from the part during finishing. Insulated sections of the mold can be used to minimize this “run-out” or scrap material.

The main limitations of rotational molding can be summarized as follows:

1. The process is typically not well-suited to very large production runs of smaller parts—for smaller parts blow-molding or even injection molding may be more competitive (although high-production rates can be achieved through the use of multiple molds and machines, e.g., children’s play-balls).
2. The number of materials that are available for rotational molding is limited in comparison to other processes.
3. Material costs are higher due to the need to grind pellets of raw material into a fine powder for molding. Micro-pelletizing technology has been explored to reduce this penalty.
4. Cycle times are longer in comparison to other processes as both the mold and material must be heated and cooled. The materials used typically require more thermal stabilization and can cost slightly more than that of other processes.
5. Loading of molds and unloading of parts is labor intensive in comparison to other processes, especially for complex parts.
6. Release agents are required to ensure that the material does not stick to the mold during de-molding. This often demands constant attention by the machine operator.
7. Bosses and ribs for stiffening cannot be easily molded into parts; designers must depend more on part geometry and design to produce stiff parts.
8. Large flat surfaces are difficult to produce due to warpage. Designers will typically use ribbing and surface details to avoid them in parts.

9. The inner surface of the part is freely formed during molding. This means that the dimensions cannot be controlled with the same degree of accuracy as, for example, in injection molding.
10. The part is free to shrink within the mold during cooling; dimensional accuracy can therefore be difficult to predict.

18.3 Materials for Rotational Molding

18.3.1 Desirable Characteristics

There are a number of desirable properties that a material should have in order to be suitable for rotational molding. They include the following:

1. *Thermal stability* to prevent loss of properties during melt-compounding and grinding into powder as well as a wide processing window during molding. Most rotational molding materials are stabilized with antioxidants to reduce the effects of the long heating cycle typically used during rotational molding and to provide good service life, especially in outdoor applications.
2. For powders, the *low-shear melt viscosity* must be low enough to allow the material both to wet the internal surface of the mold and to fuse into itself in a homogeneous mass. The common measure used as a guide to the melt flow properties of materials is the Melt Index (MI) measured in g/10 min. Most commercially available rotational molding polyethylenes have an MI between 2 g/10 min and 8 g/10 min (2.16 kg/190 °C). Higher flow rates may be required for parts with complex molding details.
3. Good *impact strength* is most often critical in low temperature applications, but is required of most parts in general purpose applications. Materials will often be expected to exhibit good performance down to 40 °F (-40 °C).
4. *Environmental stress crack resistance* (ESCR) is the ability of the material to resist long-term exposure to stress-cracking agents. Materials with ESCR values in excess of 1000 h are typically considered acceptable based on one of the common test procedures.
5. *Flexural and tensile strength* must be sufficient for the final application for which the material is intended—polyethylenes have relatively low strength values while engineering materials such as nylon and polycarbonate offer better levels of performance.
6. *Elongation to failure* should be high for most applications.
7. *Free-flowing physical properties* with good heat transfer properties to allow the material to distribute evenly and quickly during the heating cycle. Poor flow properties can significantly affect the final appearance and thickness of a part.

Recent research has investigated the effect of rheology and thermal properties on sintering and bubble removal in polymers. The techniques that have been developed by researchers include testing melt viscosity against shear rates and temperature and the elastic behavior of the material under low-shear conditions. These tests represent a major step forward in the process of evaluating materials prior to molding. Conclusions from this work show that melt rheology and surface tension play a primary role in the earliest stages of material densification while diffusion of gas from within entrapped bubbles is very important during the latest stage of densification. Materials such as linear low-density polyethylene melt slowly with a gradually decreasing viscosity. This creates a three-dimensional network of particles connected at their boundaries trapping large amounts of air. Materials with lower viscosities tend to fuse more quickly, trapping less air and therefore consolidating faster.

18.3.2 Common Materials

The specific characteristics required under the low-shear, high-temperature conditions inside the mold mean that a limited range of materials is available for rotational molding in comparison to other molding processes. However, this group is gradually growing as more material suppliers and end-markets recognize the potential of the process.

From a market perspective, the main materials in use today can be ranked as follows:

- Polyethylenes (LDPE, LLDPE, HDPE, XLPE, mLLDPE, EVA) 95%
- PVC 3%
- Nylons (Nylon 6, 66, 11, 12) $< 0.2\%$
- Polypropylene $< 0.1\%$
- Polycarbonate $< 0.1\%$
- Fluoropolymers (ETFE, ECTFE, PFA, MFA, PVDF) $< 0.1\%$

There is, however, a range of polymers that have either been successfully molded over the past 30 years or are being used in small quantities for specialist applications. These include:

- Acetal copolymer
- Acrylic
- ABS (acrylonitrile butadiene styrene)
- Cellulosics

- Epoxy
- Ionomers
- Phenolic
- Polybutylene
- Polyester
- Polyester elastomer
- Polystyrene
- Polystyrene—impact modified
- Polyurethane
- Silicone

18.3.2.1 Polyethylene

Polyethylenes offer an excellent combination of ease of processing, thermal stability, and cost with which they continue to dominate the market. The development of a broad range of alternative materials for rotational molding has been slow due to two main reasons:

1. The ability of a material to reform into a homogeneous solid after being pulverized into a free-flowing powder without the need for pressure eliminates many engineering materials from the rotational molding palette.
2. Specialist materials tend to be initially more expensive than the benchmark polyethylene and are often hampered by low market demand to encourage material development.

While polyethylene satisfies the need for many varied applications, structural requirements, scratch resistance, chemical resistance, and an expanded temperature performance range are just some of the attributes that both molders and end-users alike need in order to expand into new markets. The demand for these properties will grow as the overall scale of the rotational molding market grows and will hopefully drive further research and development in new materials.

18.3.2.2 Polypropylene

Polypropylene has been used for many years in rotational molding. It has typically been hampered by difficulties in processing, poor low-temperature impact strength, and sensitivity to overcure. But, recent developments have produced grades, which are easier to mold and have reasonable impact performance at room temperature (although good low temperature performance remains elusive). Applications for polypropylene include hot (not boiling) water storage, autoclavable containers, and chemical containers where the chemical resistance of polyethylene is not sufficient.

18.3.2.3 Nylon

A range of nylon combinations can be used for rotomolding. The most common commercial grades are nylon 6, nylon 11, and nylon 12 and special grades have been developed with enhanced flame retardancy properties for use in aerospace duct work applications. They require some care in processing. But, when properly molded, they are strong, abrasion resistant, and self-lubricating, and have good impact, chemical and fatigue resistance as well as high continuous-use service temperatures. They retain their strength properties at high temperatures—values fall off as the material rises in temperature but do not dramatically fall away until the glass transition temperature (T_g) for the material is passed. Nylon 11 and nylon 12 have better resistance to oxidation that results in longer retention of properties at elevated temperatures than nylon 6.

Nylons need additional anti-oxidants or processing with an inert atmosphere (typically nitrogen or carbon dioxide) to prevent degradation. Heat stabilizers such as copper salts can be added to improve heat stability of the final molded product for applications where the service temperature exceeds 165 °F (75 °C). Nylon 6 can be molded without nitrogen if lower impact and inferior surface appearance is acceptable. Nylon 11 and nylon 12 do not require nitrogen atmospheres, although using a nitrogen bleed during molding can improve color retention and impact strength.

Liquid nylons in a caprolactam-based reaction and reaction injection molding materials such as Nyrim™ can also be rotationally molded. Raw materials, usually in two streams, are heated to a liquid state and then mixed just before being added to the mold. Rotation deposits the material on the inside surface of the mold. Control of the reaction rate is critical in ensuring that the material is evenly distributed during the curing stages of molding. The reaction generates heat that accelerates the process—an oven may not be required for some applications.

Nylon is commonly used in applications requiring high temperature resistance while retaining good strength properties; for example, car and truck duct work. It is also used where good abrasion resistance is required and where chemical resistance beyond that of polyethylene is required. High flexural strength and toughness make it a good choice for pressure vessels and excellent permeation resistance makes it ideal for solvent and fuel containment.

18.3.2.4 PVC—Liquid

PVC is available in two distinct forms for rotational molding, either liquid or dry. Liquid materials in the form of plastisol and organosol have been the mainstay of PVC molding since their introduction in 1947. Dry powders or vinyl micropellets were introduced in the early 1980s. Vinyl plastisol is the most common form of PVC used for rotational molding.

Plastisols are typically low-cost, have a wide range of hardness, are easy to automate for dispensing, can have high clarity and transparency, allow high mold surface reproduction, and are easy to color. They can be produced in FDA grades, have good chemical resistance and are very forgiving in process.

Altering the ingredients of the plastisol controls the durometer or surface hardness of a molded plastisol product. Rotomolding grade plastisols range from a Shore durometer of about 30 A (very soft) to about 70 D (hard). The inherent hardness is controlled by the properties of the materials used, and the ratio of solids (materials) to the plasticizer.

18.3.2.5 PVC—Powder

Both vinyl powders and micropellets are fairly recent additions to the PVC palette for rotational molding. They offer a wide range of hardness, do not require a pump for dispensing, are clean, can mold with uniform wall thickness, and have a lower bulk density and somewhat higher cost, but are only in limited use in the industry.

18.3.2.6 Polycarbonate

Polycarbonate was first introduced in the 1950s and was first rotationally molded in the late 1960s. It is hygroscopic and requires drying before molding and should have less than 0.02% moisture before being charged directly into the mold. Improper drying will produce parts containing “gray matter” bubbles, a yellow color, a reduction in transparency, and a loss of impact strength. Moisture decreases the average molecular weight of the polycarbonate during molding and therefore degrades physical properties.

As higher temperatures are required to process polycarbonate, heat transfer through the mold to the material can be a problem. The best results are achieved using oil-jacketed molds and finer powder than the 35 mesh (500 micron) commonly used for polyethylene. However, bubbles can still occur in parts and it is common to see textured mold surfaces used to disguise their presence. The use of a nitrogen atmosphere can reduce the yellow color caused by degradation.

The advantages of polycarbonate are its higher stiffness, toughness, clarity, and high temperature resistance (275 °F (135 °C) vs. 122−158 °F (50−70 °C)) over polyethylene. Weatherability and dimensional stability are good and the material can be ductile even at low temperatures. FDA-approved and flame-resistant grades are available. It is most commonly used for applications such as street lighting and display covers. The disadvantages are that it is high in cost, is more difficult to process, must be dried, and has low chemical resistance.

18.3.2.7 ABS

Acrylonitrile butadiene styrene (ABS) is an amorphous thermoplastic terpolymer. It has been molded in the past commercially and has been the subject of several major research projects at university level. Studies have shown that ABS (along with polystyrene and acrylic) is a material that is sensitive to degradation and one that can sinter to produce a porous and friable structure with low tensile strength and high surface porosity. Increased rubber content in ABS leads to increased difficulty in densification.

ABS offers a range of potential advantages, including good impact strength, rigidity, chemical resistance, good adhesion properties, paintability, and resistance to solvent cracking. Molded parts can be painted using a primer and topcoat combination for applications such as mannequins, toys, sanitary ware, auto components, sports equipment, and furniture.

18.3.2.8 Fluoropolymers

Fluoropolymers offer superb chemical and temperature resistance for demanding applications. They exhibit low surface tension, excellent chemical resistance to many aggressive chemicals, and good temperature resistance. They also offer good aging resistance as they are not affected by UV rays, do not undergo oxidation, and do not absorb water.

There are two distinct families of fluoropolymers: perfluorinated (like PTFE) and the partially fluorinated (like PVDF) polymers. The major types that are rotationally molded are polyvinylidene fluoride (PVDF), ethylene-tetrafluoroethylene (ETFE), ethylene-chlorotrifluoroethylene (ECTFE), and perfluoroalkoxy (PFA).

Fluoropolymers are used for demanding applications where purity, chemical resistance, and high temperature performance are required. Typical products include high purity chemical storage vessels and processing vessels. They are also commonly used to line tanks and piping components for transportation and processing of aggressive chemicals including: pump housings, vessels, columns, elbows, tees, and pipe sections with unusual shapes.

18.3.2.9 Foamed materials

Foaming of molded parts is used for increased stiffness, insulation, flotation, impact dampening, and even sound absorption. In rotational molding, there are two primary techniques used (a) polyurethane foam filling and (b) foaming the part material during molding using a chemical blowing agent.

Polyurethane foam is commonly used to fill the void inside a hollow part for strength or insulation. The foam density is typically in the range of 2−4 lbs/ft^3 (0.03−0.06 g/cm^3) and is often used to provide buoyancy in flotation devices or insulation for storage vessels. The urethane foam is created using a two-component liquid system that is metered into the part using a special mixing head and as the components react it rises to fill the void inside.

The downside of polyurethane is that there is almost no adhesion between regular polyethylene parts and the foam (some adhesion with crosslink polyethylene occurs). A number of techniques (such as plasma treatment of the polyethylene) are used to develop a mechanical bond; but over time, the interface between the foam and the part can still break down. The initial reinforcement and insulation properties can be significantly reduced. Recycling of parts is not easy and the process of filling is messy and potentially an environmental problem.

Chemical blowing agents for rotomolding have become increasingly common in recent years. These can be added by compounding in a pellet form or dry-blended with the material directly to produce a foam structure within the part during molding. This can produce increased stiffness and insulation properties in a single step; thus removing the need for secondary operations and fixtures. The most common material to be foamed in rotational molding is polyethylene although work has been carried out using polypropylene. The densities that can be achieved by direct foaming of polyethylene are typically not as low as polyurethane foam and the insulation properties not as effective. Foaming will also extend the cooling cycle substantially as the insulation slows the transfer of heat from within the part significantly.

18.3.3 Material Preparation

The rotation process exerts negligible shear on the materials used for rotational molding. As a result, molding material must be free-flowing enough to reach every surface detail and must have low enough melt viscosity properties to form a smooth finish. To achieve this, the majority of materials are molded as finely divided powders or pellets, although an increasing number of liquid materials are also used.

Materials are most commonly ground to a 35 mesh standard (500 microns) that is defined as the size through which 95% of the material will pass. The average size of the powder particles is typically around 50 mesh (297 microns) although a full range of particle sizes from very fine dust to 600 microns can be present. Powders ground to finer and coarser mesh sizes are used for specialized applications and materials.

Micropellets in the range of 0.020″−0.060″ (500−1500 microns) have been used successfully for a range of applications, but are not common. They offer good moldability and eliminate the need for grinding, which has the potential for reducing cost and eliminating the shearing action of grinding from the heat history of the material. However, extruder throughput levels are lower than for regular size pellets and this tends to offset some of the potential cost savings. Micropellets are very free-flowing and can in some cases produce uneven wall thickness distribution due to the short residence time during rotation on large flat surfaces or internal corners. A combination of 10−20% powder with micropellets can aid in producing a smooth surface and the higher bulk density of micropellets can allow more material to be placed in tight spaces.

18.3.3.1 The grinding process

The bulk of materials ground for rotational molding are polyethylenes (95%+ of the market). Polyethylene is a relatively tough material that can be difficult to divide. The most common method of pulverizing is performed using high-speed attrition mills that grind pellets approximately 3/16″−1/4″ (5−6 mm) in diameter down to the required particle size-distribution.

An attrition mill uses a stationary and a rotating disk with a series of radially serrated teeth machined into them within a mill housing. The disks are positioned opposite each other with a narrow gap that tapers down from the center of the plates to the outer edge. Figure 18.2 shows the layout of a two-stage grinding mill and its major components (PLC controls [1], material feed hopper [2], primary mill [3], secondary mill [4], piping [5], cyclone separator [6], blower [7], dust collector [8], and sifter [9]). Modern mills use horizontal operation for more uniform powder production and reduced wear on the cutting teeth. Production units use single, double, and triple mill configurations according to the throughput required.

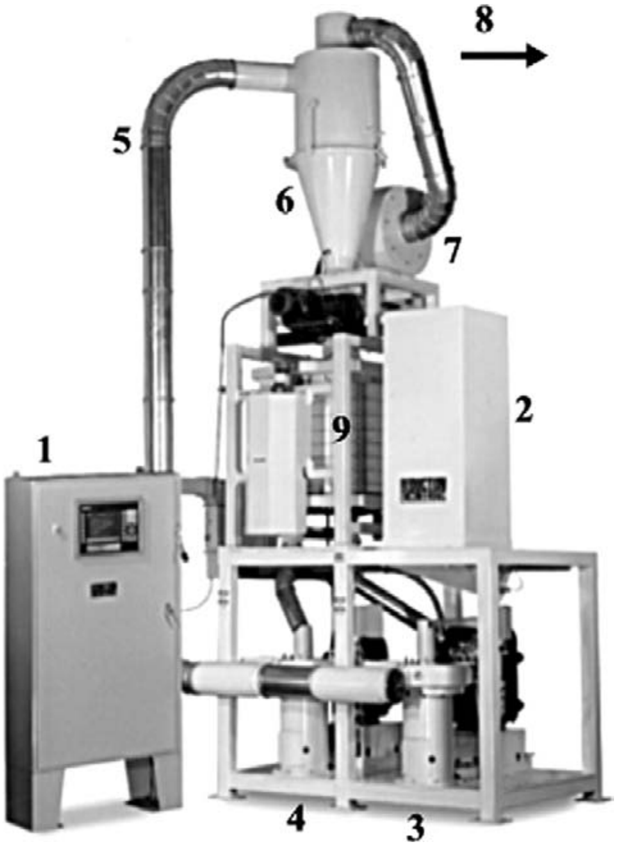

Figure 18.2 Two-stage attrition grinding mill. *(Courtesy Reduction Engineering, Inc.)*

There are a number of important parameters used to control the throughput and quality of the powders produced in typical mills, including the number of teeth on the grinding plates, the gap size between the plates, and the grinding temperature.

Cryogenic grinding

Cryogenic grinding uses liquid nitrogen to freeze material prior to feeding it into the mill and to maintain a low temperature throughout the system. It is used for soft or very tough materials that cannot be ground at normal temperatures. By freezing the pellets, they are shattered as they pass through the mill. Cryogenically ground materials tend to feel somewhat coarse in comparison to polished polyethylene powders.

18.3.3.2 Powder quality and assessment

Powder particle size, shape, and size-distribution are important factors in determining the moldability of a material. Heat is transferred to the powder by conduction with other particles and the mold and by convection with the surrounding air.

Particle shape

Figure 18.3 shows a magnified view of an improperly ground polyethylene powder. Many of the particles have tails and “hairs” attached. These can lead to a number of problems, including reduced bulk density, poor flow characteristics, and unevenness during molding. Figure 18.4 on the other hand shows a sample of powder that has been “polished” to remove tails and hairs that can interlock to cause problems. Note that while the particles are not uniform in shape, they are rounded and therefore able to flow much more easily. Also, a range of particle sizes is present; this is essential in promoting even flow and good surface reproduction during molding.

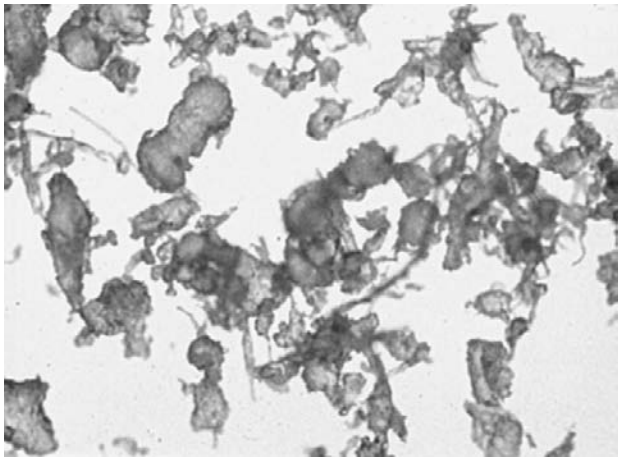

Figure 18.3 Poor powder particle shapes. *(Courtesy Wedco, Inc.)*

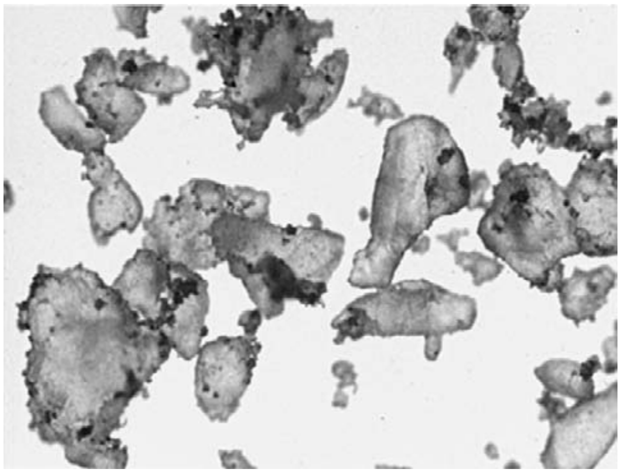

Figure 18.4 Good powder particle shapes. *(Courtesy Wedco, Inc.)*

Particle size distribution (ASTM D-1921)

Particle size distribution (PSD) is measured using a set of sieves stacked vertically with mesh sizes typically ranging from 100 mesh (150 microns) to 30 mesh (600 microns). A sample of material (typically 100 g) is shaken, vibrated, or tapped through the sieves for a fixed time period (typically 10 min) and the quantity retained on each sieve is measured. A typical size-distribution is shown in Figure 18.5.

A broad range of distributions can produce quality moldings—the main aspects requiring control are the level of fine particles (<100 mesh) and the level of coarse particles (>35 mesh). Typical quality guidelines look for a PSD with 95% < 35 mesh (500 microns) and a maximum of 15% < 100 mesh (150 microns).

Dry flow (ASTM D-1895)

The shape of the particles will affect the way in which the material will flow during molding. A measure of this flow is called the “dry flow” rate and is measured using a funnel of specified shape and dimensions. The powder that has been

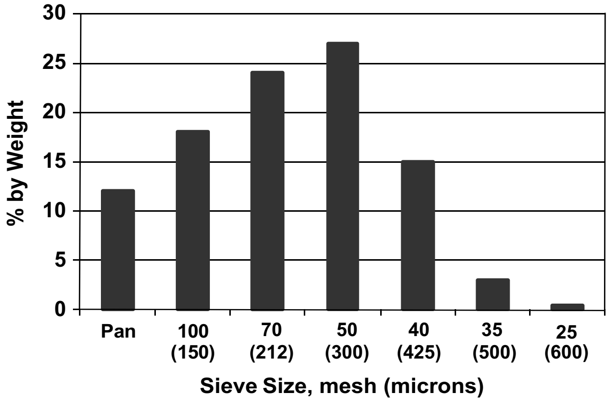

Figure 18.5 Typical powder particle size distribution.

Figure 18.6 Free flowing powder during flow rate test.

ground properly will flow through the funnel smoothly and steadily as shown in Figure 18.6. If the powder has not been ground properly and the particles are "hairy" or have tails attached, it will not flow well or even not at all in some cases. Flow rate is important since easy-flow powders will produce parts of more uniform wall thickness than powders that are tacky, sticky, or that tend to bridge.

A recommended powder flow rate is between 25 and 32 s for a 100 g sample although higher flow rates can be tolerated for large simple part shapes that do not have a lot of fine surface detail.

Bulk density (ASTM D-1895)

The bulk density of the powder is measured using a cylinder of known volume placed under the dry flow test funnel as shown in Figure 18.7. The powder is leveled off after filling the cylinder (taking care not to tamp it and cause settling) and weighed. The weight of the powder is then divided by the volume of the cylinder to calculate bulk density. Typical powders will have bulk densities in the range 0.320—0.400 g/cc. Materials that have been poorly ground with many tails will have lower bulk densities as the powder does not pack as well.

Figure 18.7 Bulk-density cylinder of known volume (40cc) filled with powder during flow rate test.

18.4 Molds for Rotational Molding

18.4.1 Mold Design Considerations

Molds for rotational molding are hollow, thin-walled, and lightweight with good heat transfer characteristics and must be sufficiently strong to withstand repeated handling. They are relatively low-cost in comparison with injection- or blow-molding tools. The choice of mold material and method of manufacture used will depend on the size, complexity, surface finish, and the number of molds required for the production run anticipated for the product.

For all their apparent simplicity, molds for rotational molding are subjected to more rigorous demands than those used in other processes. Injection, blow, and thermoforming molds are used to shape molten or softened plastic. Rotational molding tools are used to heat the raw material from ambient conditions, shape it, and then cool it back close to ambient conditions again. This thermal cycle presents a dichotomy for the mold maker in that the mold must be thin enough to allow heat to pass quickly into and out of the part and at the same time be sturdy enough to withstand the rigors of repeated opening and closing. A very thin mold will heat quickly but will distort during de-molding; on the other hand, a very thick mold will maintain its shape well but may heat at an uneconomical rate.

The range of materials that have been used for rotational molding includes:

- Sheet carbon steel (sheet is defined as up to 3/16″ (4.76 mm) thick)
- Sheet stainless steel
- Plate aluminum (plate is defined as above ¼″ (6.35 mm) thick)
- Cast and machined aluminum
- Cast and machined nickel
- Cast magnesium
- Electroformed nickel and nickel-copper
- Cast and machined Be/Cu.
- Sprayed metal
- Glass or carbon fiber reinforced epoxy
- Cast rubber

The main commercial processes used to produce molds are as follows:

- Cast aluminum
- Fabricated carbon steel
- Fabricated stainless steel
- Fabricated aluminum
- Machined aluminum
- Electroforming

Other methods used for specialist parts and prototyping include the following:

- Oil-jacketed molds
- Glass or carbon fiber reinforced molds
- Sprayed metal

The most common types in use are fabricated and cast molds as shown in Figures 18.8 and 18.9.

Four major factors must be considered when choosing the type of mold to use for a particular part: size, complexity of form, quantity of molds required, and the appearance of the molded part.

18.4.1.1 Size

Physical size may eliminate some methods of tool manufacture. Most large molds are fabricated from sheet metal, although large castings such as 18-foot (5.5 m) kayaks can be produced in single pours. Aluminum casting is often limited to the size of individual cast pieces by the capacity of the furnace used but larger molds can be made by combining several castings and welding or bolting them together. The cost of manufacturing a very large pattern for casting must also be taken into account.

18.4.1.2 Complexity of form

The geometry of the part will also affect the decision. Features such as corner radii, inserts, holes, threads, etc., may affect the choice of mold materials and also affect how a part must be mounted or how a parting line is constructed. Complex parting lines, which require more than one mold piece and cannot fit into a single plane, will complicate the manufacture of the mold.

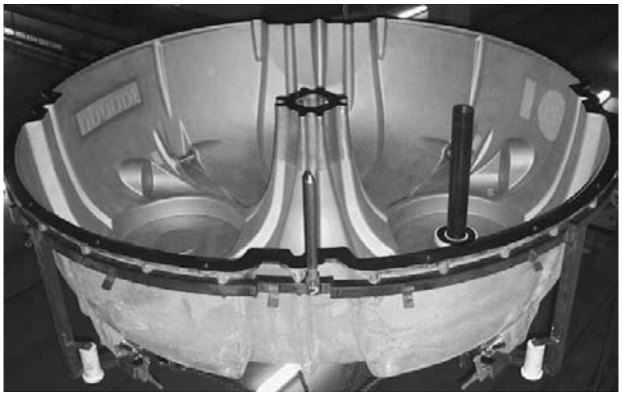

Figure 18.9 Cast aluminum mold half with parting line hardening finish. *(Courtesy Persico SpA)*

Mold inserts (cores, etc.) that are removed each time the mold is opened will affect mold construction by introducing wear points. Fixed inserts that must be interchanged less frequently are preferred.

Detailed molds that require a high degree of precision will favor machining, electroforming, or casting over fabricated methods. Chemical etching is not common but can be used on steel molds to create fine surface details and patterns.

18.4.1.3 Quantity of molds

When multiple molds are required, the level of repeatability that can be achieved must be taken into account when choosing a mold-making method. Sheet metal molds have improved considerably, but casting, electroforming, or machining offer better, more repeatable accuracy. Repeat

Figure 18.8 Fabricated sheet metal mold (upper and lower halves). *(Courtesy Rivers Metal Molds, Inc.)*

cast molds are lower in cost due to the fact that the same master pattern can be used.

High volume production runs that can use either steel or aluminum molds will often be made in cast aluminum due to repeatability. Lower volume production runs will often take advantage of the ability to use lower-cost sheet metal tools or even composite tools to produce small batches; as volumes increase, the project can be converted to cast molds.

18.4.1.4 Appearance of the product

The required surface finish for a part may also dictate which process is used to produce a mold. Some surface finish and details can be added during casting or fabrication; others can be added after the mold is finished (peening, etching). Aluminum or electro-formed molds can produce a wider range of surface finish than sheet metal molds—intricate castings and engraved surfaces can be easily incorporated onto the pattern. Sheet metal can be lightly textured after forming and can even use patterned plates and chemical etching to produce more complex finishes.

Parts requiring a highly polished finish will favor machined aluminum or nickel-plated molds. Cast aluminum and steel can be burnished to a polished finish but not a mirror finish. Designers should note that polished finishes require many hours of hand work in a mold and can add considerably to the cost of a mold. Also, finishes on cores should be considered carefully—highly polished surfaces can create a vacuum, while rough textures may provide enough grip to lock a part in the mold.

18.4.2 Mold Elements and Features

Many of the basic components of molds are similar regardless of the manufacturing process chosen. Figures 18.10 and 18.11 show how a typical cast aluminum mold might be constructed. Each mold requires a mounting plate (1) to enable it to be attached to the machine, a frame to support the mold cavity (2), posts to connect to the mold (3) (often spring-loaded), a parting line flange (4), the cavity itself (5), clamping or bolting mechanisms (6), pry points (7), a vent (8), and lifting points (9). Inserts, removable cores, and other ancillary devices can be added as necessary.

1. Mounting plate

Typically, a heavy steel plate attached to the bottom of the mold frame to allow the mold assembly to be fitted to the machine arm.

2. Framing

The frame must be strong enough to support the weight of the mold, resist the torque applied for closure, allow for ease of handling, and withstand the rigors of repeated heating and cooling. The frame will also be used as the attachment point for mounting plates, clamping, pry points, and other components.

Multiple molds can be mounted in a single frame in what is called a "spider" arrangement. The molds are connected to the frame individually and are opened simultaneously when the frame halves are separated.

Laser-cut frame sections can be designed and fabricated simultaneously as the mold is being produced to shorten the overall delivery process. Ideally, the frames should be stress relieved by heating to 1825 °F (1000 °C) after welding. Heating the frame to the typical range of 500 or 600 °F (260−315 °C) in a standard rotomolding oven will not allow the stresses in the frame to be fully relaxed.

3. Support posts

The cavity is suspended within the frame via the parting line, flanges, and support posts. These posts, or "stand-offs," should be as short as possible to prevent distortion and

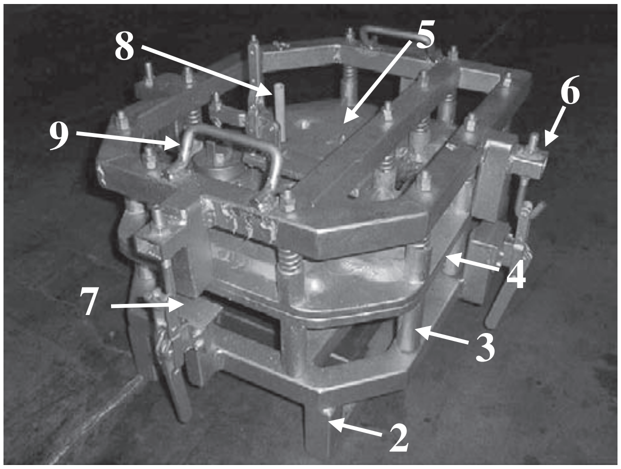

Figure 18.10 Typical mold elements.

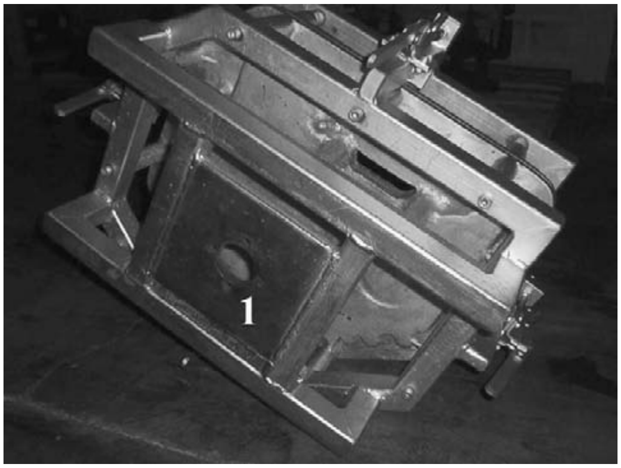

Figure 18.11 Typical mold elements.

cracking due to thermal expansion and contraction—a maximum length of 6″ (150 mm) is typical. For cast aluminum molds, one half of the mold is often spring-loaded to allow the mold to "float" within the frame to minimize distortion due to thermal expansion.

4. Parting line

The parting line is a critical part of the design of a mold. This is normally chosen about the largest dimension of the part to assist with removing the part from the mold and ideally should be flat in a single plane for ease of construction.

Several designs for the flanges along the parting line have been developed, such as tongue and groove, offset (stepped) and flat, to ensure good sealing and ease of location. Alignment pins along the parting line or a tongue and groove parting line can be useful to maintain parting line alignment as shown in Figure 18.12.

The location of the parting line should be chosen so as to allow one piece of the mold cavity to hold the total charge of material if a fill port is not acceptable. This larger mold portion is best for mounting to the machine arm.

5. Mold cavity

The simplest cavity consists of two mold pieces with a simple flat parting line. However, multi-piece cavities may be required for complex parts to allow a part to be removed. Six- or eight-piece molds are not uncommon, but usually require more care and maintenance during use.

6. Clamping mechanisms

There are a number of different types of clamping methods that can be used including: over-center clamps, quick acting toggle bolts, spring-loaded bolts (at the parting line or through the spider), captive bolts and nuts, 'C'clamps, and even vice grips. The clamping point where force is applied should be as far inbound on the flange as possible to ensure that force is applied as close as possible to the parting line.

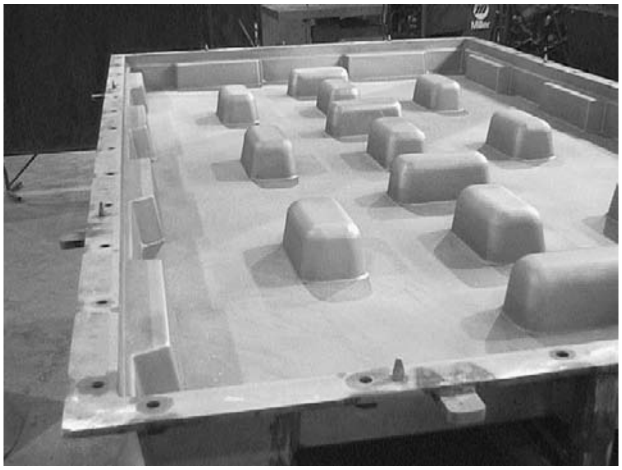

Figure 18.12 Flat bar parting line with alignment pins. *(Courtesy Rivers Metal Molds, Inc.)*

7. Pry points

Pry points are incorporated into a mold frame to provide leverage points where mold halves can be separated without damaging the parting lines.

8. Vent

A vent pipe is usually incorporated to allow equilibrium between the external atmosphere and the inside of the mold and to allow any unwanted emissions to escape and cooling air to enter the mold. The most common vent tube materials are Teflon™ tubing, steel or stainless tubing, and silicone tubing. Ideally, a vent should be in the line of draw, reach to the center of the part volume, and be located in an area that does not affect the final function of the part.

9. Lifting points

Ergonomic and safe handling of molds must be considered when attaching lifting points. When using a hoist, consider using four lifting points for balance.

10. Inserts and cores—Mold sections

Mold inserts and cores are removable or interchangeable areas of a part. These can be used to form threads, undercuts, handles, holes, etc. Steel bushings on the parting lines of cores are recommended to resist wear.

11. Fill ports

Some molds have a shallow cavity half that prevents all the material from being placed in the mold at the beginning of the cycle. A fill port is essentially a removable area of the mold that is opened after the cavity is closed to allow material to be poured into the mold. This can also be used for double shot processes when the material is added during the molding cycle.

12. Hinge mechanisms

Opening and closing molds can create wear on mold components. Removing the mold halves and setting them down may create further damage at parting lines. One way to reduce this problem is to hinge mold pieces so that they remain on the machine at all times. The hinge mechanism must open only enough to allow the part to be removed (see

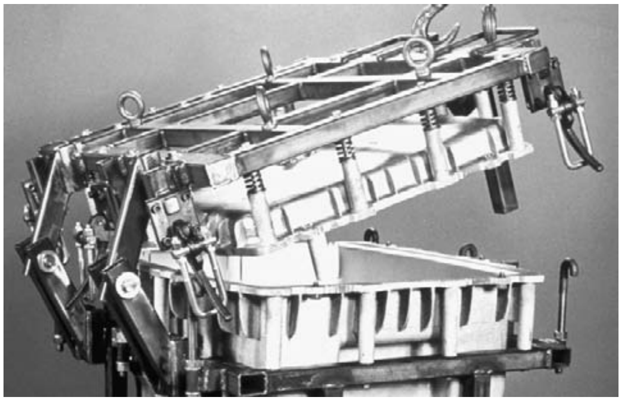

Figure 18.13 Mold hinging mechanism. *(Courtesy Wheeler Boyce, Inc.)*

Figure 18.13). This can be a major time-saving feature for mold servicing.

13. Roller guides

Another technique used to keep mold pieces together on the machine is the use of roller guides. Mold pieces are mounted on guides that allow the pieces to be separated for part removal. The guides and roller system need to be robust to withstand repeated heating and cooling cycles. Figure 18.14 shows roller supports used as guides on a machined aluminum mold.

14. Drop box

A drop box (or dump box) is used to add material during a cycle. This may be to produce a multiple-layer part or to allow extra material to be added that could not fit into the mold at the start of the cycle. The drop box is insulated to prevent the second charge of material from melting before it is added to the mold. It is connected to the mold through a Teflon™ plugged opening (typically 2—4″ (50—100 mm) in diameter). A pneumatic actuator connected through the arm of the machine is used to operate the box.

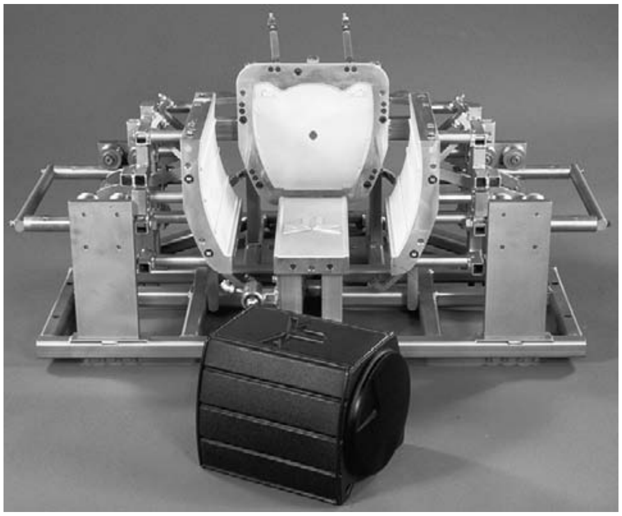

Figure 18.14 Roller Guides used on machined aluminum mold. *(Courtesy Wheeler Boyce, Inc.)*

15. Airflow amplifiers (vortex generators)

Airflow amplifiers (vortex generators) work by using high-pressure compressed air through a specially designed nozzle to entrain large volumes of air from the surrounding environment. In the oven, this can increase the flow of heat to areas of the mold thereby increasing the wall thickness of the molded part.

16. Thermal pins

Thermal pins can be used to direct heat into difficult areas on a mold. These can be passive designs that utilize pipes or tubes (all-thread) with fins attached to them to increase heat flow. The fins attract heat and concentrate it down the pin to the attachment point.

17. Insulated or shielded panels

Heat can be excluded from areas of the mold by using several methods like:

- Metal grids to break up airflow to the mold surface;
- Insulated blankets with glass or ceramic wool encased in a sheet metal box next to the mold surface to reduce heat flow;
- Woven ceramic or glass fabric attached to the mold surface; and
- Teflon™ sheet (usually on the inside surface of the mold).

Care should be taken as insulated mold surfaces will not expand as much during heating as surrounding surfaces—this can lead to distortion and cracking of the mold.

18.4.3 Mold Release Systems

During molding, the plastic part is formed at the inner surface of the mold. The interface between the plastic and the mold is critical as this will have an impact on part size, finish, and ease of removal from the mold. A mold release system is used primarily to prevent plastic from sticking to the mold surface. There are a number of types available, falling into three main categories:

1. Non-permanent

These are soaps, stearates, or silicones that are either dusted or wiped onto the mold almost every time a part is made. They can also be added by dry-blending with the plastic powder or compounded directly into the material.

2. Semi-permanent

These are principally siloxane and silazane polymer compounds that bond to the surface of the mold, providing release for a number of moldings before needing to be reapplied. These compounds are supplied in solvent and water-based formulations—they are the most common form of release agent used.

3. Permanent

These are fluoropolymers (such as Teflon™) or high temperature paint coatings that are bonded to the mold surface before molding takes place. The surface must be shot blasted, the coating material sprayed on, and then the mold baked to cure the finish in place. These coatings provide a uniform release surface that can have a high gloss or matt finish.

The choice of the type of mold release to use is most often based on cost, ease of use, and the ability to control part size. Part design may also affect this decision as simple rounded shapes are ideally suited to permanent coatings. Permanent coatings can last for many molding cycles before needing to be replaced (up to 30,000, although between 5,000 and 10,000 may be more common), but cannot be repaired in production. Semi-permanent release agents offer the ability to vary the degree of release in a mold during production.

18.5 Machinery for Rotational Molding

The rotomolding process consists of three principal stages:

1. Heating a rotating mold
2. Cooling a rotating mold
3. Servicing the mold

The basic rotational molding machine must be able to satisfy these three stages of the rotomolding process (typically simultaneously) while providing controlled rotation of the molds being used.

There are a number of methods of heating that have been used including the following:

- Forced hot-air convection
- Direct (open) flame heating
- Molten salt spray
- Hot oil heating—direct conduction
- Infrared heating
- Electrical heating
- Microwaves

The heat transfer method selected must be engineered to promote uniform temperatures within the mold-residence area to ensure that the mold heats up evenly so that even distribution of material occurs inside the mold.

The primary goals of the cooling stage are to:

- uniformly cool the material within the mold;
- control the rate of cooling to produce good part properties and dimensional stability; and
- reduce the mold and part temperature to a safe handling temperature.

Cooling is normally carried out in a separate chamber although single station machines can sometimes combine both heating and cooling in a single chamber.

Coolers are commonly equipped with water sprays, cooling fans, and exhaust fans to remove the heat from the area. Water spray is generally a very fine mist to envelop the molds to maintain uniform cooling throughout the mold-residence area in the cooler. Large water droplets tend to agglomerate at different areas of the molds promoting uneven cooling and creating stresses in the molded parts that can cause warping or uneven shrinkage. Large water droplets can also enter the mold and cause water spots or streaks in the molded part.

18.5.1 Rotation Mechanisms

During the heating and cooling stages, the molds must be rotated to ensure that even material distribution takes place on the inside surface and that material does not sag when molten. The raw material begins as a pool of powder or liquid that remains at the bottom of the mold under the force of gravity. The speed of rotation must be fast enough to allow all inner surfaces of the mold to pass through the pool during the fusion phase of the process. The required ratio of rotation between the horizontal axis and the vertical axis is a function of part shape and size. The ratio must be such that all inner surfaces of the mold pass through the pool of raw material to create the desired wall-thickness characteristics in combination with heat transferred through the mold wall—a ratio of 4:1 is the most common starting point for many shapes.

Rotation can be accomplished by two principal means:

1. Biaxial rotation: Biaxial rotation is created by simultaneously turning the mold 360° in both the horizontal (major) and the vertical (minor) axis. The mold is mounted on an arm assembly that is geared to allow rotation on both axes.
2. Rock and roll rotation: Rock and roll rotation is accomplished by continuously rotating the minor

axis 360° while tilting the major axis back and forth at least 45° in two directions. The major or horizontal axis is the "rock"; the minor or vertical axis is the "roll." The speed of the roll is variable to help the flow of the material, and the speed and frequency of the rock is variable to assure the desired wall thickness distribution.

The most common form of molding is using biaxial rotation and there are two styles of arms commonly used for creating this motion: straight and offset (dropped) arms.

1. Straight arm: This configuration allows two molds or spiders (a framed group) of molds to be mounted directly opposite each other on either side of the central concentric shafts. This can allow a large number of small parts to be mounted simultaneously within the two rotating volumes as shown in Figure 18.15.
2. Offset (dropped or cranked) arm: The arm is offset (dropped) to allow a larger mold to be mounted on the machine. The main arm (horizontal axis) is rotated and power to the minor rotation (vertical axis) is transferred via a set of gears and chain drive through the arm. Figure 18.16 shows a typical offset arm arrangement.

18.5.2 Machine Styles

There are a number of different styles of machines that are commonly used in rotational molding including the following:

- Open-flame rock and roll
- Rocking oven
- Shuttle
- Clamshell
- Vertical oven
- Carousel
- Oil-jacketed molds

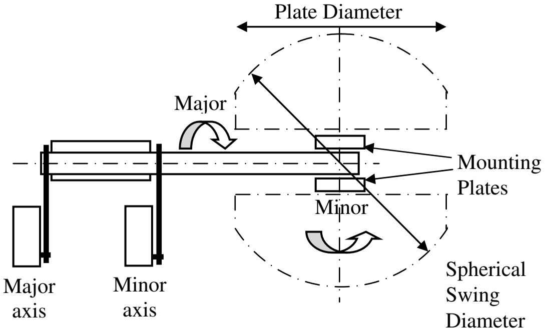

Figure 18.15 Straight arm configuration showing spatial volume available for two mold spiders.

Figure 18.16 Typical offset (dropped) arm arrangement. *(Courtesy Ferry Industries Inc.)*

Each style may be suited to different sizes of parts and different volumes of production. Simple open-flame machines offer the lowest entry cost to the process while single station shuttle machines and clamshells offer efficient use of limited space. Rock and roll machines dominate water tank production and large shuttle machines are common for the more extreme sizes of tanks produced. As production demands increase, multiple arm shuttles become more useful and offer flexibility in terms of multiple molds-in process.

However, with three functional stages to the rotomolding process, the most efficient machines for the majority of small to moderate size applications will consist of three stations to allow all three phases of the process to be performed simultaneously: oven station, cooler station, and servicing station.

Generally, the three stations are arranged in a circular pattern with three mold-carrying arms indexing from station to station around a common center-point. This style of machine is called a "Carousel style" because it operates similarly to carousels at amusement parks. It is also referred to as a "turret" machine—Figure 18.17 shows a typical layout in production.

The three-arm, carousel-style machine has one mold-carrying arm for each of the oven, cooling, and servicing stations. Modern machines provide for independent programming of the process variables for each of the arms on the machine. Molds that are mounted together on an individual arm must have compatible cycle times, temperatures, cooling rates, rotation speeds, etc. However, this compatibility need not extend from arm to arm. Products with different oven processes, cooling processes, and servicing requirements may be run on a common machine by varying

Figure 18.17 Three-arm turret machine showing oven (1), cooler (2) and servicing (3) stations. *(Courtesy Ferry Industries Inc.)*

oven temperature, cooling rates, rotation speeds, etc., for the individual arms; however, differences in cycle times may affect production throughput.

Different configurations of turret machine are used to accommodate longer cooling or oven cycles. A four-arm, four-station layout is shown Figure 18.18. The additional station is used to allow the cooling cycle to be extended—this is useful, for example, for thick parts or parts which are foamed.

Another configuration of the carousel-style machine is the "independent-arm" configuration. The independent-arm configuration allows more flexibility in the molding process by allowing each arm to index to the next station while not disturbing the position or process stage of the other arms. This configuration typically has five stations consisting of one oven, one intermediate station (or wait station), one cooler, and two servicing areas, and can be equipped with three or four arms. Figure 18.19(a) shows a three-arm, five-station layout while Figure 18.19(b) shows the same configuration with four arms.

Arms on an "independent machine" are not, of course, truly independent; the station ahead of the current station must be free in order for an arm to advance.

The latest innovation for machinery in rotational molding is that of full automation. Figure 18.20 shows a single station machine produced by Persico SpA in Italy, which uses hot

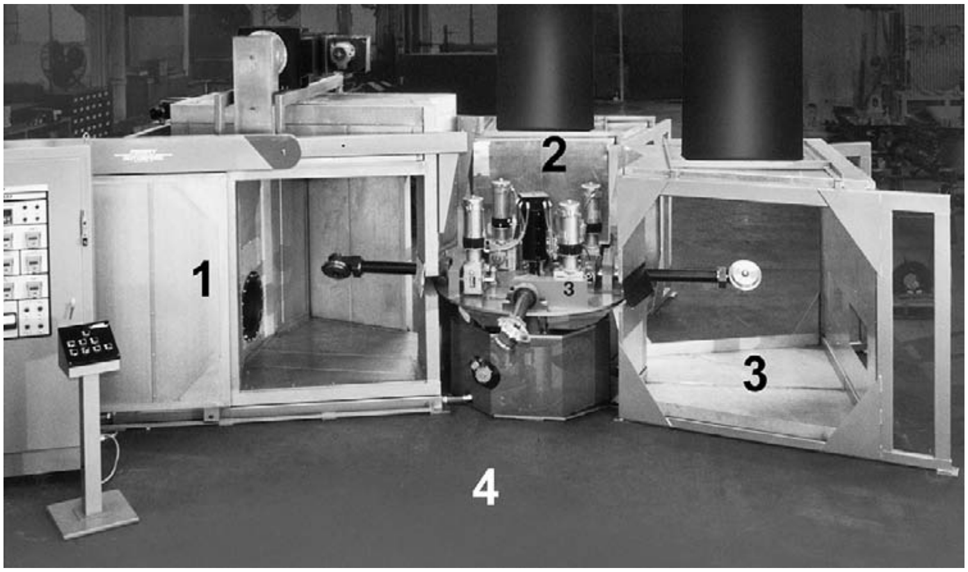

Figure 18.18 Four-arm turret machine showing oven (1), cooler A (2), cooler B (3) and servicing (4) stations. *(Courtesy Ferry Industries Inc.)*

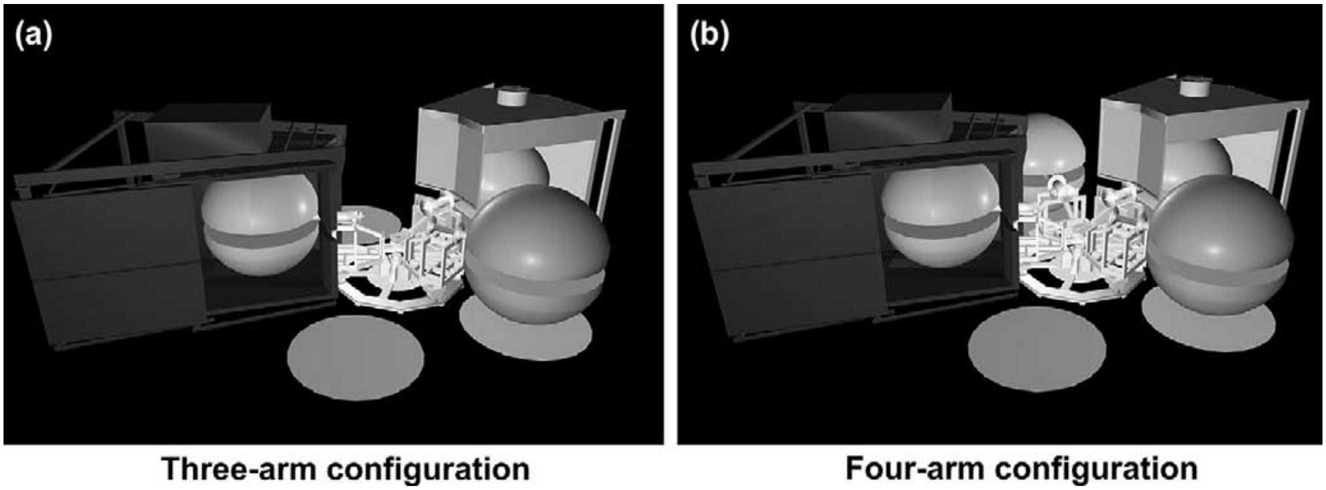

Figure 18.19 Independent arm machine layouts. *(Courtesy Ferry Industries Inc.)*

and cold oil directed through channels in the mold to melt and cool the material inside. By directing heat only to the mold surface, features which cannot be used in the harsh environment of a traditional rotational molding machine can be used, including ejector pins, automated venting, and lifting pins. All functions such as material delivery and part extraction can be fully automated.

18.5.3 Process Control

Traditional process control for rotational molding has used oven temperature and time and cooling time with air and/or water times as the principal parameters with no direct control of the events taking place within the mold. This changed in the early 1990s with the introduction of Rotolog and direct temperature measurements within the mold. Figure 18.21 shows typical temperature data measured during a molding cycle for polyethylene. In this case, two thermocouples were used; one measuring the external environment to which the mold was exposed and the second measuring the internal temperature of the mold (the enclosed inner air volume).

Examining the external temperature profile first, at the beginning of the process both the internal and external temperatures are similar. As the mold progresses into the oven, the temperature of the environment rises rapidly. The profile and rate of recovery of the oven temperature are dependent upon the size and performance of the oven burner and the design of the oven itself. The environment temperature settles around the set point of the oven. Variation in the temperature during this stage of the cycle is due to the rapid movement of air in the oven and the rotation of the mold past the hot-air inlet. Once the oven cycle is over, the environment temperature drops rapidly to the temperature of the cooling bay. Temperatures in the cooler are dictated by ambient conditions and any special cooling system employed. For

Figure 18.20 Fully automatic rotational molding machine. *(Courtesy Persico SpA)*

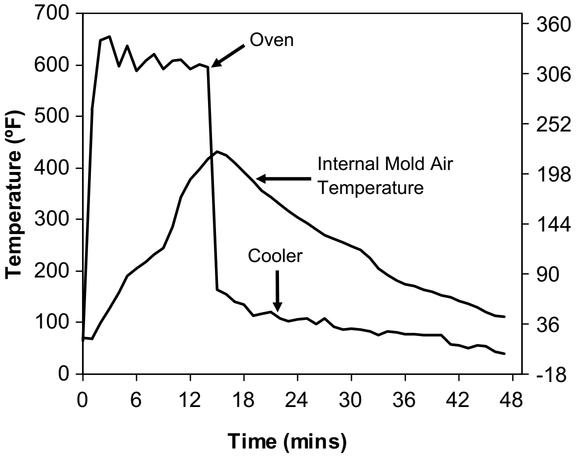

Figure 18.21 External and internal temperature profiles during a typical molding cycle for a polyethylene part.

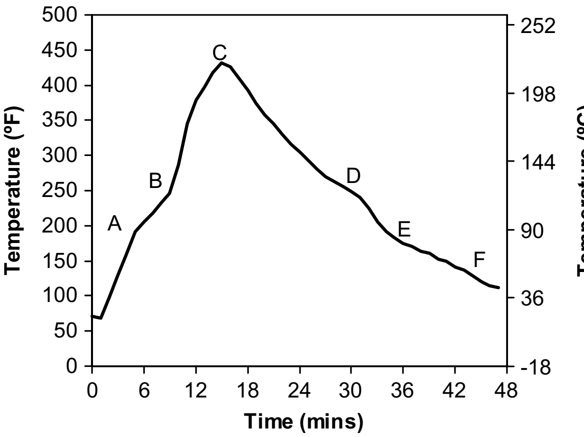

Figure 18.22 Internal air temperature profile during a typical molding cycle for a polyethylene part.

enclosed coolers, heat radiating from the mold can raise the surrounding temperature initially—this falls over a period of time as fans and/or water are used to cool the mold.

Looking at the internal air temperature profile in more detail as shown in Figure 18.22, a number of consistent transition points can be observed for polyethylene during molding.

Key points in the molding cycle:

A. Powder begins to adhere to the mold surface.
B. Powder has completely adhered to the mold surface.
C. Peak internal temperature that can be related to part properties.
D. Crystallization of polymer.
E. Part separates from the mold surface.
F. De-molding point for solidified part.

At the start of the process, the material and air inside the mold are at ambient conditions dictated by the residual heat left in the mold from the previous cycle and the temperature of the material as it is placed in the mold. As rotation and heating begin, energy is transferred through the mold and into the air and material masses within the mold. The material does not stick immediately but flows as a powder until the material mass and the mold surface are sufficiently hot to allow smaller particles in the material to begin sticking to the surface. This occurs at Point A.

As heating continues between Points A and B, material fuses to the mold in successive layers. The absorption of energy by the melting process (as material is converted from a powder to a solid molten mass) causes the rate of increase in temperature of the internal air to slow down, thus producing a plateau. At the end of this plateau when all the material has adhered to the mold surface, energy is once again transferred directly to the internal air and the temperature rises again more rapidly.

Heating continues until Point C. This peak temperature can be related to the final properties of the final molded part; the ultimate degree of "cure" or "cook" can be related to the peak internal temperature observed within the mold during the cycle. This peak will occur sometime after the part leaves the oven depending upon the "thermal inertia" in the mold and part wall thickness. Increases of 30–40 °F (16–22°C) or more into the early stages of cooling are not uncommon for thick parts.

As cooling of the mold commences, the temperature of the part inside falls. The rate of temperature drop of the air inside the mold lags the external surface temperature of the mold. This rate is dominated by the cooling method employed (typically fan cooling only during the early stages of the cooling cycle) and the ambient conditions (cooling in summer can be dramatically slower than in winter).

Cooling continues until the material reaches crystallization. At this time, energy released during the formation of a crystalline structure maintains the temperature within the part producing a second plateau similar to the melting plateau found during the heating stage of the cycle. This occurs at Point D.

Beyond the crystallization point, cooling continues using water and/or air until the part is safe to handle. Recent work has shown how temperature changes in this region can be related to separation of the part from the mold surface due to shrinkage, which can be observed through changes in slope of the temperature profile—Point E.

The characteristic shape of this curve is consistent for almost all polyethylene parts, only the relative times and temperatures at which the transitions occur will change, depending upon mold material, part material density, part thickness, and size.

For other materials, the characteristic shape of the internal temperature profile is similar but will vary according to the melting temperature of the material. Amorphous materials such as polycarbonate do not exhibit a crystallization plateau during cooling.

Rotolog™ is a radio-frequency-based temperature measuring system that is an ideal tool for diagnosing cycles and problems during molding. A number of similar systems have been developed recently (some of which can be used for extended periods through the use of cooling blocks inside the electronics or via slip-rings through the arm of the machine) and the message of direct process control has been spreading.

Another approach using non-contact infra-red data collection called IRT (Ferry Industries, Inc.) has also been developed, which enables the machine to directly map the surface temperature across the molds being used and convert this information into control data without the need to encumber operators with electronics and cables.

18.6 Design for Rotational Molding

As with any plastic process, one must understand the basic part requirements and the process being used to manufacture the part in order to have a successful design. There have been relatively few publications on the design of rotationally molded parts despite the fact that rotational molding offers considerable design freedom with generally fewer restrictions than other processes. It can produce both open and closed shapes ranging in size from 1 to 2″ (25−50 mm) in diameter to 20 ft (6 m) long × 7 ft (2.2 m) diameter tanks. Parts can range from simple shapes such as balls and containers to complex fuel tanks and machine housings. These can vary in thickness from 1/16″ (1.6 mm) to 2″ (50 mm) and, within the limits of mold/powder volume, the part wall thickness can be varied using the same mold. Single wall or double wall parts for insulating properties can be produced. And parts can be colored or transparent, flexible, or stiff.

The decision to use rotational molding over other processes is usually dictated by the following:

1. Material

Rotational molding has a limited number of common materials that are relatively straightforward to mold—polyethylene, nylon, polycarbonate, and PVC are the most common. Specifying a material will usually depend upon strength requirements, how rigid or flexible it needs to be (surface properties), operating temperature, color, and UV requirements. Other materials may require special handling or processing controls.

2. Number of parts

Rotational molding is ideally suited for small runs but can be justified for runs of up to 50,000−100,000 parts per year. Beyond this (depending on part size and form), a more automated process may be a better alternative. However, if rotational molding is the only process suitable, high volumes can be achieved by using multiple molds and machines (e.g., the toy industry). Throughput rates for rotational molding must be considered as they are lower than for blow-molding or injection molding. This means that multiple tools might be required, narrowing the gap for justification.

3. Complexity of shape

The complexity of shapes that can be produced by rotational molding is almost unlimited. It offers the potential to convert complex metal parts consisting of multiple sections into single parts. Fuel tanks for vehicles are an excellent example of how traditional parts which require many steps to form can be converted to a single molding operation, resulting not only in cost savings but also in a better design with fewer operations to monitor and fewer connections that can potentially fail.

4. Size

Large parts are typically the domain of rotational molding although the capabilities of injection molding, blow-molding, and thermoforming are constantly increasing in size and thickness. Large tanks between 500 and 20,000 gallons (1,890−75,000 l) are eminently suited to rotational molding, but other processes are increasing their capability in terms of volume. Parts the size of trashcans are now commonly produced by injection and blow-molding where volumes justify the investment in tooling and equipment. However, parts required in relatively low quantities are often more easily justified for rotational molding due to the lower cost of tooling vs. other processes.

There are many aspects to the design of rotationally molded parts. This chapter will take a look at the fundamental areas of wall thickness, draft angles, tolerances/shrinkage, and warpage/flatness.

18.6.1 Wall Thickness

Rotational molding has the advantage that the wall thickness can be varied after the mold is made, however, it is best to have a nominal wall thickness in mind when the part is being designed. Parts are formed against the outer surface of the part (inner surface of the mold) without cores that allows wall thickness to be varied easily. Similar changes in other processes would mean substantial mold modifications. However, it should be remembered that thicker parts tend to shrink more than thinner parts and may therefore cause fit problems. Also, thicker parts will require longer oven and cooling cycles.

The distribution of wall thickness is affected by heat transfer rates, the ratio and rates of rotation of the mold, mold wall thickness and material, powder characteristics, and release agent. The major factors are heat transfer and ratio of rotation. Maintaining a uniform wall thickness is very important as it aids in uniform cooling rates and reduces the possibility of warpage. Despite the fact that the internal surface of the part is free-formed in rotational molding, the distribution of material within a molded part will generally be quite uniform. Wall thickness variation is normally quoted at ±20% for most commercial applications. However, careful adjustment of the mold and molding parameters can achieve ±10% (with a possible corresponding increase in costs). When specifying wall thickness on a rotationally molded part, it is best to set a nominal wall thickness along with a minimum thickness. Also, the part weight should be specified with a tolerance since it controls the wall thickness. Figure 18.23 shows how external corners (E) attract more material and are thicker than internal corners (I). Away from corners, wall thicknesses will generally be more uniform except at the center of large flat surfaces where parts tend to be thinner.

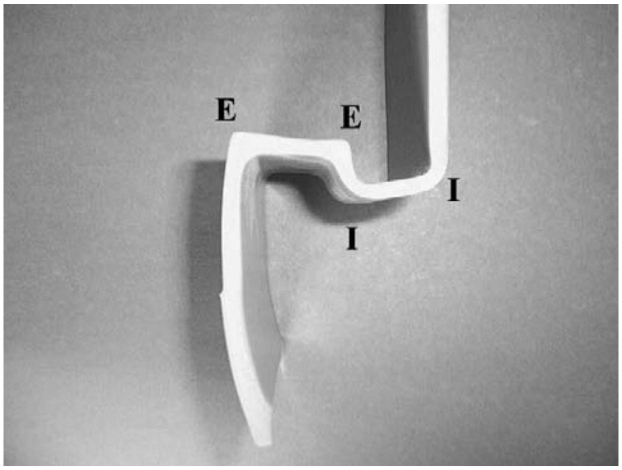

Figure 18.23 Cross-section of molded part comparing build-up of material at internal (I) and external (E) corners.

Variation of wall thickness has a direct impact on the way in which rotationally molded parts are dimensioned. Since the wall section may vary and in many cases cannot accurately be predicted before a part is made, the part must be dimensioned to an external feature. If an internal dimension is required, then allowances for the upper tolerance of wall thickness variation must be made. Designers used to specifying injection molded parts with controlled surfaces both inside and outside of the part can find this difficult to deal with. However, extrusion blow-molding and twin sheet thermoforming share the same limitations and rotational molding actually maintains more uniform wall thicknesses than either one of these competitive processes.

Typical molded parts have wall thicknesses in the range of 0.0625″ (1.6 mm) to 0.5″ (12.5 mm). Parts as thin as 0.020″ (0.5 mm) have been produced for aircraft applications but require special controls; thicknesses up to 2″ (50 mm) can be found in large tank applications.

Liquid systems such as PVC can be produced in very thin layers by controlling the rotation of the mold—parts as thin as 0.010″ (0.25 mm) can be produced. The typical range of thicknesses is 0.0625″ (1.6 mm) to 3/8″ (10 mm).

Controlling the flow of heat to a particular area can deliberately induce variations in the wall thickness of a part. This can be achieved by utilizing shielding material (wire mesh) or insulation (ceramic or glass wool) on the outside of the mold to slow down heat transfer, or by increasing heat transfer by preheating of the mold or by the use of airflow amplifiers. Painting of the outer surface of the mold either black or silver can also help attract or deflect heat in specific areas.

18.6.2 Draft Angles

It is possible to produce parts with zero draft in rotational molding as the material shrinks away from the mold wall during cooling. However, in most cases it is best to have draft on a part to help in removal from the mold. For a large hollow part, draft may not be needed on the outside surface, but if one degree of draft will not affect the function of the part, then draft should be used.

The actual angle will depend on the material being used. Materials with high shrink levels (crystalline) such as polyethylene and nylon will move away from the cavity much more than low shrink-level materials (amorphous) such as polycarbonate. Also, materials such as nylon and polycarbonate are much more rigid than polyethylene and therefore require more draft to allow easy removal. Table 18.1 lists recommended draft angles for a range of materials. For recesses or holes, 3° draft is the minimum and 5° is better.

Figure 18.24 shows a detail that is shrinking onto a mold core instead of moving away from it; greater draft angles are needed to allow the part to be removed from the mold. The forces generated by plastic as it shrinks onto cores can be quite significant. In general, the use of larger draft angles is recommended.

Adding surface texture and other features to a mold may influence the de-molding process and require a larger draft angle. A common rule of thumb for texture is that one additional degree of draft is required for each 0.001″ (0.025 mm) of textured depth.

Table 18.1 Recommended draft angles per side for various materials

Material	Outside Surfaces		Inside Surfaces	
	Minimum	Better	Minimum	Better
Polyethylene	0°	1°	1°	2°
PVC	0°	1.5°	1°	3°
Nylon	1°	1.5°	1.5°	3°
Polycarbonate	1.5°	2°	2°	4°

Source: Glenn Beall (1998)

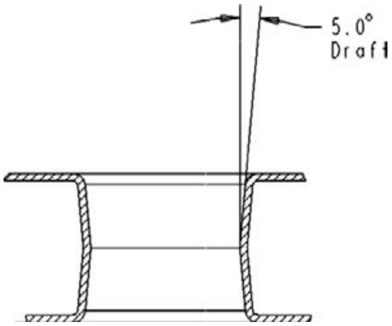

Figure 18.24 Core cross-section showing increased draft.

18.6.3 Tolerances and Shrinkage

Tolerances for rotationally molded parts are generally given as a percentage of the dimensions or an inch per inch value (cm per cm). The designer should endeavor to use the broadest tolerance possible that can be tolerated by the final application. Overspecifying tolerances inevitably leads to higher costs and rework of molds or parts.

Two design variables have a major effect on final part dimensions. The first is the quality and accuracy of the pattern; this is often minimized by the use of CNC machined patterns or CNC machined molds. The second variable is the shrinkage value that is used for making a pattern. Determining this value requires an understanding of the material being used, the size and thickness of the part, the complexity of the part design, and the effect of processing variables.

It can be difficult to anticipate the actual part shrinkage as variables in the molding process such as color, wall thickness distribution, release agent, and cooling cycles can vary. Large parts typically have greater amounts of shrinkage and will therefore be more difficult to hold to close tolerances than small parts. Thicker parts will also vary more due to higher levels of shrink than thinner parts. The best approach is to use shrinkage data gathered for similar-shaped parts using similar parameters. Note that the inside surface of rotationally molded parts are free-formed and should not have dimensions with tolerances applied to them.

Crystalline materials such as polyethylene and nylon will shrink most and will also be susceptible to variations in the molding cycle. Amorphous materials such as polycarbonate and PVC are able to withstand cycle variations with lower variation in part dimensions. The design of the part can be critical in determining how a part will shrink during cooling. Cores, changes in geometry, and any feature that restricts the free shrinkage of the part will distort it to some extent. Recommended free-shrink and restricted shrink tolerances are given in Table 18.2 for a range of common materials.

Adding reinforcement to materials will affect the shrinkage of parts. Fibers or glass spheres can significantly reduce shrinkage (down to around 0.5% for polyethylene). Higher draft angles (up to 7−8°) are also recommended.

18.6.4 Warpage and Flatness

Large flat surfaces are a major problem in rotationally molded parts as they tend to distort during cooling due to

Table 18.2 Recommended shrinkage tolerances

Material	Standard	Free-Shrink (in/in or cm/cm)	Restricted Shrink (in/in or cm/cm)
Polyethylene	Ideal	0.020	0.015
	Commercial	0.010	0.008
	Precision	0.005	0.004
PVC	Ideal	0.025	0.015
	Commercial	0.020	0.010
	Precision	0.010	0.005
Nylon	Ideal	0.010	0.008
	Commercial	0.006	0.005
	Precision	0.004	0.003
Polycarbonate	Ideal	0.008	0.005
	Commercial	0.005	0.003
	Precision	0.003	0.002

Ideal tolerance = minimum care required.
Commercial tolerance = possible with reasonable care.
Precision tolerance = possible with difficulty and added cost.
Source: Glenn Beall (1998)

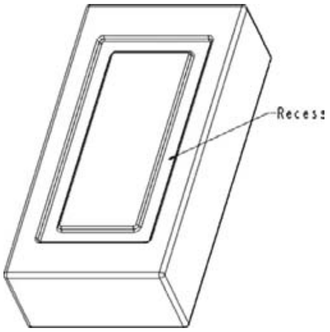

Figure 18.25 Recessed panel used to offset warpage.

uneven wall thickness and uncontrolled release. The problem is most apparent in highly crystalline materials such as polyethylene. If possible, flat surfaces should be broken up with additional design details such as that shown in Figure 18.25.

Creating steps or recesses within a large flat surface reduces the part distortion by both reinforcing the surface and distracting the eye. When large flat surfaces must be used, a slight crown of around 0.015 in/in (0.015 cm/cm) can be added to the surface. A crown helps to keep the surface from oil canning and minimizes distortion. Smooth or polished surfaces will exacerbate distortion while a heavy texture or the use of "stone-effect" materials will improve the cosmetic appearance of a flat surface even if it is slightly distorted. The use of internal pressurization can also help control part distortion by forcing the part against the mold during cooling.

As with general-size tolerances, the tolerance that should be applied to the flatness of a part will be dependent upon the material used, the size and thickness of the part, and the complexity of the part design. Control of the cooling cycle is also critical. Guidelines for the flatness tolerances are given in Table 18.3 for a range of common materials. Note that stiffer materials such as nylon and polycarbonate are less prone to distortion than materials such as polyethylene.

Table 18.3 Recommended flatness tolerances

Material	Standard	Flatness Tolerance (in/in or cm/cm)
Polyethylene	Ideal	0.050
	Commercial	0.020
	Precision	0.010
PVC	Ideal	0.050
	Commercial	0.020
	Precision	0.010
Nylon	Ideal	0.010
	Commercial	0.005
	Precision	0.003
Polycarbonate	Ideal	0.010
	Commercial	0.005
	Precision	0.003

Ideal tolerance = minimum care required.
Commercial tolerance = possible with reasonable care.
Precision tolerance = possible with difficulty and added cost.
Source: Glenn Beall (1998)

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[1] P.J. Nugent, Rotational Molding: A Practical Guide, Reading, Pennsylvania, October 2001.

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19 Thermoforming

Jim Throne, Consultant
Dunedin, FL 34698, USA

19.1 Introduction

Thermoforming is a generic term that refers to a process that begins with an extruded sheet of plastic. The process involves heating the plastic sheet to a temperature range where it is soft or malleable. The sheet is then stretched against a cool single-sided mold. When the sheet has cooled to the point where it retains the shape of the mold, it is removed and the excess plastic is trimmed from the formed product.

Thermoforming represents a group of sheet-forming processes that includes vacuum forming, drape forming, billow of free bubble forming, mechanical bending, matched mold forming, billet molding, pressure forming, and twin-sheet forming.

Thermoforming is one of the oldest methods of forming useful articles. Beginning in the 1870s, thin sheets of cellulose nitrate were fitted into metal molds and heated with steam [1]. The molds were quenched in water and the formed shapes were removed and trimmed to shape. Products included baby rattles, mirror cases, and sharps piano keys.

By the 1930s, thermoformed products included bottles by Fernplas Corporation, relief maps by US Coast and Geodectic Survey, and cigarette tips using an automatic thin-sheet thermoformer made by Klaus B. Strauch Company. World War II saw a rapid increase in thick-gauge cast acrylic thermoformed products for aircraft gun enclosures and windscreens. After the war, cast acrylic was used to produce bathtubs by Troman Brothers of the UK and cellulose acetate was introduced in rigid packaging.

19.2 Thermoforming Characteristics

The thermoforming process is usually segmented into thin-gauge and thick-gauge markets. Thin-gauge markets tend toward disposable products such as rigid packaging. Thick-gauge markets tend toward permanent or industrial products.

If the beginning sheet is less than about 1.5 mm in thickness, it is called thin-gauge sheet. It is usually extruded in roll form, with the rolls being 1 to 1.5 m in diameter. The rolls may weigh as much as 1800 kg and may contain as much as 3000 m of sheet. The sheet is fed continuously into thermoformers that are often called roll-fed thermoformers.

If the beginning sheet is greater than about 3 mm in thickness, it is called thick-gauge sheet. It is usually extruded and cut or guillotined into discrete pieces that are stacked on pallets. These pieces are then fed, either manually or automatically, into thermoformers that are called cut-sheet machines.

Sheets having a thickness between 1.5 and 3 mm are often too expensive to be used for disposable products and too thin to be used in structural applications. There is a growing market, however, in this mid-gauge sheet in certain under-the-hood automotive applications and in large-volume, deep-draw drink cups.

It is estimated that the 2007 North American thermoforming market was about 2700 million kilograms with an estimated value of about US $13,000 million. Approximately 20% of this market was “industrial products,” or products that have structural characteristics [2]. The top five industrial product markets are transportation, recreation, electrical/electronic, medical, and storage and dunnage. In 2007, in North America, there were about 250 thick-gauge companies, running 2800 machines, and employing 14,000 people.

Approximately 80% of the North American market was thin-gauge “disposable products.” Rigid packaging represents more than two-thirds of all thermoformed products and includes blister packs, point-of-purchase containers, meat and poultry trays, hot and cold drink cups, convertible-oven food serving trays, medicinal unit dose containers, egg cartons, and rigid form-fill-and-seal containers for everything from foodstuffs to hardware supplies. In 2007, in North America, there were about 500 thin-gauge companies, operating 700 plants, running 5000 machines, and employing 35,000 people [3].

Therefore, in 2007, there were about 750 companies, operating about 1000 plants, and employing nearly 40,000 people in the North American thermoforming industry. It is estimated that the European thermoforming industry is about 60% of the North American industry. Recent estimates put the South American industry at about 20%, China and Southeast Asia at about 40%, India at about 20%, and the rest of the world at about 20% of the North American industry. From this, it is estimated that the 2007 worldwide thermoforming market was about 7000 million kilograms, with a rough estimated market value of about US $30,000 million.

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19.3 Thermoformed Product Characteristics

Thermoforming is a low-temperature, low-pressure process in which the sheet is handled as a rubbery solid or elastic liquid. Molds are usually single-surfaced. Mold materials are relatively inexpensive and are often fabricated in relatively short times. Thick-gauge thermoforming produces a limited number of products at production costs below those produced by other processes such as injection molding. Thin-gauge thermoforming produces millions of products at production costs below those produced by other processes. Thin-gauge products traditionally have surface area-to-thickness ratios as large as 100,000:1. No other process can produce similar results.

In contrast to these advantages, thermoforming has several disadvantages. The incoming material is an extruded sheet, with the extrusion process adding 50% or more to the cost of the formed product. Thermoforming generates substantially more trim than other processes and that trim must be ground and re-extruded at additional cost.

Thermoforming is a differential stretching process, meaning that as the sheet is stretched, only that portion of the sheet that is free of the mold is stretched. As a result, the wall thickness of the formed product is nonuniform (Figure 19.1) [1]. Although some improvement in wall thickness is achieved by mechanical or pneumatic stretching of the hot sheet prior to pulling it against the mold surface, wall thickness tolerance is typically 10−20%. Because local areas of formed products are designed to minimum critical thickness, many portions of the formed products contain more plastic than necessary to meet the design criteria. Regarding product surface quality, only one side of the product contacts and replicates the mold surface. As noted, the thermoformed sheet is in a rubbery solid or nearly solid state when it is stretched at relatively low-pressures. Nearly all applications use unfilled or unreinforced sheet. Because the sheet is usually stretched in its solid, rubbery elastic state, the thermoformed products are under substantial residual stress. As a result, substantial distortion can occur if formed products are subsequently heated to near-forming temperatures. This is discussed later.

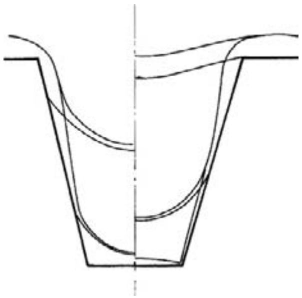

Figure 19.1 Variation in wall thickness for simple vacuum forming into a female or negative cavity.

19.4 The Thermoforming Concept

As noted, thermoforming begins with an extruded sheet of plastic. If the sheet is discrete, it is fixtured on all four edges in a clamp frame. If it is in roll form, it is clamped along its two continuous edges. The clamped sheet is fed into an oven where it is heated until pliable and at a pre-selected forming temperature range. The hot sheet is then moved to a forming press where it is stretched onto or into the cool shaping mold. The formed product and the plastic surrounding it are cooled until removed from the mold without distortion. The product is mechanically trimmed from the plastic surrounding it. The product is inspected, and stacked or crated. The trim is reground and the regrind is mixed with virgin plastic to be extruded into sheet. Each of these steps will be considered in detail below.

The forming step is the most complex part of the process. The earliest and simplest forming operations are drape forming and vacuum forming. In drape forming (Figure 19.2), the hot plastic sheet is draped over a male or positive mold. Vacuum may be used to pull the sheet tight against the mold surface. In vacuum forming (Figure 19.3), the plastic sheet is clamped against the rim of a female or negative mold. Vacuum is used to pull the sheet into the mold cavity (see Figure 19.1 also). Another rather simple forming operation is billow forming. The hot clamped plastic sheet is inflated with air pressure. The height of the bubble is

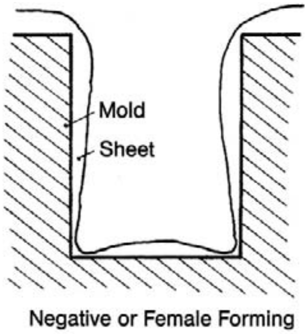

Figure 19.2 Vacuum forming into a female or negative cavity.

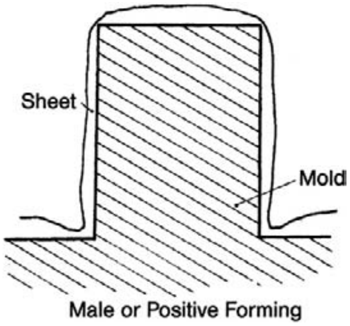

Figure 19.3 Drape forming onto a male or positive mold.

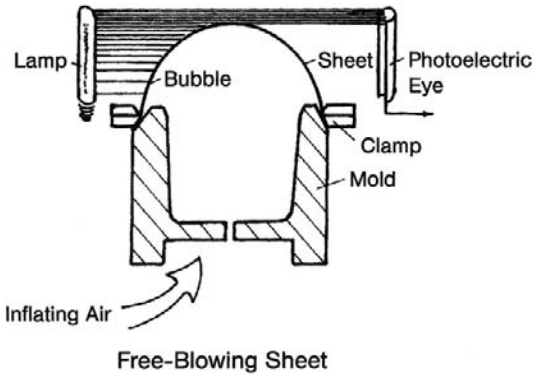

Figure 19.4 Freely blown bubble.

controlled by the air pressure and cooling fans that act to rigidify the bubble. The inflation process is often controlled with photoelectric eyes (Figure 19.4).

As noted earlier, thermoformed products have nonuniform wall thickness. To achieve more uniform product wall thickness, two general prestretching methods are used in the industry. Pneumatic prestretching is used with thick-gauge sheet [5]. As shown in Figure 19.5, the hot sheet is drawn by vacuum into an empty box called a draw box. The male or positive mold is lowered into the bubble and vacuum is applied, pulling the sheet against the mold. Mechanical prestretching or plug assist is used with both thin- and thick-gauge sheets. As shown in Figure 19.6, a solid element called a plug is pressed into the hot sheet, stretching it toward the bottom of the female or the negative mold. When the expected extent of prestretching has been achieved, vacuum is applied between the mold and the stretched sheet and often air pressure is applied between the plug and the stretched sheet. This presses the sheet against the mold surface.

In all forms of thermoforming, hot sheet is pressed against the mold surface by applying greater air pressure on one side of the sheet than on the other. Vacuum forming, for example, applies up to one atmosphere differential pressure or 0.1 MPa across the sheet. In pressure forming, somewhat of a misnomer, differential pressures to 1 MPa are often used to press the plastic sheet against the mold surface. Pressure forming is used in thick-gauge sheet forming when the sheet at its forming temperature is too stiff to replicate the mold surface. This is particularly the case when very sharp radii and highly textured product surfaces are required. Pressure forming is used in thin-gauge sheet forming to reduce cooling cycle times by rapidly pushing the sheet from the plug and pressing it hard against a cold mold surface. It is also used to fabricate filled or reinforced plastic products.

Matched molds are used when both surfaces of the sheet must replicate the mold or when the hot sheet is too stiff to stretch into the mold (Figure 19.7). Low-density foam sheet cannot be heated to the forming temperature of the unfoamed plastic without extensive cell collapse. As a result, foam is matched-mold-formed at pressures of about 0.3 MPa. As mentioned, thick-gauge filled and reinforced plastics are often matched-mold-formed. Filled plastics and short-glass fiber-reinforced plastics are formed at pressures of about 1 MPa. Long- and continuous-glass fiber-reinforced plastics and carbon-fiber-reinforced plastics are often formed at near-compression moulding pressures of up to about 10 MPa.

Thick-gauge twin-sheet forming is being developed to compete with products that are manufactured using rotational and blow molding. Typical applications include pallets and recreational products. Depending on the nature of the plastic, the two halves of the product can be separately thermoformed and welded together with heat or solvents. In Europe, twin-sheet-formed products are formed by simultaneously heating two sheets of plastic in a single clamp frame (Figure 19.8). When the sheets are at forming temperature, air is forced between the sheets, pressing them against molds and the press is closed to form the peripheral pinch-off.

In North America, thick-gauge twin-sheet-formed products are formed in sequential fashion on rotary thermoforming presses. The first sheet is heated and formed into the lower mold. The second sheet is heated and formed into the upper mold. Then the press closes to form the peripheral pinch-off (Figure 19.9). Thin-gauge twin-sheet forming has

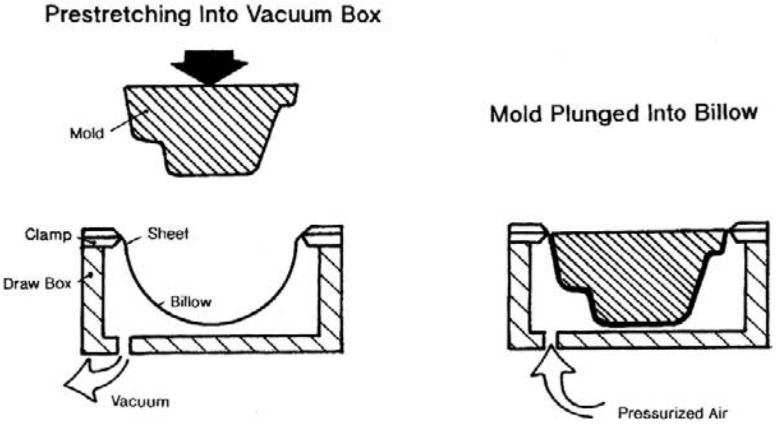

Figure 19.5 Vacuum draw box with male or positive mold.

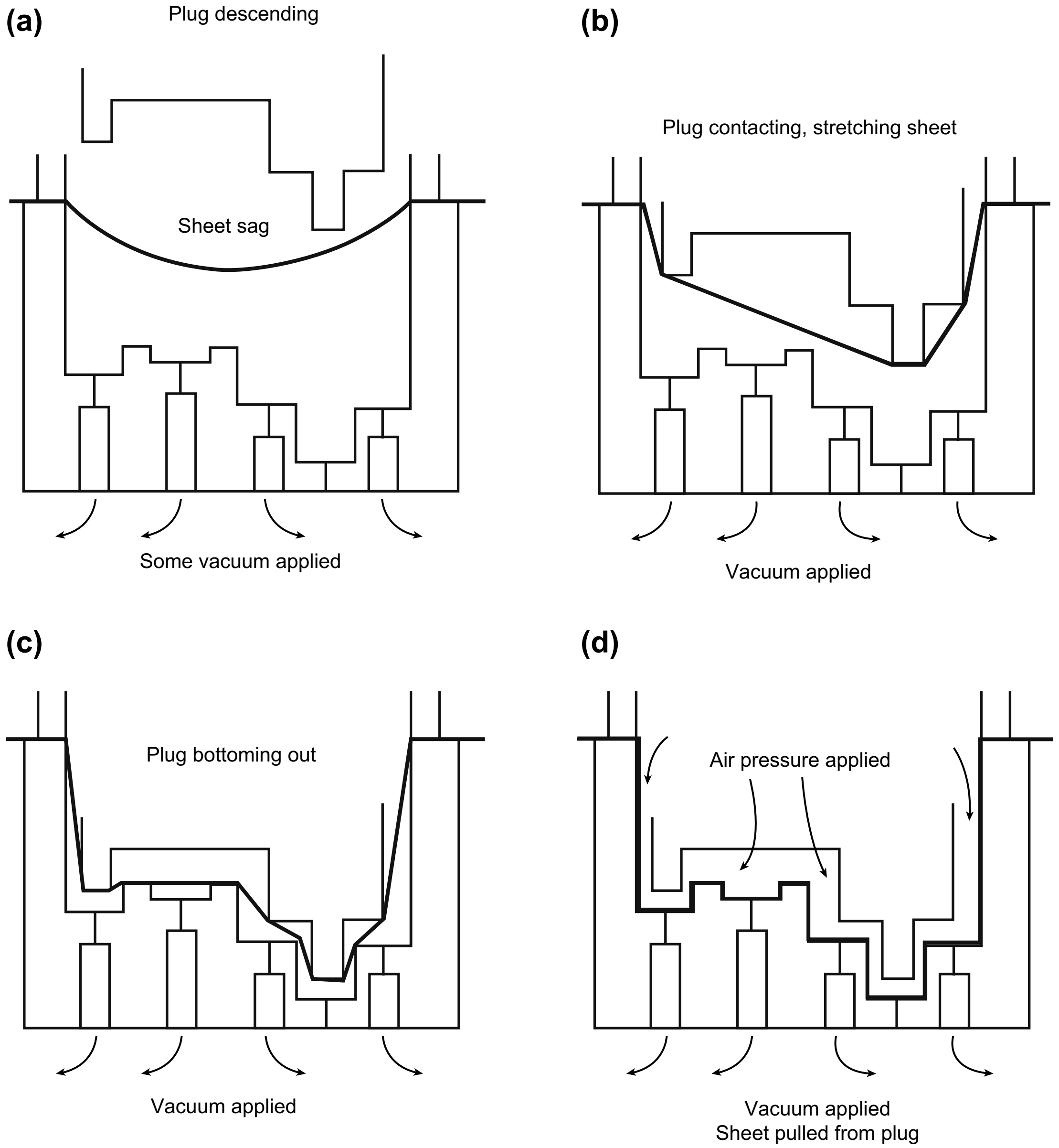

Figure 19.6 Plug assist sheet formed into a female or negative cavity.

been used to produce lightweight bottles, medical room devices, and air bladders in running shoes.

Contact forming is restricted to roll-fed thin sheet. The sheet to be heated is brought in contact with a heated plate by vacuum. When the sheet reaches its forming temperature, which is the same temperature as the heated plate, the plate and sheet are pressed against the female or negative mold. A combination of vacuum and air pressure pushes the sheet from the plate to the cool mold cavity (Figure 19.10). When the sheet is cool, the mold drops away and the sheet moves to a trimming fixture.

Often, contact forming is used as the first part of a process known as rigid form-fill-and-seal or RFFS (Figure 19.11). The formed products are conveyed with the trim-in-place through a filling operation, a sealing operation, and a trimming operation, where the products are removed from the trim. RFFS is used extensively in the manufacture of pharmaceutical unit dose packages and foodstuff unit servings.

Mechanical heating and bending of plastic sheet is also a thermoforming process. It was used extensively by crafters in the 1920s to produce household products from picture frames to bud vases. Today it is used in combination with computer-aided high-speed multiaxis routers. The routers cut the flat sheet into several pieces, some of which are line-bent into angles. The pieces are then solvent-welded or glued into functional products that may represent early design prototypes of the final product. Often, this method is used to produce a few to perhaps a dozen finished products to meet the customer's needs.

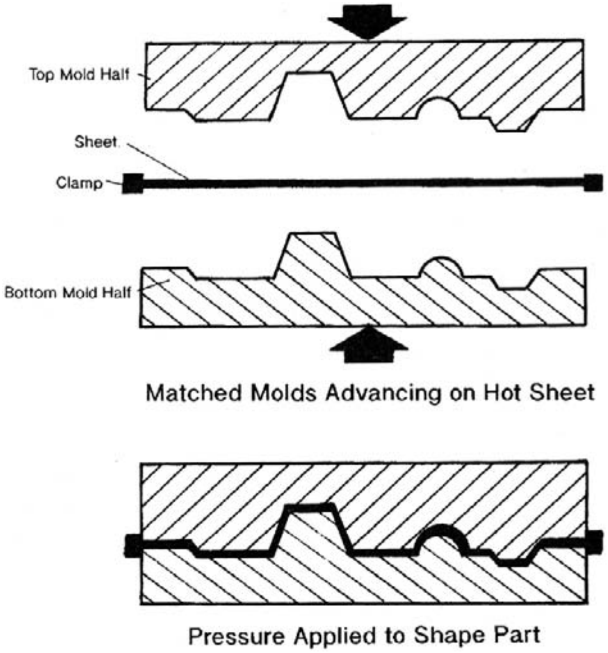

Figure 19.7 Matched-mold thermoforming.

19.5 Thermoforming Machinery

Nearly all thermoforming machines have the following elements:

- Sheet-handling system
- Method of rigidly clamping sheet
- Oven(s)
- Forming press
- Pneumatic or mechanical prestretching (optional)
- Load/unload elements
- Vacuum box
- Pressurization system (optional)
- Condition monitors and process control

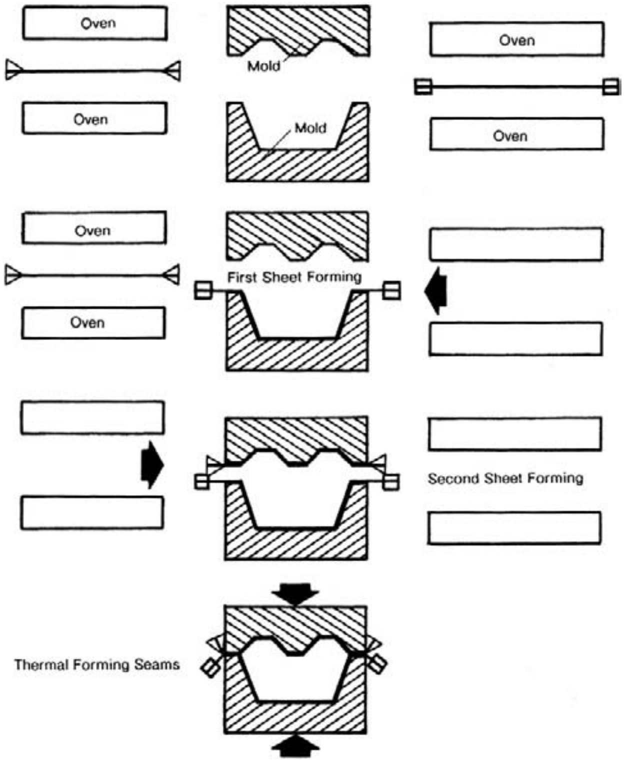

Figure 19.9 Sequential twin-sheet production sequence.

- Safety elements
- Method of trimming the product from the web

As noted, there are two general categories of machinery: thin-gauge or roll-fed thermoformers and thick-gauge or cut sheet thermoformers.

19.6 Thin-Gauge Thermoforming

19.6.1 Machinery

A typical thin-gauge thermoformer is shown in Figure 19.12. The roll is placed on a roll stand that usually

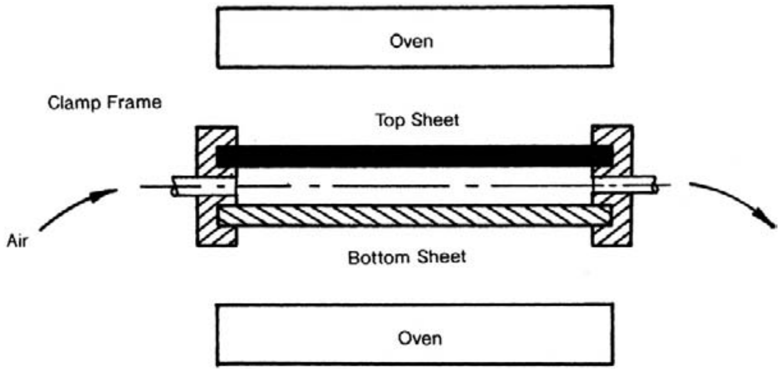

Figure 19.8 Simultaneous twin-sheet production.

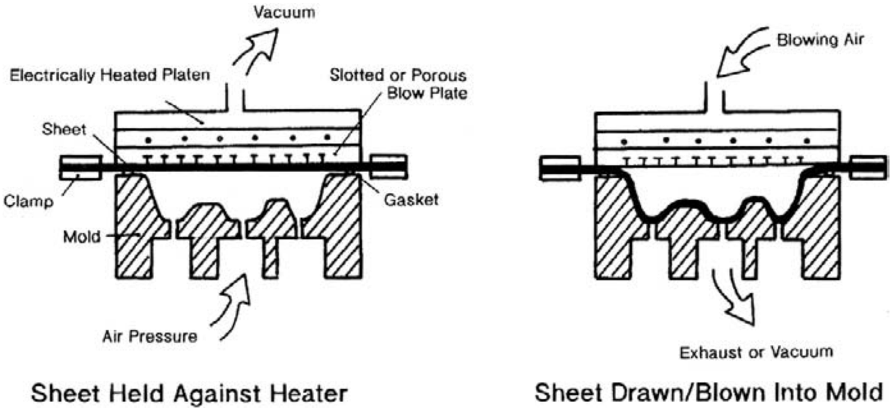

Figure 19.10 Trapped-sheet, contact heat forming.

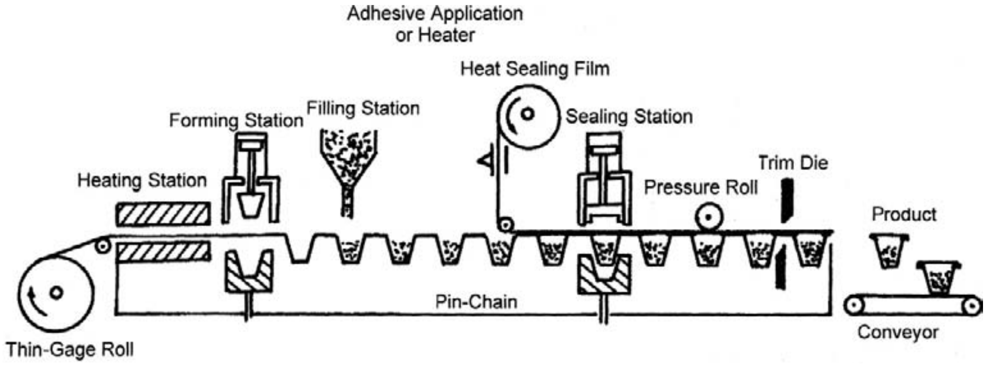

Figure 19.11 Rigid form-fill-and-seal (RFSS) schematic.

has passive breaking or a roll speed governor to prevent uncontrolled unspooling. It may also be equipped with an end-of-roll alarm and rapid roll changeover capabilities.

The sheet is fed into the machine where it engages pins that are spaced along the lengths of parallel or near-parallel, continuous cycle-link chains. The pin-chains convey the impaled sheet through the machine. The pin-chains are usually shielded from oven heat and are outside the edges of the mold in the forming press. The pin-chains may be lubricated but are often designed to run dry for medical and food product applications. The pins are held vertically by guides. For certain plastics such as polystyrene, brittle chips may be vacuumed prior to the sheet reaching the oven and forming stations. In-feed non-stick or non-scratch engagement shoes are used to position the sheet prior to engaging the pin-chains. Many machines are equipped with automatic chain adjustment, allowing the pin-chains to diverge slightly in the heating and forming portions of the machine. The sheet is advanced through the machine in a start-stop fashion with the total time of each advance being seconds. The pin-chains are servo-driven so that the sheet moves smoothly through acceleration, deceleration, and constant speed during indexing.

19.6.2 Oven

In thin-gauge thermoforming, many products are molded at once. Forming cycles are determined by the time a “shot” or portion of the continuous sheet resides in the forming press. One important criterion is temperature uniformity across the sheet. To achieve this, most thin-gauge thermoforming machines have modular sandwich ovens that allow more than one shot to reside in the oven. For many plastics such as polypropylene, a preheating oven that consists of a series of up-and-down roller-driven loops is recommended. The preheating oven is placed between the takeoff-stand and the in-feed pin-chain rail to the thermoformer. Energy consumption is a major expense in all forms of thermoforming. As a result, all oven modules are often thoroughly insulated and the sides usually come to within 25 mm of the machine framework that holds the pin-chain rails. Baffles are often used between oven modules and usually between the last oven module and the press frame. The types of heaters used in thin-gauge thermoforming ovens are discussed below.

Modern ovens have means of changing both the top and bottom sheet-to-heater gaps. Whenever the chain travel is interrupted, the ovens are quickly and automatically

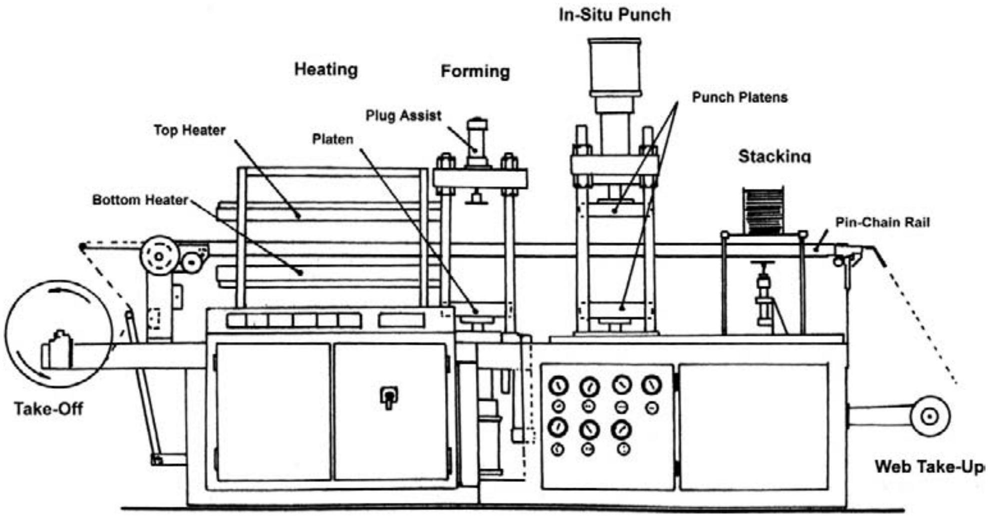

Figure 19.12 Thin-gauge roll-fed thermoformer (Kiefel).

retracted, either horizontally or by flying open in clamshell fashion. Rapid disconnects are used for individual or bank heater elements and for thermocouples. Insulated infrared temperature measuring devices are usually inserted through top and bottom oven wall surfaces. Sag bands are either low-friction coated rods or continuous wires that index with the pin-chains. They are parallel to and between the pin-chain rails and minimize sag on very wide sheet. Because all shots in the oven and forming press are contiguous, each shot is exited from the oven to the forming press based on clock time rather than sheet temperature. Some sheet temperature control is achieved by adding highly responsive heaters at the oven segment closest to the forming press.

19.6.3 Forming Press

The heated sheet temperature may fall 10 °C or more between the time it exits the last oven section and the time the forming press closes on it. The forming press is a machine with many functions. The press can be closed and clamped pneumatically, with servo-mechanical linkages, or electrically. Platen locking devices and pneumatic bladders are used when high forming air pressure is needed. Platen screws are usually self-lubricating, continuously lubricated, or unlubricated if the press is used to produce medical, pharmaceutical, or food containers. Clean-room thermoforming requires that thermoforming machines be all electrical with unlubricated sliding elements and self-leveling platens. If products are to be trimmed while on the mold face, provisions must be made for protecting, sliding, and locking elements from trim detritus.

In addition to providing sufficient space for the mold, the press must include space for a pressure box and other elements such as plug assist plates, cavity isolator plates, trim-in-place die plates, and ejector-ring plates. Water and vacuum lines should be properly located and should be easy to disconnect. Programmable logic controls or PLCs are needed for adjustment of all rate-dependent ancillary features such as plug assist, cavity isolator, pressure box, and trim-in-place sequence. Many newer machines are equipped with computer controls that provide for rapid set-up after mold changeover. The press platens must allow easy mold removal and installation.

As noted, thin-gauge thermoformed products, particularly deeply drawn products, often require cavity isolators, plug assist, and pressure forming [6]. Plug travel is usually adjustable and each plug is often easily adjusted and replaced. For certain plastics, the plugs may need to be internally heated. As a result, the electrical leads must be easily connected and disconnected. Plug shape and plug material are discussed below.

19.6.4 Trimming

There are three general methods for trimming products from the sheet:

- In-place trimming, where the trim die resides on the mold and is activated once the products have been formed (Figure 19.13).
- In-machine trimming, where the sheet containing the formed products is indexed to a trimming press located on the machine frame (Figure 19.12).
- In-line trimming, where the sheet containing the formed products is indexed completely from the trim machine to a separate trim press (Figure 19.14).

With the first two methods, the trim die is notched to allow the products to remain attached to the sheet until it is moved to the product removal station. Products are usually directly punched from the sheet to a collection table in in-line trimming.

In-place trimming is most effective with thin sheet (<1 mm) and narrow sheet. The advantages of in-place

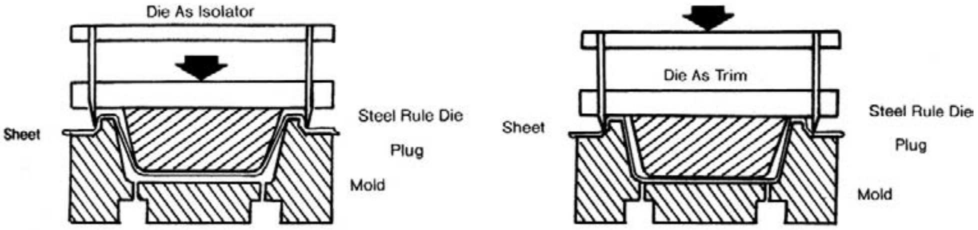

Figure 19.13 Thin-gauge trim-in-place mold and trim die assembly.

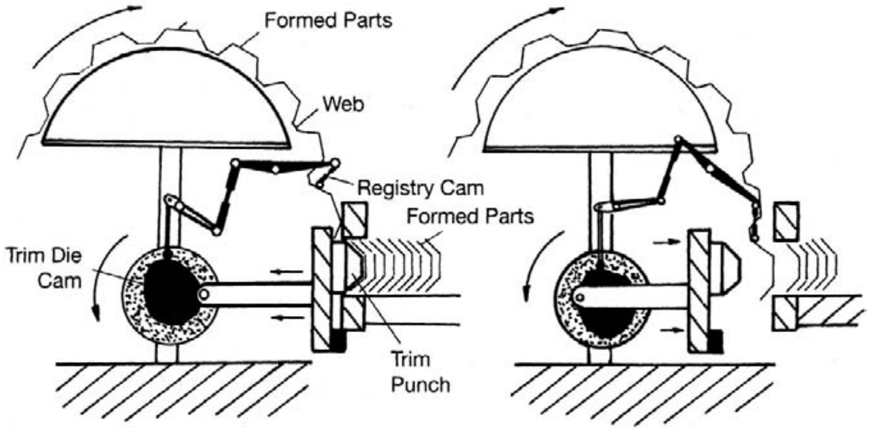

Figure 19.14 Canopy in-line thin-gauge trimming press with cam-operated punch-and-die trim.

trimming are that the trim die acts as a cavity isolator, the formed products remain in the mold cavity and are therefore in perfect registry, the plastic is soft and, as a result, the trim forces are low, and there is often less trim dust. The trim die is usually a hardened steel rule that is rigidly mounted in a plate that is integral to the mold structure.

The disadvantages of in-place trimming include the following:

- Higher mold cost.
- Difficulties in determining the quality of the trim die edge.
- Problems in aligning the trim die with the mold.
- Increased on-mold time to allow for the trimming to complete.
- The real possibility that a product may separate from the trim, remain in the mold cavity, and interfere with forming the next product.

In-machine trimming is also most effective with thin, narrow sheet. As with in-place trimming, sheet thickness is ~1 mm or less and the trim die is usually hardened steel rule. Often the sheet containing the products is usually fixtured and trimmed downstream of the forming press. Although the products may be tabbed or notched before moving to a stacking operation, the stacker may be part of the entire in-machine trimming station. Because the forming and trimming stations are separate, the mold cost is lower than that for in-place trimming, and there is greater versatility in adjusting the trim to achieve registry. In-machine trim presses are easier to inspect and maintain and trim dies are easier to inspect than in in-place trimming. However, in-machine trim presses may take longer to set-up and align than in-place trimmers. Product warp and shrink can lead to inaccuracy in trim lines. If the product trim line is critical, the products are often fixtured during trim press action.

There are two general types of in-line trim presses [7]. The canopy trim press (Figure 19.14) is more common. The sheet containing the formed products is directed from the pin-chain rails of the forming machine into the trim press via locating and registering elements. The sheet is indexed vertically between the punch and die, with the products seated in the punch pockets. The horizontal reciprocating die engages the sheet, squeezing the trim area between it and the punch rim. The products are completely cut from the trim and are pressed through the punch cavity onto a nearly horizontal collection table. The collected products are nested, automatically counted, and packed.

Typically, products are collected on the press side away from the reciprocating die. To locate, seat, and trim deeply drawn products such as drink cups, the products must be presented to the press with the products pointing up. This means that either the products are formed in the up position in the forming press or the sheet containing the formed products must be rotated 180 degrees between the thermoformer and the trim station.

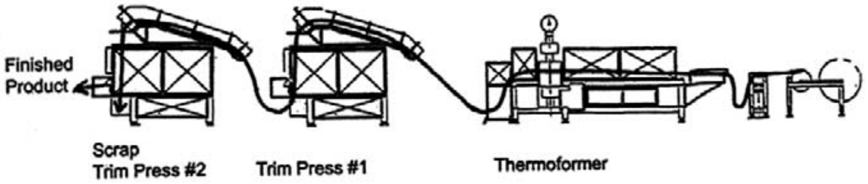

Figure 19.15 Tandem thin-gauge trim presses where first press punches holes and slots and second press separates product from web.

Canopy machines are difficult to set-up. Typically, only a single row of products is cut at a time. As a result, the trim press cycles is far shorter than that of the thermoformer, meaning that frequent maintenance and punch and die interference alignment are often required.

Flatbed presses horizontally accept the sheet containing the products. The products nest in the punches on the lower platen. The dies vertically reciprocate into the punch, completely trimming the products from the trim. The products are collected from below the lower platen. The vertical flatbed press is easier to set-up and maintain than the horizontal canopy press. It can also trim more than one row of products, although stacking and collection can be more complicated.

Products such as point-of-purchase and berry box rigid containers often require multiple punch steps. The first punch forms holes or slots in the product. The second punch separates the product from the trim. Although multiple punches can be accomplished on a single trim press, there is always a concern about the first punch trim-out causing problems with the second punch. As a result, tandem trim presses are usually used (Figure 19.15). Set-up and alignment of two presses often take substantially more time than the set-up time of the thermoforming forming press.

Figure 19.15 shows one method of web take-up. The roll is replaced when the spool has reached a specific diameter. For longer production runs, the web or trim is guillotined either at the end of the thermoformer or at the end of the in-line trim press. The trim strips are either collected and baled or are fed directly to a grinder/chipper for shipment to the extruder.

19.7 Thick-Gauge Thermoforming

19.7.1 Machinery

As noted, both thin-gauge and thick-gauge thermoforming machines have essentially the same functional elements. There are two general types of thick-gauge machines—shuttle presses and rotary presses. Shuttle machines are very versatile and are capable of forming very large products (Figure 19.16). As a result, they represent about 70% of the total number of machines. Shuttle presses are economically inefficient because one set of products is fabricated for every two cycles of the machines. Rotary presses, such as the three-station (Figure 19.17), are quite energy efficient, but are more expensive than equivalently dimensioned shuttle presses, require more care in setting up, and are typically limited in the size of the product that can be handled in the rotary clamp frame.

As with thin-gauge thermoformers, machine criteria include the following:

- Platen dimensions
- Depth of draw
- General nature of the forming process such as vacuum, pressure, matched mold, plug assist, and twin-sheet capability
- Nature of the motive power for moving the platen and for indexing the clamp frame
- Types of heaters and methods of temperature control
- The overall type of process control

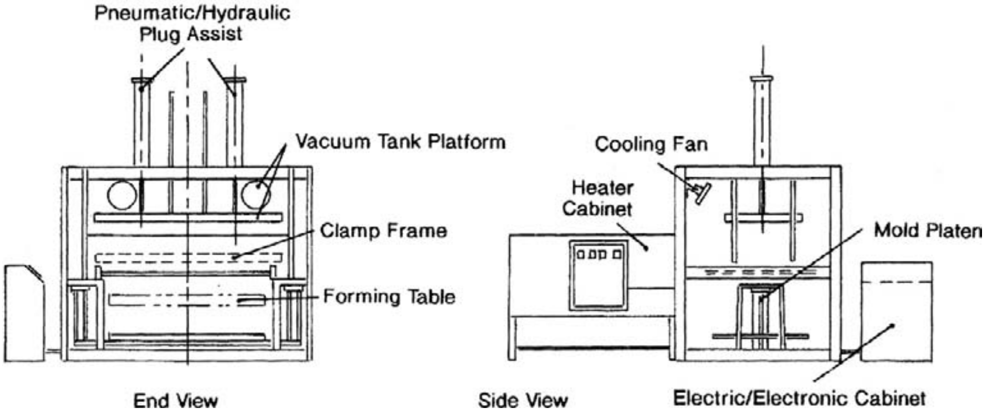

Figure 19.16 Thick-gauge shuttle thermoformer schematic.

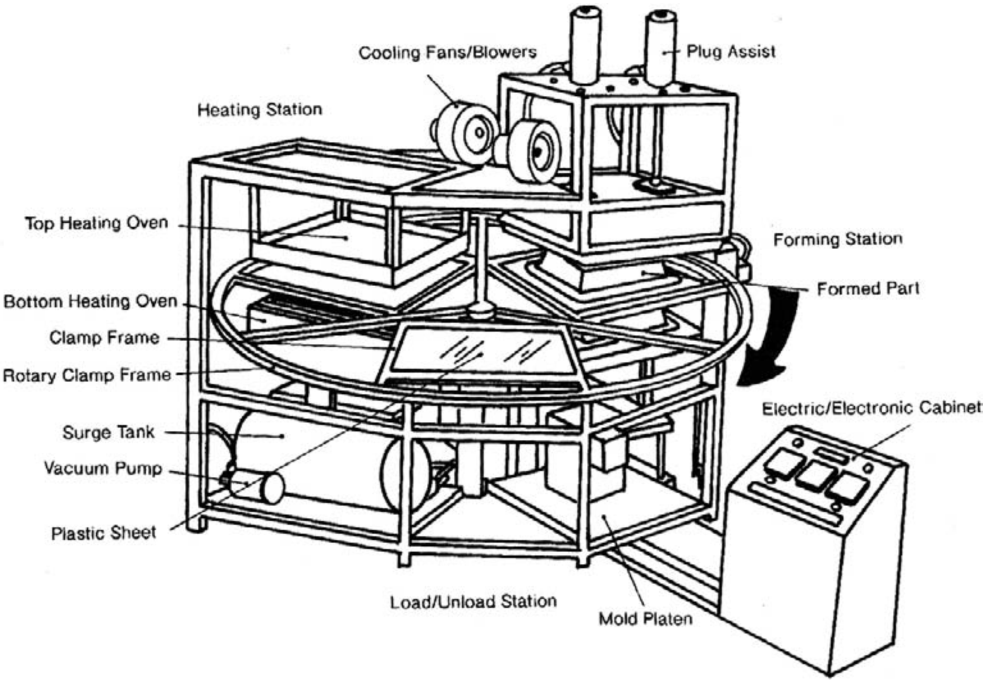

Figure 19.17 Thick-gauge three-station rotary thermoformer schematic.

Other features may include automatic heater-to-oven adjustment, drop-side ovens, vacuum draw box, automatic sheet loading, through-oven temperature monitoring, sag monitoring, and automatic fire suppression.

The shuttle press is the simplest commercial thermoforming machine. The sheet is loaded in a four-sided clamp frame that is shuttled from the load/unload station into the oven (Figure 19.16). When the sheet has reached its forming temperature, it and the clamp frame are shuttled out of the oven to the forming station that also serves as the load/unload station. Depending on the complexity of the process, the sheet may be mechanically or pneumatically prestretched prior to contacting the mold. The mold is usually, but not always, located beneath the heated sheet and the sheet is either lowered onto the mold or the mold is raised onto the sheet. The formed sheet is held against the mold surface until sufficiently cooled. The sheet and its formed products are then separated from the mold, the clamp frame is opened, and the sheet is removed to an off-line trim station.

As noted, when a sheet is being heated, there is no sheet being formed, and when a sheet is being formed, no sheet is being heated. As a result, products are produced only every other cycle. One way to increase shuttle press efficiency is to use two ovens with the load/unload/forming station between them (Figure 19.18). When one sheet is being formed, another is being heated. This technology is also used to produce twin-sheet thermoformed products.

Cabinet shuttle machines are common outside of North America. Instead of the sheet moving into and out of the oven, the sandwich heaters horizontally move across the

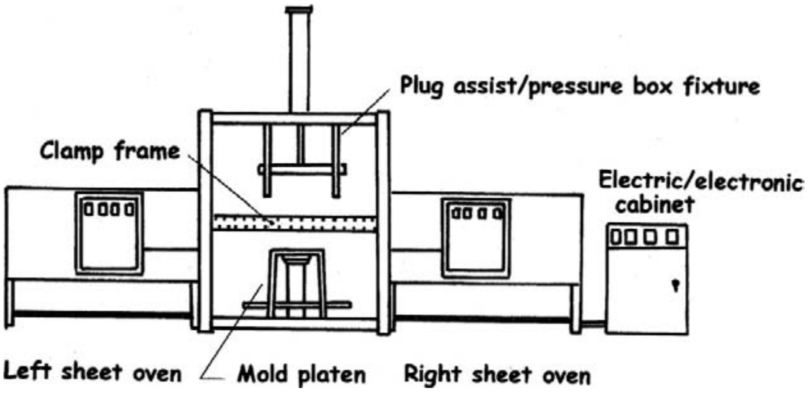

Figure 19.18 Thick-gauge double-oven shuttle thermoformer schematic.

sheet while the sheet remains poised over the mold. When the sheet is at forming temperature, heaters are retracted and the mold is raised onto the sheet to form the product. This technique also allows for plug assist and pressure forming.

The rotary machine is used for long production runs. The heart of the machine is the carrousel and turret that transports the sheet from station to station. The three-station machine (Figure 19.16) consists of a sandwich oven, a forming station, and a load/unload station. For many materials such as high-density polyethylene, the heating station often controls the overall cycle time. As a result, four-station machines are used, with the fourth station being a preheating oven. A second oven is often recommended while heating and forming hygroscopic plastics such as ABS and polymethyl methacrylates. As with the shuttle machines, the sheet is clamped on all edges at the load/unload station. It is indexed into the oven by rotation of the turret. When the sheet has reached its forming temperature, it is indexed to the forming press. When the product is formed and sufficiently cooled, it and its trim are rotated to the load/unload station, where it is removed to the off-line trimmer.

The four-station rotary thermoforming machine is used in North America to produce twin-sheet products. This is accomplished by having two molds in the forming station—one on the lower platen and one on the upper platen. The first sheet is loaded in the rotary clamp frame and indexed into the first oven. When it has reached a predetermined temperature, the second sheet is loaded in the next clamp frame and the two sheets are indexed. The first sheet moves into the second oven and the second into the first oven. When the first sheet has reached forming temperature, it is indexed to the forming press, while the second sheet is indexed into the second oven. The first sheet is vacuum formed into the lower mold where it is held until sufficiently cooled. At that point, the clamp frame is opened and the first sheet is released where it resides on the lower mold. The second sheet at its forming temperature is then indexed into the forming press, where it is vacuum formed into the upper mold. The upper and lower platens are then mated. Air pressure is introduced between the two product halves to ensure their continuing contact with their respective mold surfaces. Often, auxiliary forming bars in the molds are activated, applying pressure to produce a peripheral seal on the two halves of the product. When the product halves are sufficiently cool, the platens separate and the twin-sheet product, still held in the upper sheet clamp frame, is rotated to the load/unload station for removal.

The cut sheet may be manually inserted into the clamp frame of the thick-gauge thermoformer, but vacuum pick-up and placement devices are more common for long production runs. Pneumatic or mechanical tables are used to lift very heavy or large sheets. Pneumatic clamp frame closures are usually used. The closure edges are often toothed or barbed to ensure that the sheet does not extrude from the grips during heating or forming. Of course, all clamp frame elements are designed to withstand high oven temperatures (up to 450 °C) for long cycle times (several minutes) and many cycles (more than 10,000) without sticking, binding, or leaking air or fluids.

The clamp frame must be robust enough to support the largest and heaviest sheet without oscillating or bouncing. The indexing acceleration, constant speed, and deceleration must be smooth without vibration or banging. Most turrets are equipped with a positive stop arrangement to ensure positive positioning of the carrousel at every operating station.

19.7.2 Oven

Energy costs are usually very important economic considerations in thick-gauge thermoforming. Modern ovens are provided with appropriate side baffles or curtains to minimize drafts and optimize energy usage. Heaters are equipped with rapid electrical disconnects and thermocouples. Ovens have provisions for in-oven infrared temperature measuring, and are equipped with photoelectric devices to detect excessive sheet sag. For very large sheets and high sheet sag, oven sidewalls should pneumatically drop when the sheet is ready to be transported out of the oven. Modern machines have provisions for rapid emergency shutdown. Baffles between the sheet and the heaters, high-velocity air blown across the sheet, and carbon dioxide fire suppression means are recommended. More advanced thermoformers may include intermittent vacuum or air lift of the sheet to minimize sag. Heater characteristics are discussed below. Until very recently, sheet exited the oven on time. With advances in process control and infrared temperature monitoring, sheet is frequently exited on temperature.

19.7.3 Forming Press

The modern thick-gauge forming press is robust enough to adequately accommodate the weight of molds on both upper and lower platens. In addition, the machine must be capable of supporting a steel-reinforced pressure box, plug assist plates, and on some machines, trim-in-place, and forged trim dies. Modern machines have two-stage closing sequences that allow smooth acceleration and deceleration of the platens to minimize banging and chatter of molds as they enter the hot sheet. Overhead air and oil lines should be enclosed or self-sealing to minimize oil vapor contamination of the hot sheet. Platen cogs and screws should be enclosed to minimize dirt collection in the flights. The platens should be self-leveling or have easy means for leveling. All vacuum, air pressure, and coolant lines should be equipped with oversized rapid disconnects. When a pressure box is used, the press should have pneumatic interlocks to prevent premature depressurization when the box is pressurized. As the platen size increases, locking bayonet toggles and air bladders are often used during pressure forming.

Mold changeover is often labor intensive. For very large machines, process adjustments may be far above or below floor level. Permanently mounted caged ladders are used for overhead access. Special breathing apparatus is needed for set-up of controls that are more than a meter below grade. If the carrousel is far above the operators' reach, automatic load and unload features are used.

Two prestretching methods are commonly used in thick-gauge thermoforming. Mechanical prestretching uses solid plugs that are driven into the sheet prior to the sheet touching the mold surface. The rate and extent of travel of the plugs are part of the automatic process sequence. The thick-gauge plug shapes and materials are discussed below.

In pneumatic prestretching or bubble stretching, the hot sheet is clamped over a hollow shape that acts as a blow box. The sheet is then inflated with air pressure of up to 70 KPa with the height of the bubble monitored and controlled with a photoelectric eye or a microswitch. For male or positive molds, the sheet is drawn with vacuum into a draw box. The mold is then immersed into the prestretched sheet. Again, the extent of prestretching is monitored and controlled. The shape of the prestretched bubble is determined by the variation in temperature across the sheet surface.

Improvements in thick-gauge process control include advanced programmed logic control and computer-aided control systems that monitor energy usage, index sheet on temperature, and sense sheet sag, pressure box pressure, brownout, power surge, and a myriad of other tasks. In addition to single-point infrared temperature measurement through the oven wall, newer optical devices scan the entire sheet as it exits the oven. The two-dimensional thermal image that is produced is used to adjust individual heater temperatures.

19.7.4 Trimming

Very few thick-gauge products are trimmed from the web in the thermoforming machine. Off-line trimming methods include the following:

- Guillotines of the type used to cut extruded sheet
- Band saws
- Rotary or table saws
- Handheld manual trimmers or routers
- Milling machines or three-axis machines
- Multiaxis routers or five-axis machines
- Robotic trimmers

Guillotines, band saws, table saws, and handheld routers are only used if a few number of products need to be trimmed. Numerically controlled trimmers are used when hundreds or thousands of products need to be trimmed.

In addition to simply removing the product from its trim or web, it is often necessary to drill holes or machine slots, vents, or cutouts in the product. Computer-controlled multiaxis routers, developed first for the metalworking and woodworking industries, have become the workhorses of thick-gauge trimming. The milling machine, standard in metalworking, is a three-axis or XYZ machine. The product is held in a fixture that is moved on a horizontal or XY plane. The milling head is moved vertically on the Z plane. Drilling and milling sequences and tool paths are programmed into the machine computer for each product. Because the milling head is constricted to a single direction, complex trim lines are difficult to achieve without frequent repositioning of the product on the XY plane. Linear cutting speeds are about 2.5 m/min with cutting head speeds of 3000 rpm.

Five-axis machines were developed by the woodworking industry. Again, the product is held in a fixture that moves on the XY plane. The machining head moves in the Z direction but it can also gimbal in two other directions (U, V). [If it gimbals in three other directions (U, V, and W), the machine is called a six-axis machine.] This operation can be demonstrated by rotating one's wrist. These additional degrees of freedom allow the milling cutter to move diagonally or horizontally into the product and even machine underneath an overhanging portion of the product while the product remains affixed to the XY platform. The movement of the multiaxis router is carefully controlled to minimize overshoot and vibration. Five-axis linear cutting speeds are up to 25 m/min and router tip speeds are up to 40,000 rpm.

There are two keys to successful multiaxis routing. The first lies in the fixture holding the product during trimming. Vacuum used to secure the product to the fixture must hold the product rigidly even when holes, slots, and other intrusions are routed and the product is released from the surrounding trim. The second is in cutter design. The cutter surface should separate a small portion of plastic from its surroundings without melting, generating fine dust or fibers, or causing microcracks, and it must clear the cut portion of plastic from the kerf before separating the second piece from its surroundings. Cutters are selected based on the speed of routing and the fracture or softening behavior of the plastic being routed.

Robotic trimmers are similar to the robots used in the transportation industry. They were initially recommended when very heavy, very rigid products needed to be trimmed. The advantage of a robot is its very long arm that extends from a capstan or spindle. The arm has a nearly 360-degree rotation as well as movements above and below the horizontal plane. A very small, high-speed motor is positioned at the end of the arm, with its motion similar to that of the six-axis router. The product is mounted on a turntable and the entire assembly is computer-controlled. As the product is rotated, the arm moves horizontally in and out and vertically up and down. A robotic trimmer usually occupies less floor space and indications are that it requires less maintenance than an equivalent sized multiaxis router. The robot trimming accuracy is not quite as good as that of multiaxis routers.

19.8 Other Thermoforming Technologies

19.8.1 Rigid Form-Fill-and-Seal

As noted earlier, thermoforming is used extensively in rigid form-fill-and-seal packaging for pharmaceuticals and unit servings of foodstuffs. A traditional RFFS operation is shown in Figure 19.18. Typically, sheet in the 0.25–0.5-mm thickness range is continuously pulled from a roll through the entire system from the outfeed end. The sheet is usually heated by direct contact with the heater. It is formed into nesting cavities into which are placed the appropriate products. A film is heat-sealed across the cavities and the sheet containing the filled cavities is trimmed from the web. The film is not adhered to the web and is stripped from it prior to the web being chipped for recycling.

For wide or thicker sheet, a conventional thermoformer is used, with the formed products being carried on the web into the filling, sealing, and trimming stations. Many RFFS machines are built for specific applications. For medical and pharmaceutical dose packaging, the machines are usually constructed of stainless steel with oil-less and greaseless slides. These machines are frequently steam-sterilized. In many RFFS operations, thermoforming is usually a minor part of the process, with the major operational efforts focusing on controlling the dosing and sealing operations.

19.8.2 Wheel Machines

Wheel machines are designed specifically for dedicated products such as picnic plates, dual-ovenable food trays, and take-away coffee lids [8]. The wheel is a horizontal cylinder that contains dozens to hundreds of female or negative molds. The sheet is continuously extruded through the sheet die directly onto the slowly turning wheel. Vacuum pulls the sheet into the cool molds. As the wheel turns, the formed products are cooled. When the products are sufficiently cooled, the sheet containing the products is stripped from the wheel and fed to a conventional in-line trimmer.

19.8.3 Coupled Extrusion and Thermoforming

For dedicated products, the sheet extruder can be directly coupled to the thermoformer (Figure 19.19). Although this extruder-thermoformer combination is used for both thin- and thick-gauge products, its greatest advantage is with the thick-gauge sheet where the sheet does not need to be cooled to room temperature and then reheated to its forming temperature in the thermoformer. Unfortunately, there are major disadvantages with this combination. The cycle time of the thermoformer controls the rate of extrusion. If the thermoformer cycle is interrupted, either the extruder must be stopped or the extruded sheet must be cooled and collected in some fashion. The major issue is usually mismatched capacities. Typically, the throughput of the thermoformer is small and the sheet is wide, meaning that the extruder is usually small and the ideal width of the extrusion die too narrow.

19.8.4 Matched-Mold Forming

There are two types of matched-mold forming. The high rigidity of filled- or fiber-reinforced plastic sheet at the plastic forming temperature often precludes even the use of pressure forming into single-surface molds. Special purpose shuttle machines with forging presses, dual platens, and positive mold lock-ups are designed to squeeze the sheet between matched steel tooling at pressures exceeding 1.4 MPa.

Low-density thermoplastic foam cannot be heated to a forming temperature appropriate for the plastic without excessive cell collapse and poor product quality. Inadequate heating yields low secondary expansion and products that do not replicate the mold cavities with just vacuum. Pressure forming will collapse the foam cell structure. As a result, foam sheet is usually heated in roll-fed machines on traditional pin-chain rails. The ovens are usually extended in length and have heaters that gradually heat the sheet to temperatures where the increasing internal gas pressure in the cells expands the foam to as much as twice its original

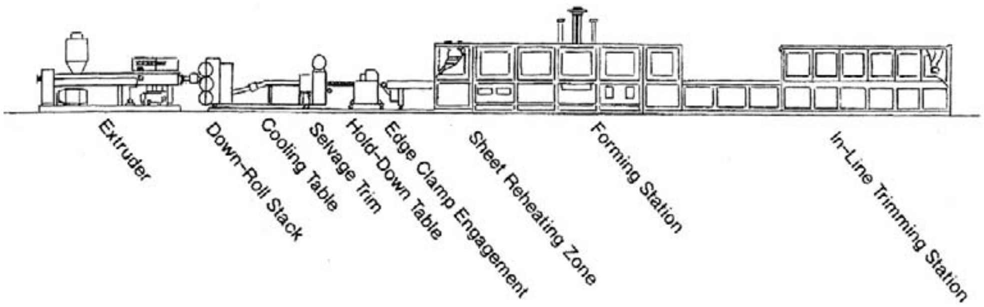

Figure 19.19 Extrusion-thermoforming line, thick-gauge.

thickness. The sheet is then fed into matched tooling in the forming press. Forming pressures rarely exceed 0.34 MPa.

19.9 Heaters

There are three modes of heat transfer in thermoforming. Energy is conducted from the sheet surface to its interior, from the sheet to the mold, and for very thin sheet, by direct contact of the sheet with a heated plate, prior to vacuum forming. Convection is air movement across a solid surface. Very thick sheet is often heated in a large forced hot air convection oven. Thin-gauge preheaters are often forced hot air ovens. Radiant heat is the most common and usually the most efficient way of heating sheets of nearly all thicknesses [9]. Because air surrounds the sheet while it is being radiantly heated and because air is in contact with one sheet surface while the other is contacting plug or mold surface, all three energy transfer modes occur in nearly all forms of thermoforming.

19.10 Electric Rod Heaters

In the early days of thermoforming, the primary heating element was the rod or linear heater, being a solid wire embedded in compacted powdered inorganic oxide, which was centered in a carbon steel sheath. Rod heaters are still used in thermoforming. Because energy is emitted uniformly around the rod, reflectors are used to redirect the energy toward the sheet. Heater technologies continue to evolve. Newer linear heaters include quartz and halogen heaters. The quartz tube heater is a nichrome metal tape or wire that is centered in an evacuated quartz glass tube. Quartz glass is essentially transparent to infrared radiation. When the wire is energized, it emits radiant energy that passes through the glass. The halogen heater is a tungsten tape or wire that is centered in a quartz glass tube that has been filled with a halogen gas. The gas prevents rapid deterioration of tungsten. Quartz tube and halogen heaters must have reflectors to redirect the radiant energy toward the sheet. Metal rod heaters respond very slowly to power input changes. Quartz tube and halogen heaters respond very quickly and are often on-off temperature controlled. Quartz and halogen heaters are quite fragile and the glass is easily etched by off-gassing from the plastic.

19.11 Electric Plate Heaters

Flat heaters direct the radiant energy primarily in the sheet direction. The simplest flat plate heater is a metal plate that is backed with a serpentined nichrome wire that is embedded in magnesium oxide. Temperature control is usually by rheostat or other proportional controller. Ceramic heaters are essentially firebricks or tiles with embedded nichrome wire. The surface is usually a chemically resistant, nonporous glaze. Because these heaters tend to be small in size, they are often clustered or ganged, with one or more of the heaters containing an embedded thermocouple for temperature control. Metal plate heaters use nichrome wire partially embedded in porous ceramic material. The heated wire radiates to the metal plate that is carbon steel, stainless steel, or even aluminum. The plate, that may have a low-friction coating, re-radiates to the sheet surface. The quartz cloth heater is similar in structure, except that the quartz cloth contacts the heated wire surface. Again, quartz is essentially transparent to radiant energy. Metal plate and quartz cloth heaters tend to be large. Flat panel and ceramic heaters are slow to respond to the changes in energy input.

19.12 Gas Combustion Heaters

Gas combustion heaters are often used as preheaters in thick-gauge thermoformers. Natural gas and propane are the preferred gases. There are two general types of combustion heaters. In the direct combustion unit, the radiant energy from a direct flame impinges on the sheet. Because the energy output is so great, the burners are placed at some distance from the sheet or a series of nickel screens are placed between the burners and the sheet. The nickel screens act as re-radiators.

Catalytic gas combustion radiant heaters have generated substantial interest. The combustible air-gas mixture is introduced to the heater directly below a porous bed of catalyst that is similar to the catalyst used in automotive exhaust systems or camper heaters. Combustion and radiation occur at the catalyst surface. Catalytic gas systems are desired for their uniform surface temperature and low operating cost. Lack of temperature modulation is the major problem with gas combustion heaters. The catalytic gas system needs many gas lines and controls as well as an electric heater that must preheat the catalyst bed prior to initiating combustion. As a result, the initial installation cost is very high compared to the all-electric heating systems.

In thermoforming, energy cost is second only to the cost of plastic sheet. The economic factors that are important in selecting the appropriate heater combinations are:

- *Day-to-day running cost.* In North America, natural gas costs are about one-fourth those of electricity.
- *Maintenance cost.* Heater efficiencies, replacement of reflectors, required cleaning, replacement of broken quartz glass heaters, and incomplete gas combustion are some major issues here. Ease of identification of burned-out heaters is also important.
- *Initial installation cost.* Large panel heaters require fewer connections than ceramic heaters. Catalytic gas combustion heaters require electrical and natural

Table 19.1 Infrared heaters

Item	Metal Rod	Ceramic	Quartz Tube	Catalytic Gas
Radiant efficiency	55%	85%	60%	80%
Initial efficiency	Low	Medium	High	High
Maximum temperature	760 °C	760 °C	870 °C	500 °C
Longevity	Long	Medium	Medium/low	Medium
Manufacturing cost	Low	Medium	Medium	High
Installation cost	Low	Medium	Medium	High
Retrofit capability	Excel	Good	Good	Poor
Operating cost	Low/medium	Medium	Medium	Lowest
Power response	Low	Medium	High	Low
Loss of effectiveness	High	Medium	High	Medium/high
Pattern/zone capability	Poor	Excel/good	Excel	Poor
Chemical attack	High	Low	Medium/high	Low
Breakage	Low	Low/medium	Medium/high	Low
Temperature control	Good/poor	Good/excel	Excel	Poor

gas installations and extensive gas control and monitoring.

- *Heater versatility.* A wide temperature range is important if many types of plastics are to be formed. Rapid temperature response is needed if the process requires frequent interruptions. Ease in zoning or patterning the heater output is important if many sizes of sheet are heated or if the product is very complex. Reliability and constant energy output are needed for long production runs.
- *Level of control.* Smaller heaters allow for greater versatility in energy input into the sheet. Very small heaters such as ceramic elements are often ganged together. With advanced computer controls, energy input to individual heaters is feasible. This is particularly useful when dealing with thick-gauge products that are very complex and require very careful local temperature control. However, burned-out heaters can only be detected if each heater has a monitored thermocouple. Slowly-responding heaters are usually proportional-controlled. Rapidly responding heaters are controlled with either simple on-off relays or traditional PID controllers. As thin-gauge thermoformers form many products at once, local temperature control is quite limited. Often auxiliary heaters are located along and inside the pin-chain rails to ensure that the sheet nearest to these elements is heated to the same level as the rest of the sheet. Auxiliary heaters are used at the exit of the last oven as a fine adjustment of the sheet temperature just before the sheet enters the forming press.

Table 19.1 gives comparative ratings of the infrared heaters that are most commonly used in thermoforming.

19.13 Thermoforming Mold Materials

The thermoforming mold is usually single-surfaced. Aluminum is the preferred material for longer production runs for both thin- and thick-gauge thermoformers. The mold serves several purposes and has several requirements:

- It allows the production of the product that meets the customer's all dimensional specifications.
- It provides a dimensionally stable surface against which the hot sheet is pressed.
- It removes heat from the hot sheet in a rapid, reliable, and consistent manner.
- It is a modest pressure vessel.
- As the sheet is pulled against it, it must have means to remove air from the cavity in a controllable fashion.
- It must be robust enough to withstand repeated formings at elevated pressures and temperatures.
- It must resist attacks from gases emitted by the plastics.
- It must resist erosion from filled- or fiber-reinforced plastics.
- It must be dimensionally stable during extended periods of storage.
- It is often a machine with sliding cams and slides.

- It often includes platens that contain cavity isolators, plugs, ejection rings or bars, and trim-in-place dies and anvils.

There are two general categories of molds. Prototype molds are used to produce a few to a hundred products. These molds are generally made of easily worked materials such as plaster, wood, and even paper. Production molds are used for long production runs.

19.14 Production Mold Materials

Very large thick-gauge molds are usually made of atmospheric or foundry cast aluminum. A-360 series aluminum is easy to melt, pour, machine, and weld, and has good corrosion resistance [10]. The mold is usually foundry sand. Properly cast aluminum is relatively free of surface and subsurface pores and locally soft areas. The casting is usually 15−25 mm in thickness and is nearly uniform in thickness. When the casting has cooled, it is deflashed, the risers are machined away, coolant lines are welded or soldered to the back of the casting, vent holes are drilled in, and the positive surfaces are finished. Sand or grit blasting is a common finishing method.

Thin-gauge molds usually contain many cavities. The development of computer-controlled milling machines has allowed the machining of many cavities into a single plate of aluminum. Al 6061 T aluminum is preferred although Al 7075 T, a tougher, higher temperature aluminum, is used for higher temperature plastics such as polycarbonate and for filled and reinforced plastics. Coolant channels are usually gun-bore drilled into molds that are designed for deeply drawn products. For shallow products, a flat cooling plate is mounted between the mold and the vacuum box.

Other mold materials include:

- Prehardened P20 steel, often used for very high temperature plastics, plastics that require very high forming pressure, and fiber-reinforced plastics
- Cold electroformed nickel, used for products that require very high or very fine surface details [11]
- Stainless steel, particularly 304 stainless steel, used for thermoforming corrosive plastics.

19.15 Prototype Mold Materials

There are many occasions when only a few to a few dozen products are needed. Traditional vacuum forming uses low-pressures and relatively low sheet temperatures. As a result, many common materials often serve as thermoforming molds. There are two general types of prototype molds.

Deductive mold materials are removed to form the desired shape. Inductive mold materials are built up to form the desired shape. Hardwoods, fiberboard, and industrial plaster are examples of deductive materials, which under certain circumstances can also be used inductively. Syntactic foam, thermoset plastics, papier mache, and sprayed white metals are normally considered to be inductive materials.

To withstand repeated compression during vacuum forming, the prototype mold material should have a compressive strength of around 25 MPa. Most woods [12] and industrial plasters [13] achieve this strength. Sisal, glass fibers, or hemp is used to reinforce thin plaster molds. Medium-density fiberboard is a pressed wood fiber product that is easily sawed, shaped, and drilled with common woodworking tools. It is somewhat porous, meaning that vacuum can be drawn directly through thin sections without the need of vacuum holes. Syntactic foam is a composite of fly-ash, phenolic, or hollow glass spheres in polyurethane, phenolic, or epoxy resin that may be foamed. Syntactic foams are available in plank or board at densities of 200−800 kg/m^3, and are easily shaped with carbide-tipped cutters and routers. These foams are more expensive than other prototype mold materials and so find greater use as plug materials.

Glass-reinforced epoxy and thermosetting polyesters are also used. These materials have excellent compressive strengths but they are usually restricted to 125 °C continuous use temperatures. Papier mache is very inexpensive, uses readily available materials, is easily shaped and worked, and can be used to produce a few products before deteriorating. An epoxy coating is recommended to improve its heat resistance and product surface quality [14]. White metals such as zinc and zinc alloys are sprayed as molten drops directly against a pattern as fragile as a paper doily. Sprayed metal molds are often made in a few hours [15]. The mold surface often replicates the pattern surface with great detail. Water lines are usually soldered in place (Figure 19.20). Thin metal shells are often backed with high-temperature epoxy.

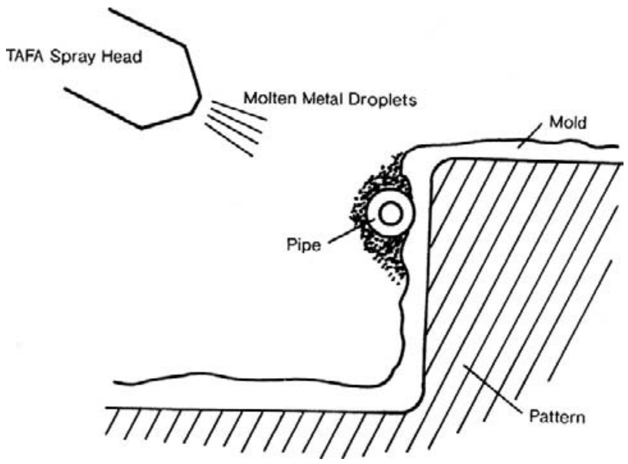

Figure 19.20 Method of fastening coolant line to back of sprayed zinc metal mold.

19.16 Mold Design

Cooling, cavity venting, undercuts, and surface texture are important elements in the design of thermoform molds. Thin-gauge coolant aspects were discussed earlier. Thick-gauge thermoform molds tend to be thin shells. Coolant lines are soldered or mechanically affixed to the non-product side of these molds. Metal-filled epoxy is often used around the coolant line and between the coolant line and the mold surface to ensure adequate conduction heat transfer. The key in all coolant-line designs is uniformity in mold surface temperature during operation. Manifold cooling lines are always preferred over serpentine lines. Many coolant lines are preferred over a few lines. Ideally, coolant temperature rise, inlet-to-outlet, should not be more than 3 °C.

To produce a quality product, air must be quickly and efficiently removed from between the sheet and the mold surface. This is accomplished with vacuum or vent holes drilled through the primary mold surface. For thin-gauge molds, these holes are connected to machined vacuum channels, a plenum, and/or a vacuum box beneath the mold structure. For thick-gauge molds, the void behind the thin-shell mold acts as an air reservoir. The vacuum box or air reservoir is connected to the vacuum pump through vacuum lines, solenoid-actuated rotary valves, and a vacuum or surge tank (Figure 19.21). The number of vacuum holes is determined by the volume of air trapped between the sheet and the mold surface. The rate of evacuation must be rapid enough to allow the sheet to stretch without riding on a cushion of exhausting air. Because the plastic is stretched last into two- and three-dimensional corners of the mold, vacuum holes are always needed in these regions. However, they are also needed in flat areas to prevent local air trap and in rim and lip areas to ensure that the sheet remains tight against the mold surface during stretching. Spring-loaded valves, often connected to a high-velocity low-vacuum source, are placed in the very bottom of very deep molds to accelerate air evacuation. To minimize drawdown of the sheet into a vacuum hole, the vacuum hole diameter should not exceed the thickness of the sheet covering it. Porous sintered metals are used when vacuum hole mark-off is unacceptable [16]. For thin-gauge products, porous aluminum with micron-sized pores is available in machineable and castable forms [17].

Because thermoforming is a relatively low-pressure, single-surfaced process, undercuts are commonly designed into both thin- and thick-gauge products. Thin-gauge products are often flexible enough to be pulled from minor undercuts such as detents. If necessary, ejector pins or rings are used. Moveable mold elements are used with undercuts of thick products or for plastics that are stiff at product removal time. Simple moving elements are hinged to swing away as the product is withdrawn. For severe undercuts, pneumatic cylinders are activated to move elements away as the product is pulled from the mold cavity. Orphan mold elements exit with the product are removed and are reassembled in the mold for the next cycle.

Grit or sand-blasted mold surfaces having roughness dimensions of 200—300 microns are usually acceptable for nonappearance products. Chemically etched surfaces yield texture dimensions to 100 microns or less. Vacuum-formed products usually do not replicate mold surface details of less than about 50 microns. Mold surface texture details as fine as 10 microns can be replicated when the sheet is pressure formed.

Whenever a hot sheet touches a cooler mold surface, it deglosses to a matte finish. If the surface must remain glossy, it can be formed free of the mold. Freely blown skylights and domes are examples. To achieve a glossy surface on a product that has touched a mold surface, the surface is often flame treated or polished with 2400 grit Crocus cloth.

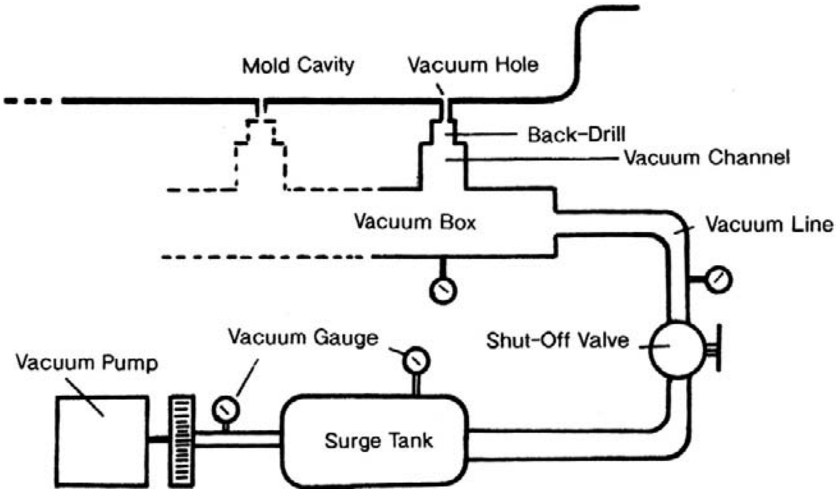

Figure 19.21 Vacuum system from mold cavity to vacuum pump.

19.17 Plug Materials

Plugs or mechanical prestretching devices are considered part of the mold. Plugs are made of syntactic foam, solid polyamide or ultrahigh-molecular weight polyethylene, heated aluminum, or felt-covered wood. The choice of the material depends on whether:

- The process is production or prototype.
- The final plug design is evolving.
- The plastic sheet is chilled and therefore marked by certain materials.
- The plug temperature needs careful control.
- The sheet is very thick.
- The sheet is very hot.

Even though plugs are used in both male or positive and female or negative thermoforming, they find greatest use while prestretching a sheet into a cavity. Plugs are usually, but not always, made of materials that have some thermal insulating capacity such as syntactic foams and wood. Heated, temperature-controlled plugs are used for some plastics such as crystallizing polyethylene terephthalate and oriented polystyrene. Plugs usually, but not always, have a shape similar to the mold. The actual plug shape is usually determined by the amount and location of the plastic to be redistributed.

19.18 Other Mold Features

To ensure that the same amount of plastic is drawn into or over a mold with each cycle, molds are designed with ridges or grooves that lock the sheet against the mold edges before sheet prestretching. Two- and three-dimensional corners of products should be designed with chamfers rather than radiuses. To ensure flat, uniform thickness in local areas of the formed product, the hot sheet is pressed between the mold surface and a coining press. Coined areas are used in thick-gauge products for assembly purposes and in thin-gauge products for flat, dimensionally accurate sealing areas.

In sequential twin-sheet thermoforming, after the two product halves have been formed, peripheral and interior segments of the product are mated under substantial pressure. Often, secondary heaters are used to keep the mating surfaces hot. Secondary hydraulic elements are used to apply force sufficient to extrude some of the plastic from the welding area, thereby ensuring an integral seal. Various sealing configurations are shown in Figure 19.22.

19.19 Plastic Materials

Any plastic that can be manufactured in sheet form can be thermoformed into useful products. The plastic sheet is heated and formed as a rubbery solid or an elastic liquid. Therefore, the solid or elastic liquid properties of the plastics are more important than their viscous properties.

The majority of thermoformable thermoplastics is amorphous, meaning that at a specific temperature, called the glass transition temperature, the plastic changes from a brittle, glassy state to a ductile, rubbery state. Polystyrene, acrylonitrile-butadiene-styrene, polyvinyl chloride, and polycarbonate are examples of thermoformable amorphous plastics.

Some thermoformable thermoplastics are semicrystalline. In addition to glass transition temperatures, these plastics melt at specific temperatures. Polyethylenes and polypropylenes are examples of thermoformable semicrystalline plastics. Semicrystalline plastics such as polyethylenes are normally thermoformed at temperatures just above their melting temperatures as elastic liquids.

Polystyrenes and the family of styrenics—high-impact polystyrene, acrylonitrile-butadiene-styrene (ABS), styrene-acrylonitrile (SAN), oriented polystyrene (OPS), and others—are workhorses in thermoforming. Polyvinyl chloride and other vinyls—flexible PVC, ethylene vinyl acetate, and others—are noted for their fire retardancy and ultraviolet resistance. Other commonly thermoformed plastics include acrylics such as polymethyl methacrylate, polycarbonate, polyethylene terephthalate, and semicrystalline plastics such as polyethylene, rubberized thermoplastic olefins, and polypropylene. There are niche applications for thermoformed

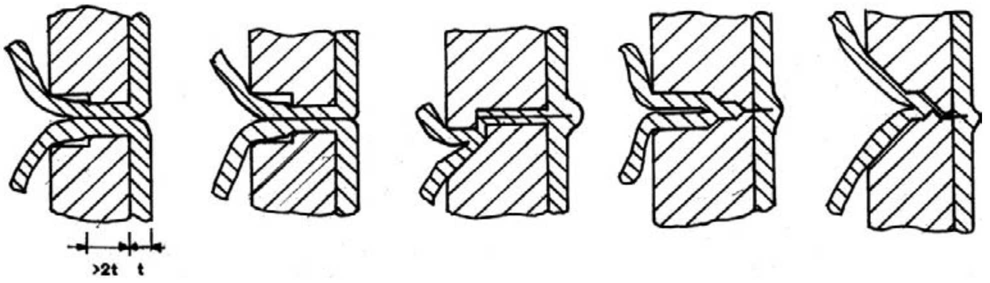

Figure 19.22 Cross-sections of twin-sheet sealing areas. First two schematics show effect of increasing pressure on sealing area thickness.

products of fluoropolymers, polyamides, thermoplastic polyurethanes, polysulfone, polyethylene sulfide, and high-nitrile resin.

19.20 Thermoforming Window

The key to successful heating and stretching a thermoplastic is its thermoforming window. The thermoforming window is the temperature range over which the plastic is pliable enough to be stretched and shaped into the desired product. Amorphous plastics have relatively wide thermoforming windows. Semicrystalline plastics have very narrow thermoforming windows. The forming field is envisioned in Figure 19.23, as the interaction of sheet extensibility, sheet temperature, and applied force. The abscissa is the extensibility of the plastics, a temperature-dependent material property. The ordinate is the applied stress or applied force per unit area. The curved lines represent the plastic elongation as a function of temperature and applied stress. The upper horizontal bound is the maximum applied stress. The right vertical bound is the maximum design elongation of the plastic. The upper curve of the forming window is the lowest forming temperature of the plastic. The lower curve is the highest forming temperature of the plastic. The cross-hatched area represents the forming area.

The thermoforming window is technically identified as a plateau or near-plateau in the temperature-dependent elastic modulus of a given plastic. Amorphous plastics such as polyvinyl chloride and cycloolefin [18] demonstrate broad plateaus at reasonably high modulus values (Figure 19.24), whereas homopolymer polypropylene shows no such plateau. Time-dependent extensional viscosity is another measure of the formability of a crystalline plastic. Polyethylene strain-rate hardens as it is elongated (Figure 19.25). As a result, it is thermoformed above its melting temperature range as an elastic liquid. Homopolymer polypropylene does not strain-rate harden (Figure 19.26) and so cannot be thermoformed above its melting temperature range [19]. Branched or copolymerized polypropylene behaves more like polyethylene (Figure 19.27), and so is thermoformed above its melting temperature range.

19.21 Semicrystalline Plastics

When a semicrystalline plastic is heated and formed above its melting temperature range, it must be recrystallized on the thermoforming mold. The rate of recrystallization is important when determining processing cycle times. Polyethylenes recrystallize rapidly at temperatures only a few degrees below their melting temperatures. Polypropylenes recrystallize slowly and often at temperatures tens of degrees below their melting temperatures. Product distortion and warping can result when slowly recrystallizing products are removed too early from the thermoforming mold. Polyethylene terephthalate is a very slowly crystallizing plastic. It is amorphous when extruded into thin sheet. It remains amorphous if it is heated rapidly and formed on a cool mold. If it is modified with a crystallizing nucleant and is formed on a heated mold, the resulting product is semicrystalline. As a food container, it will withstand 200 °C oven temperatures for up to 1 hour.

19.22 Bio-based Plastics

There is growing interest in bio-based plastics [20]. Amorphous polylactic acid is thermoformed into thin-gauge

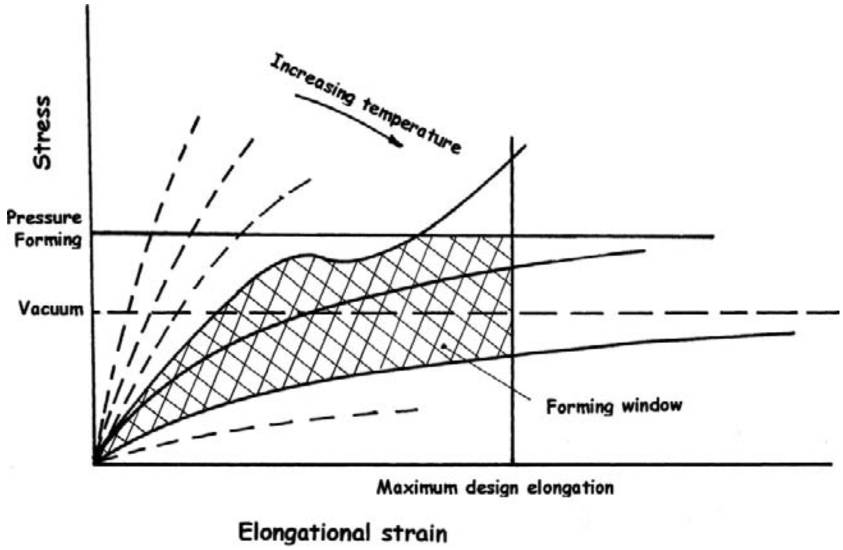

Figure 19.23 Schematic of thermoforming window, showing upper and lower temperature-dependent stress–strain curves, maximum applied processing stress, and maximum design elongation.

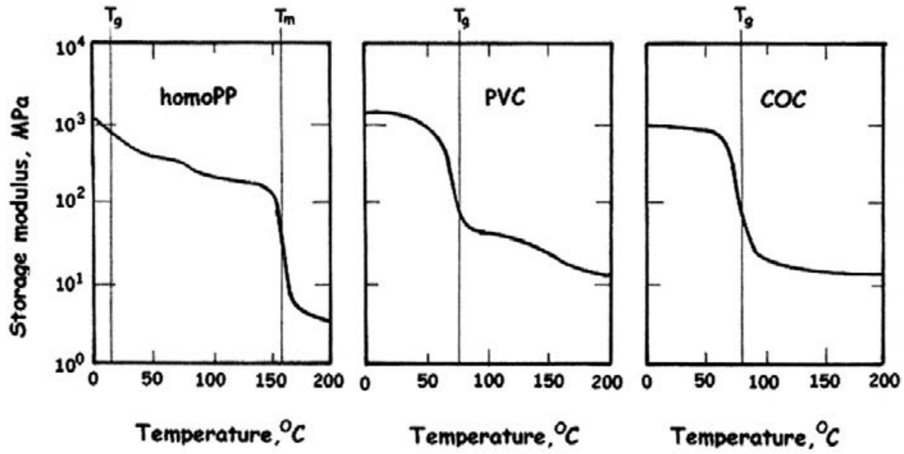

Figure 19.24 Temperature-dependent elastic or storage modulus for three thermoformable plastics. Homopolymer polypropylene (*left*), polyvinyl chloride (*center*), and cycloolefin (*right*). *(Courtesy Ticona Topas Advanced Polymers, Florence, KY.)*

disposable packaging products. It extrudes and thermoforms as a stiff polystyrene. It is moisture sensitive and the formed products tend to be brittle. Its low glass transition temperature of about 60 °C restricts its use in hot-fill containers. Semicrystalline polylactic acid has the same glass transition temperature, a melting temperature of about 170 °C, and a temperature-dependent elastic modulus plateau of 90–140 °C. The thin-gauge semicrystalline sheet is thermoformed using conventional forming pressures and warm molds. It has a practical hot oil distortion temperature of 140 °C [21].

Polyhydroxybutyrate, polyhydroxyvalerate, and blends have melting temperatures of 145–175 °C [22]. Early results indicate that these microorganism-based plastics are processible in traditional thermoforming equipment. Other bio-based plastics include modified polyesters, and older plastics such as polystarches, plastics from gluten- and gliadin-based amino-acids, casein, and, of course, cellulosics. Acceptance of bio-based plastics depends on their long-term competitive price/performance characteristics and on legislative actions against traditional plastics.

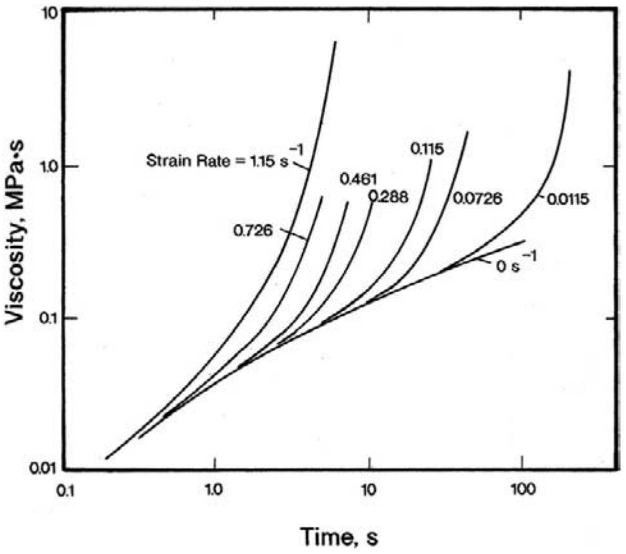

Figure 19.25 Time-dependent elongational viscosity for high-density polyethylene, showing effect of strain-rate hardening.

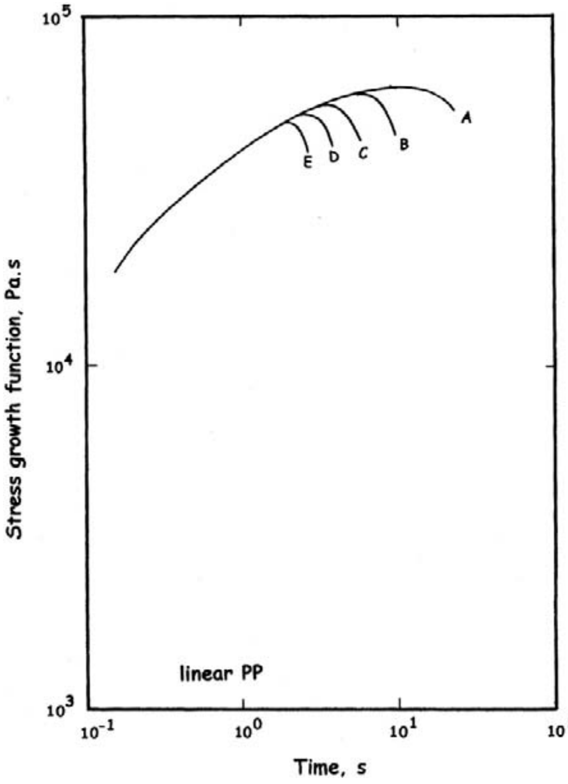

Figure 19.26 Time-dependent elongational viscosity for homopolymer polypropylene, showing absence of strain-rate hardening. Strain rate values in second^{-1}: A = 0.1, B = 0.3, C = 0.5, D = 0.7, E = 1.0.

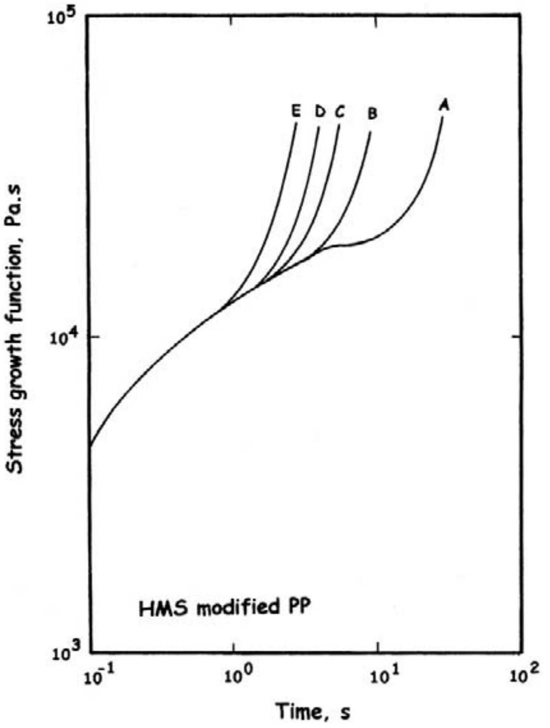

Figure 19.27 Time-dependent elongational viscosity for high-melt strength polypropylene, showing presence of strain-rate hardening. Strain rate values in second^{-1}: A = 0.1, B = 0.3, C = 0.5, D = 0.7, E = 1.0.

19.23 Filled and Reinforced Plastics

Particulate-filled thermoplastic polyolefins are used in vehicle applications. Talc, calcium carbonate, and kaolin are typical fillers. Fillers do not change the transition characteristics of the plastic. Fillers increase the temperature-dependent elastic moduli of the plastics, increasing the forces required to form the plastics in the plateau temperature regions. Matched-mold thermoforming is necessary if the product cannot be formed using a conventional pressure box over a single-surface mold.

Short-fiber-reinforced thermoplastics also do not alter the transition characteristics of the plastics but also increase forces required to form the plastics. Again, matched-mold thermoforming is recommended. Long- and continuous-fiber-reinforced thermoplastics pose an additional processing problem. Although the reinforced sheet can be drawn into shallow shapes using matched-mold pressure forming, fibers are inextensible. As a result, products will exhibit resin-rich and resin-poor areas. Nonuniformity in reinforcement implies nonuniformity in physical properties across the product.

19.24 Multilayer Products

Thermoforming is used to form products from multilayer sheets. Thick-gauge products include polyvinyl chloride-polymethyl methacrylate sanitary structures and polymethyl methacrylate- and fluoropolymer-capped ABS exterior transportation components. An example of a family of thin-gauge products is polystyrene-ethylene vinyl alcohol-polyolefin barrier packaging. Heating and stretching of multilayer sheets often require trial and error to minimize interlayer de-lamination, excessive barrier film thinning, and incomplete replication of the mold cavity.

19.25 Foamed Plastics [19]

High-density thermoplastic foam sheet is usually produced by adding a chemical foaming agent, as either a masterbatch or a blended powder, to the plastic at the extruder hopper. The chemical foaming agent is a technically pure chemical having a very sharp decomposition temperature. Sodium bicarbonate is widely used to foam products that are used in contact with medicines, pharmaceuticals, and foodstuffs. It decomposes to produce carbon dioxide and water vapor. Azodicarbonamide is used to foam plastics used in industrial applications such as electrical trays. It decomposes to produce nitrogen and other volatiles. The density of high-density foam sheet is typically 80—90% of the density of the unfoamed plastic sheet. It is heated and thermoformed in a manner similar to that of the unfoamed plastic sheet.

Low-density thermoplastic foam sheet is thermoformed into products that are used primarily for thermal insulation, as in fast food takeaway containers, or for shock mitigation, as in egg cartons. The density of low-density foam sheet is typically 20% or less of the density of the unfoamed plastic sheet. Low-density foam sheet is usually produced by metering low-boiling liquids into the molten plastic through a port in the extruder barrel. Fine cells are achieved by adding small amounts of chemical foaming agents and other cell nucleants such as talc to the plastic at the extruder hopper. Low-density foam sheet must be carefully heated to achieve secondary foam expansion and to prevent catastrophic cell collapse. The heated, expanded sheet is formed in match molds. The sheet is primarily drawn into the mold by the folding and collapse of cell walls rather than by stretching of the plastic.

19.26 Thermal Characteristics of Plastics

The amount of energy needed to heat a plastic from room temperature to its forming temperature depends on whether the plastic is amorphous or semicrystalline (Figure 19.28). More energy is required to heat semicrystalline plastics than amorphous ones because crystallites must be melted before the plastic becomes formable. It takes nearly twice the energy to heat high-density polyethylene to its 180 °C forming temperature as it takes to heat polystyrene to the same forming temperature.

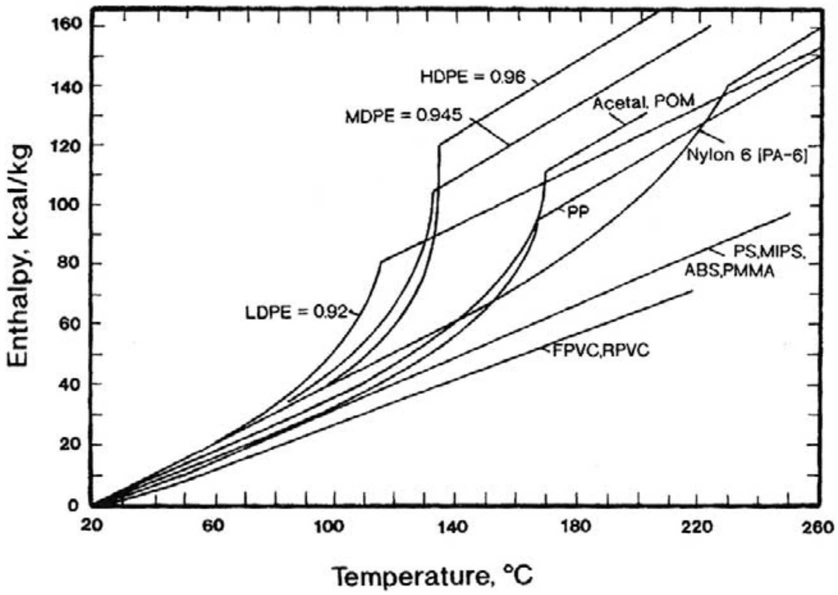

Figure 19.28 Enthalpies of thermoformable plastics.

As noted, thermoforming heaters mostly operate in the far-infrared region, in the wavelength range of about 3—10 microns. Inbound radiant energy is reflected by, absorbed by, or transmitted through the sheet. Nearly all plastics volumetrically absorb radiant energy. The chemical composition of a given plastic dictates the nature of energy absorption and by difference, the nature of energy transmission. This is shown in Figures 19.29—19.31 for

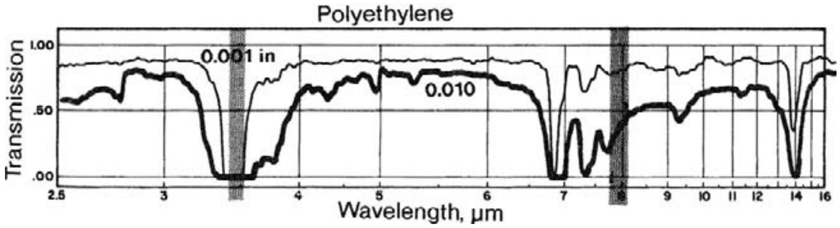

Figure 19.29 Infrared transmission spectrum for polyethylene.

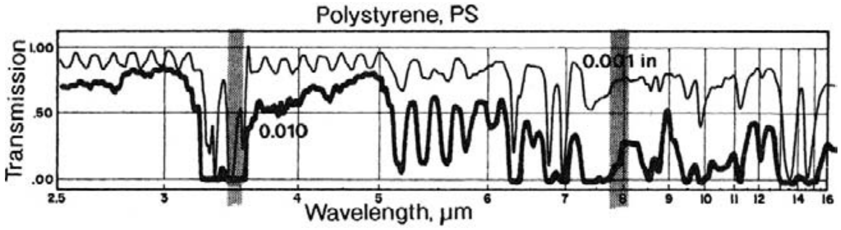

Figure 19.30 Infrared transmission spectrum for polystyrene.

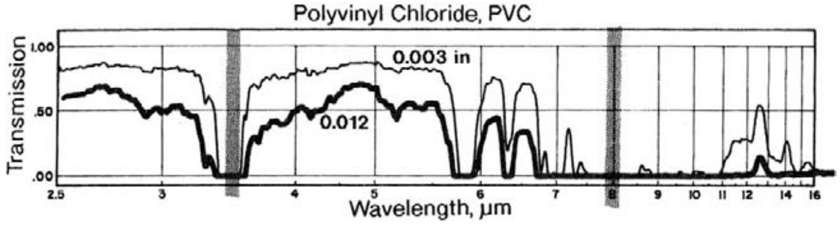

Figure 19.31 Infrared transmission spectrum for polyvinyl chloride.

polyethylene, polystyrene, and polyvinyl chloride. Thick plastic sheets absorb all inbound radiant energy. Very thin plastic sheets absorb only a fraction of the inbound radiant energy.

19.27 Product Design

The purpose of every thermoforming operation is to produce saleable products at a profit. Before a decision is made to thermoform a product of a specific design, the following concerns must be addressed [23]:

- Will the finished product meet all required and specified design criteria?
- Can the product be produced at the minimum cost for the projected market size?
- What are the consequences if the product fails to meet the minimum requirements?
- Can the product be recycled or disposed of in an environmentally friendly fashion at the end of its useful life?

Secondary concerns such as scrap disposal, reliability or availability of proper machinery, and reliability or availability of a trained labor force may alter the manufacturing process.

Before thermoforming is selected as the appropriate process to manufacture the product, certain criteria must be met:

- Can the candidate plastic be satisfactorily extruded into quality sheet?
- Can the sheet be heated to its forming temperature without excessive sag?
- Is the plastic too stiff at its forming temperature to be formed with conventional thermoforming equipment?
- Can the sheet be heated to its forming temperature without discoloration or degradation?
- Can the sheet be stretched into the desired shape?
- Is the market too large?
- Is the market too small?
- Can the regrind be reused to produce sheet for the same products?
- Are the product wall thickness variations too severe or abrupt?
- Are the product wall thickness dimensions too critical?
- Are there other processes that are better suited or more competitive economically?

Several general parameters affect thermoformed product design.

19.28 Shrinkage

As noted, thermoforming is a single-surface forming method employing low-pressure and low-temperature. The formed product is the result of rigidifying a hot rubbery sheet against a cold mold. There are two forms of shrinkage in thermoformed products. The first is thermal shrinkage, being the result of the formed product cooling from its forming temperature to room temperature. All plastics exhibit this general temperature-dependent density increase. Semicrystalline plastics formed above their melting temperatures exhibit additional density increase as they recrystallize. The rate at which plastics return to their stable room temperature density depends strongly on the rate at which they are cooled. If a product is pressed against a very cold mold and removed quickly, it will achieve its stable density at some time after it has been trimmed and even packaged for shipment to the customer.

Orientation shrinkage occurs in addition to thermal shrinkage. Residual stresses have been locked into the product during cooling against the mold surface. They relax over time. Because the stress field is not uniform, the product may exhibit distortion, warp, and dimensional variation. Residual stress relaxation is a vexation in the trimming operation. It is often the cause of product rejection by the customer.

19.29 Draft Angles

Draft angles are very important in thermoforming product design. If the product is formed onto a female or negative mold, it shrinks away from the mold sidewalls. As a result, true female or negative products can be thermoformed with vertical walls having zero draft angles. If the product is formed onto a male or positive mold, it shrinks onto the mold sidewalls. A draft angle of 1–5 degrees is recommended for all male or positive products. The more the plastic thermally shrinks, the greater the draft angle must be. On textured male molds, the draft angle should be increased about 1 degree for every 5 microns of texture depth.

Many products have both negative and positive elements. During cooling, the positive elements act to pull the plastic toward them and away from the negative elements. This can change the final dimensions of the product. Draft angles must be carefully chosen to minimize this effect. Using a plug to position the stretching sheet very close to the mold surface helps mitigate this effect as well.

19.30 Corner

As noted, plastic is stretched last into horizontal two- and three-dimensional corners. The sheet that is drawn into a three-dimensional corner decreases in thickness in direct proportion to the corner radius. In many applications, corners

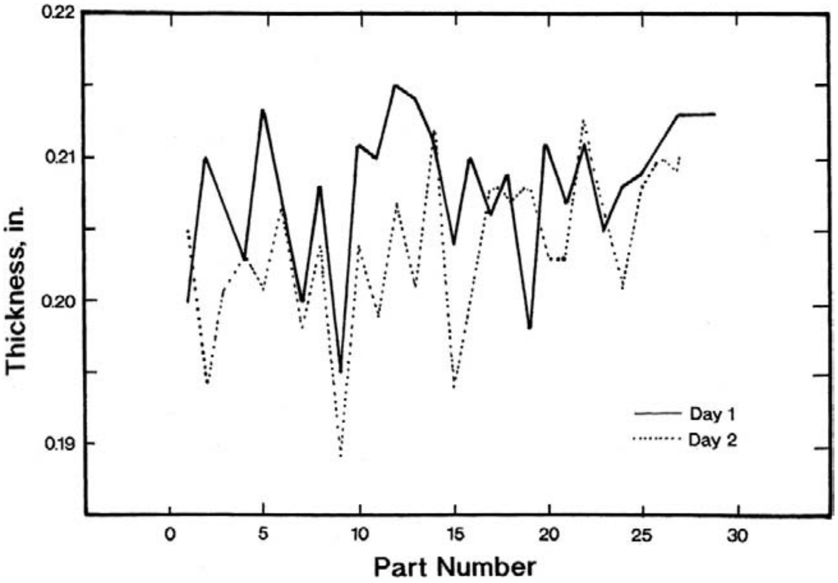

Figure 19.32 Product-to-product wall thickness variation on thick-gauge thermoformed product. Variation is about 10%.

are most vulnerable to impact. In thermoforming, corners of large radius are always recommended. Chamfers, being flattened areas with 45 degree angles to all intersecting walls, are substantially stronger than radii and are always preferred for three-dimensional thermoformed corners [24].

19.31 Dimensional Tolerance

Thermoforming, along with blow molding and rotational molding, is a single-surface forming process. Thermoforming is a differential process. Stretching takes place only on that portion of sheet that is not in contact with the mold surface. The thickness of the plastic on the mold surface decreases as the sheet stretches. In addition, there are many vagaries in the forming process:

- Sheet thickness variation
- Level and quality of regrind
- Random thermal cycling of heaters
- Sheet sag
- Variation in ambient air temperature in both the oven and the forming station
- Sheet that exits from the oven on time rather than on temperature
- Plug temperature variation, and so on

For thick-gauge sheet, local wall thickness of the forming product can be manipulated by prestretching and by changing local heater temperatures. The latter is called zoned or pattern heating. For thin-gauge sheet, local wall thickness can be manipulated by mechanical prestretching.

Wall thickness tolerance for commodity products such as thin-gauge drink cups and thick-gauge dunnage is typically 20%. Wall thickness tolerance for high-performance products such as thing-gauge lidded containers and thick-gauge equipment housings is typically 10% (Figure 19.32). A 20% variation in wall thickness results in a 60% variation in stiffness. If the product must meet a minimum sidewall strength, for example the median product wall thickness must be 120% or more of the minimum thickness.

Rim rolling is an important method of stiffening thin-walled thin-gauge thermoformed cups. Cups are indexed through a device that heats and presses the trimmed rim of the cut against a curling screw (Figure 19.33). The rolled rim dramatically increases the hoop strength of the cup and provides a smooth surface for the user.

19.32 Operational Aspects of Thermoforming [25]

19.32.1 Safety

prior to machine transfer to the new ownerThe thermoforming process involves high temperature, high mechanical forces, high pressures, many pinch points, high voltage, combustible plastics, and electrically and electronically timed start-stop elements that can maim and kill. Extensive protocols with detailed safety practices are required for machine set-up, maintenance, and operation. All permanent and temporary employees must be trained on all aspects of the thermoforming process. All plant-floor personnel must be provided with appropriate safety equipment such as earplugs and heat-resistant gloves. No one should be permitted on the plant floor without proper protective gear. All operating

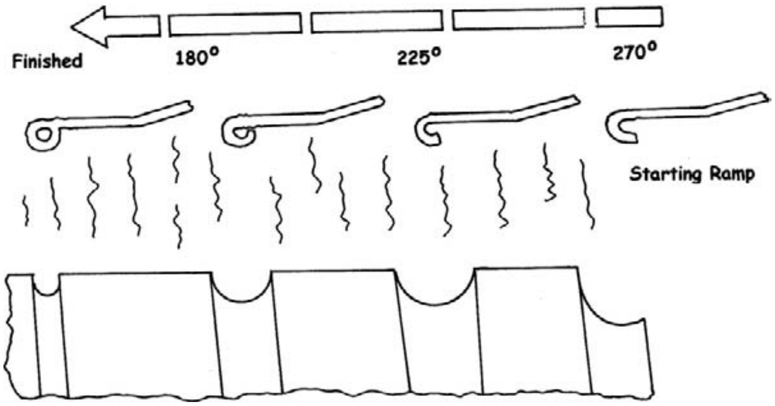

Figure 19.33 Typical heating sequence for polystyrene cup rim rolling.

features of the equipment must be disabled before anyone enters the operating theater of the equipment. One safety program emphasizes "Lock it and Pocket it!" in which two locks are used to disable all electrical and mechanical machine functions. One key is held by the person entering the machine and the other by a plant supervisor.

19.32.2 Machine Set-Up

The set-up protocol for a new machine is different from that for a used machine. When purchasing a new machine, that the machine builder will offer a thorough training session that includes hands-on operation. The machine builder will often send an experienced operator with the new machine to the plant site, oversee installation and initial start-up, and will floor-train all machine operators. The purchase of a used machine requires additional steps. If possible, the machine should be inspected and run at its current location prior to purchase. The original machine builder should be contacted before the machine is purchased to obtain operating and safety guides. The builder may wish to inspect the machine and may recommend upgrading and refurbishing prior to machine transfer to the new owner. The machine also may need to be brought up to current OSHA standards.

19.32.3 Mold Set-up

A specific protocol is recommended when purchasing a new mold. The completed mold assembly should be inspected at the mold maker to insure that the basic design features are in place. Specifically, the entire mold surface should be inspected for texture uniformity. All vent holes should be open. Coolant lines should be free of chips. Coolant should be run through the coolant lines and pressurized. All mechanical actions should move effortlessly. In-mold trim fixtures should work smoothly and be easily adjusted. Plugs should be easily adjusted and removed. Logos and date stamps should be keyed for easy adjustment and replacement. Pick and lift points should be clearly marked on mold edges and the mold should hang uniformly when lifted. All air and coolant lines should be equipped with over-sized quick disconnects.

A different type of inspection is needed for the reinstallation of a mold that has been in storage for some time. Even though the mold assembly—the mold, its vacuum box, plug plate, plugs, air and coolant line quick disconnects, and its pressure box—may have been stored as a single unit, often bits and pieces are scavenged for other molds. Installation may be delayed until the missing pieces are found or replaced. The same is true with trim dies, trim fixtures, and elements of stackers. It is vital that the mold and press set-up protocols are stored with the mold. If these are stored electronically on a disk or chip, a paper printout of the access codes to the protocols is required to ensure that the appropriate software is available. An example of the product should also be placed in the mold cavity.

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20 Process Monitoring and Process Control: An Overview

Mark Berry[1] **and Nick Schott**[2]
[1] PPD Tech, 10 Buttonwood Rd, Bedford, NH 03110, USA
[2] University of Massachusetts Lowell, Lowell 854, USA

20.1 Introduction

The objective of this chapter is to provide a general background on how process monitoring and control technologies and strategies are applied to two major plastics processes: injection molding and extrusion. While the term “process control” could apply to anything that provides some aspect of machine control, this discussion is limited to devices and methods which are applicable to some of the unique aspects of plastics processing. It is not the intention to discuss the technical details of data acquisition (DAQ), such as signal conditioning and analog to digital conversion or control architecture. Some historical perspective is provided along with recent developments and current research, which should provide an indication of the direction of future developments in process monitoring and control in the plastics industry.

20.2 Historical Factors Affecting the Development of Process Monitoring and Controls

20.2.1 The 1970s: Impact of Statistical Process Controls

It is widely known that statistical process control (SPC) methods were originally developed in the US, led by Shewhart and Deming [1], but it was Japanese companies, such as Toyota that embraced these techniques and developed the robust systems, which ultimately changed how manufacturing is managed today. The definitions of acceptable quality and productivity have changed. While 97% quality was acceptable in 1970, we now think in terms of “six sigma,” which refers to defect level of 3.4 parts per million. Manufacturers had to adjust, first by learning how to not ship defective products and SPC proved to be an effective tool in that quest. Implementation of SPC-based quality systems has certainly improved the product quality of many plastics manufacturers. It has been well documented, notably in Philip Crosby’s 1979 landmark “Quality is Free,” [2] that improving quality reduces the “cost of nonconformance” and should yield a significant savings to the manufacturer. However, it was soon learned that if SPC methods are used simply as sampling tools to “certify” that a production lot of parts will be within specification, the savings would be limited to simply preventing the cost of a customer return. To accomplish improved productivity as well, product data ultimately needed to be linked to process data.

20.2.2 The 1980s: Digital Controls Provide a More Consistent Process: Unique Aspects of Polymer Rheology More Widely Understood

The adoption of more microprocessor-based control systems yielded a more consistent process for extrusion and injection molding. Also, several key factors became more widely recognized: (1) The material viscosity changes throughout an extended run, due to changes in material lots, variation in additives, regrind levels, or degrees of dryness. (2) Changing external conditions such as room temperature, humidity and mold, and die temperatures affect the process. (3) The key process parameters would need to be very consistent in spite of these changing material characteristics and conditions. These demands have led to major changes in machine controls and a more technical approach to processing. In injection molding, earlier work by Hunkar®, Moog®, and others led to major changes in how the molding process is approached, with a much greater emphasis on closed-loop controls with a particular emphasis on injection ram speed control [3]. With servo control providing a tightly controlled ram velocity, processing techniques were improved, with more emphasis on the melt flow behavior in the individual cavities in the mold. RJG® and others emphasized the concept of “decoupling” the stages of mold filling by controlling the filling stage separately from the packing stage [4].

With extrusion, technology provided improved temperature controls, die controls and takeoff equipment, and cooling techniques. Programmable logic controllers (PLCs) allowed the development of control systems for parison profiling as well as screw speed control based on melt pressure measured at the die. All of these developments have contributed to the development of thinner sheet and very small diameter, multilumen, and multimaterial medical tubing.

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20.2.3 The 1990s: Computers, Globalization, and Higher Material Costs

With the rapidly increasing processing power of computers, improved operator interfaces and distributed control systems improved overall controls available to processors. Real-time process and product data and SPC tools became much more accessible and better utilized. However, in this period, perhaps the two most important factors affecting the adoption of process monitoring and control strategies have been (1) the drive for lower cost offshore sourcing and (2) increasing material costs. While the effect of international sourcing was probably greatest on western injection molders, the effect of increasing material costs has been universal. For extruders, ever thinner walls and higher output remained the primary goals. Microprocessor-based controls helped with improved gravimetric and loss-in-weight feed systems.

With western injection molders, an effective survival strategy was the primary focus. In the injection molding industry, there was much less demand for "low tech" producers in the higher cost countries. Molders were typically producing more and more complex parts in higher cavitation molds and with faster cycle times. Labor costs had to be minimized and technology was utilized more to accomplish that. A more technical approach to molding gained much wider acceptance [5], which considered the sources of the variations and tried to minimize their negative effect on a consistent process. For example, the more tightly controlled injection speed allows the processor to take advantage of the shear effect on viscosity of the polymer melt and to operate in an area where there should be less process variation due to other drifting parameters [6]. The use of pressure transducers became more accepted as an effective means to better understand the cavity filling process with the ultimate goal of fingerprinting an optimized process. This technology was advanced by Kistler® and others with the introduction of piezoelectric sensors, which could be positioned in a variety of positions with direct, indirect, and contact-free pressure measurement to monitor the filling process [7]. These advancements, along with advances in control technology, have led to improved open-loop and closed-loop control methods. Closed-loop systems for injection molding based on using cavity pressure to determine the switchover point from machine velocity control to pressure control became more widely used. Cavity pressure was also being utilized to manage the opening and closing of valve gates in large molds with complex flow paths.

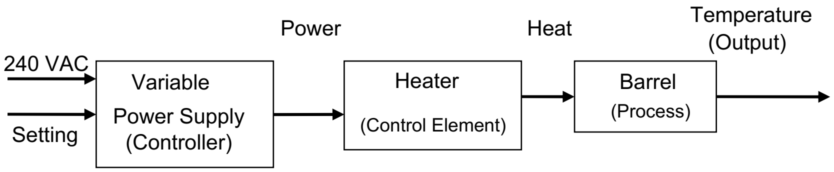
20.2.4 Early Twenty-first Century: More Powerful Computers; More Technical Approach to Processing

Process monitoring and control technology have continued to develop, with better utilization of computer hardware and software to provide improved ease of use and reliability. The 16-bit and 32-bit systems provide more speed, more data storage, and more complex control algorithms. Systems are becoming easier to implement and use with the introduction of more advances such as advanced user interfaces, and wireless transducers and transmitters. Processors have generally accepted that to be able to manage and optimize any process one must understand the process at the most fundamental levels. In injection molding, closely monitoring what is actually happening in the mold cavity itself is gaining wider acceptance, with continued improvements in pressure sensor technology as well as in melt temperature measurement. While cavity pressure is the most commonly used in-mold sensor, Priamus® has emphasized the utilization of melt temperature in the cavity as an important control characteristic, using a temperature to capture the arrival of the melt front to a specific location, to determine when to instruct the molding machine to execute the switchover from ram velocity control to pressure-based control [8]. There is also work being done which combines the output of both cavity pressure and melt temperature to characterize an acceptable process window. All of the above approaches are based on the notion that the primary machine process parameters as well as material flow properties and environmental conditions all vary over time and are interrelated in ways that are far too complex to provide a basis for a simple process adjustment. It is generally agreed that the cavity filling experience of the melt is the best determinant of the quality of the product. While more processors believe that the best process control model for injection molding should include measurements made in the mold during the cavity filling step, there is still considerable debate as to how this is best accomplished.

20.3 Basic Concepts: Open-Loop and Closed-Loop Controls

- *Open-loop controls*: Process control technologies have been incorporated into plastics machinery as they became available to industry. For instance, earlier machines often managed nozzle temperature with a variable voltage transformer which provides power to a resistance heater, delivering from 0% to 100% of the available voltage. The output of the controller is constant at any given setting. Since there is no feedback loop included, this would be an example of open-loop control as illustrated in Figure 20.1. In practice, the actual temperature of the nozzle body might be measured by a separate thermocouple (TC) probe and be monitored by the technician who would make adjustments as necessary, based on his experience. The technician might also measure the melt directly with a pyrometer, to make the decision on how much to change the voltage level (amount of voltage provided to the heater band). In this case, the resultant control

Figure 20.1 Open loop heater control block diagram.



model would be an intermittent (manual) closed-loop control as in Figure 20.2.

- *Closed-loop controls*: While open-loop control systems for heaters are still used in some situations, virtually all molding machines and extruders have utilized closed-loop controllers for barrel temperature control. Figure 20.3 shows a block diagram which describes a general closed-loop system. The system is defined as the combination of hardware and software that is carrying out the manufacturing and control process. We have described a set point as a setting that is entered as a constant value, representing the desired value of the controlled variable. In closed-loop control systems, corrections are made based on actual measured outputs. In Figure 20.3, the circle with the X is called a comparator or summing junction that algebraically adds the set point and the measured output value. The first block represents the controller, typically a microprocessor which calculates a corrective action based on the algorithm that has been developed. In turn, the controller sends out a command signal for the corrective action which is carried out by a final control element, which is a piece of hardware which can introduce energy into a system. Examples of control elements (actuators) are cartridge heaters, heater bands, servo valves, and servo motors. The final control element will put out a corrective action which, when combined with the upsets to the system, provides a combined system input. The upsets are random disturbances that cannot be predicted ahead of time that disturb the process. The output is the actual value of the controlled variable. This output must be measured by a transducer to give an electrical signal which is fed backward to the comparator also known as a summing amplifier. So, in this case the controller also receives a feedback signal from the sensor. If the feedback signal deviates from the set point, the controller then adjusts its output to the control element based on the established algorithm. Typically, the amount of the correction is proportional to the amount of the deviation from the set point. In the case of barrel temperature control, as illustrated in Figure 20.4, the transducer is typically a TC and the control element a heater band. This block diagram uses a summing junction (circle with X) to show the combination of planned and unplanned inputs to the system. The same basic diagram would also apply for a closed-loop control system for thickness control on an extruder. In this case the transducer would be a thickness gauge and the control element might be takeoff line speed or there could be a more complex combination of control elements.
- *Set point control*: Most process control is done with feedback set point control. This means that the controlled variable is measured as an output of the

Figure 20.2 Intermittent (manual) closed loop control block diagram. [9]

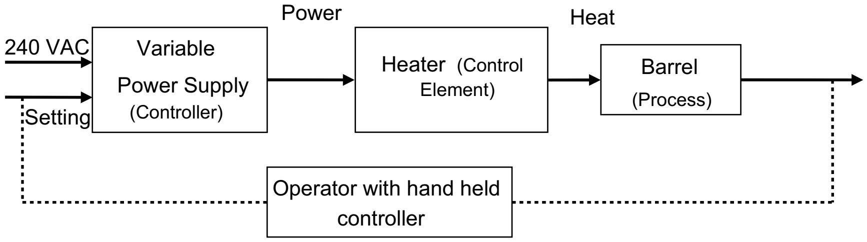
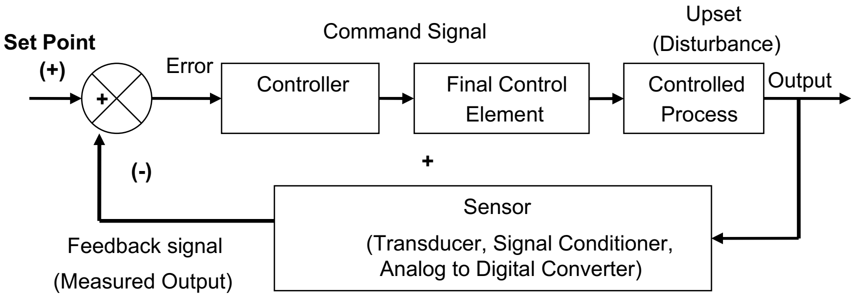


Figure 20.3 Typical closed loop control block diagram.



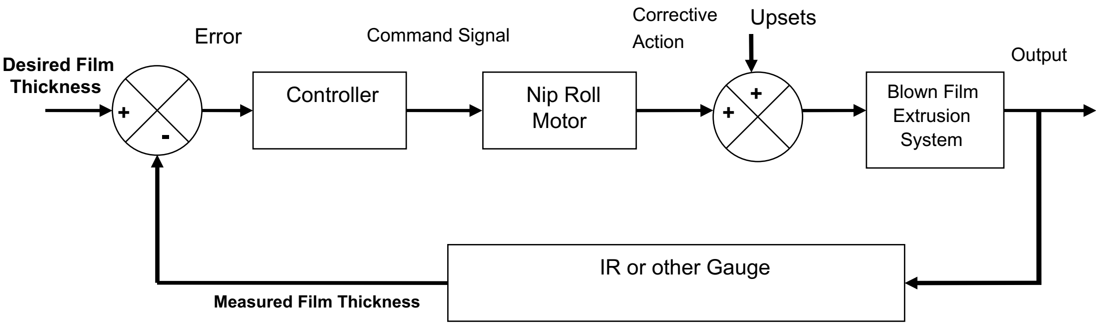


Figure 20.4 Closed loop, negative feedback, set point control loop diagram for temperature control.

process and the signal is sent back to be compared with a set point (desired value). The generated error is the difference between the set point and the measured value. The error signal is acted on by the controller to make a corrective action which is sent as a command signal to a final control element. In this kind of control loop, the error is corrected only after it has occurred. The closed-loop negative feedback control works best if the "distance velocity lag" or "dead time" (DT) is very short. Figure 20.4 illustrates a typical closed-loop, negative feedback, control loop.

- *Distance velocity lag (DT):* The DT is the minimum delay time that occurs after a process input change, before the effect of the change is seen in the output. When there is enough of a time lag in a process, it is possible to measure an "upset" and make a correction before the error occurs in the process. An example would be a "feed forward" process, such as flow-based system, where material is supplied at a feed hopper and there is a lag time before the material reaches a die. Another example is a feed belt conveyor system where material flow is managed with weight scales. Any upset in the mass flow can be corrected by speeding up or slowing down the conveyor or belt. The same would also be true if a TC is located in an extruder barrel where the temperature change has to travel a given distance. A long "dead time" makes it more difficult to control. For example, a slow response temperature transducer requires more time to acknowledge and respond to display a temperature shift.
- *Time constants*: Every system has a time constant, based on the grouping of the physical variables of the system. The time constant is the time that is required to respond to a system "upset" and the longer the time constant, the greater the time that is required to settle down to a new steady state. A small time constant allows a faster response to an upset in the process conditions. A typical example is a small wire TC which takes less time to heat up, giving a small time constant. This situation also provides a simple example of a typical trade-off in designing a system. While a small wire, exposed TC may have the desired time constant, it may not be robust enough to be of practical use in that situation. Increasing the wire size or covering the junction of the wires will make the TC more robust, but the time constant is greatly increased with the changes. In the case of a TC that senses melt temperature, the time constant will have units of time and is defined as

$$\tau = mC_\mathrm{m}/hA$$

where τ is the time constant; m, mass of TC junction; C_m, specific heat of the junction; h, heat transfer coefficient between fluid and junction; and A, area of the junction.

- *Servo control:* While set point control is used when it is desired to maintain a constant output of the controlled variable, many processes require a time varying output. That is where servo control comes into play. Instead of a constant value set point, the input is a time varying variable and the control loop must try to follow that input as closely as possible. For example, a cruise missile in which the altitude and velocity continuously change to prevent the missile from running into an unplanned object (e.g., mountain vs. the target). An extrusion blow molding example would be parison wall thickness control, to vary the thickness as needed to yield the contoured shape of the finished bottle with a more uniform wall thickness. An example of servo control in injection molding is ram velocity control, where the ram speed is controlled, perhaps being changed several times during the injection stroke. In the hydraulic injection molding machine, a servo valve constantly adjusts a hydraulic spool, adjusting the amount of hydraulic fluid, in response to information from position transducers. In the electric molding machine, a servo motor's rotation is controlled based on the linear transducer's travel of the ram.
- *Control algorithms*: We have discussed that in closed-loop control systems a corrective action is taken by the controller in response to feedback from a transducer. The exact corrective action depends on the algorithm which has been developed. The simplest control approach is a two position control which turns the

control element on and off based on the monitored value of the output. With an on/off strategy, the process value will typically oscillate above and below the set point. The most common controller is the PID (proportional, integral, and derivative) loop controller which is able to detect an early trend, adjust quickly, and prevent an over-correction. A PID controller can maintain temperatures within 1 °F. The controller provides the means to define the control algorithm by assigning a constant for each of the three control modes. Typically, most of the adjustment is accomplished with the proportional control element, with the control action, $u_{\mathrm{p},}$ being proportional to the error, e, between the set point, s, and current measured output, o. The constant of proportionality is referred to as the proportional gain, K_{p}

$$u_{\mathrm{p}} = K_{\mathrm{p}}.e = K_{\mathrm{p}}\,(s - o)$$

With proportional control alone, there tends to be trade-off between the time needed to implement the correction and over-corrections leading to loss of control. As the proportional controller responds to changing conditions, such as heat loss by convection, there is a tendency to stabilize not at the set point but at a point some distance from it. This error, called a "steady state error" can be corrected with the integral control mode of the controller, which provides an integral or "reset" correction which shifts the proportional band up or down as needed to stabilize at the set point. The integral action, u_{I}, is based on the integral gain, K_{I}:

$$u_{\mathrm{I}} = K_{\mathrm{I}}.\int e.\mathrm{d}t$$

With integral control alone, the output will tend to respond slowly at first, overshoot, and then oscillate back and forth around the set point, since the corrective action is based on the response only to the integral of the error. A long time is needed to finally settle at the set point. Combining proportional and integral (PI) control can improve the degree of control but PID controllers go a step further, adding a derivative mode whose control action, u_{D}, is proportional to the derivative of the error, with K_{D}, the derivative gain:

$$u_{\mathrm{D}} = K_{\mathrm{D}}.\mathrm{d}e/\mathrm{d}t$$

The derivative component helps to reduce overshooting, since the maximum rate of change typically occurs as the output passes through the set point and therefore the derivative will also be greatest at that point. The derivative component also improves the initial control response to a changing output, since the proportional and integral require more significant error before delivering a significant corrective response [9]. PID-loop controllers are now very common in industry and have been introduced to many areas of machine control. While the implementation of PI and PID control loops is now more likely to be done through the use of digital controllers of various types and with a range of hardware and software designs, the basic control logic is the same.

20.4 Transducers Used in Plastics Processes

A transducer is defined as a device that converts energy from one form to another. Typically, it is desirable to have the physical variable converted into an electrical signal. Some of the transducers more commonly used in plastic processing are discussed below.

- Temperature transducers are used in virtually every plastic process. The devices used consist of TCs, resistance temperature detectors (RTDs), and infrared (IR) temperature detectors.
  - A *thermocouple (TC)* is an electrical circuit consisting of two dissimilar metals. If the junction points are at two different temperatures an electrical voltage (EMF) is generated. A TC is essentially a point measurement, but it has to be in physical contact with the object that is being measured. K type (nickel—chromium/nickel—aluminum) TCs are more common in Europe. The plastics industry in the US has generally settled on the J type TC (iron—constantan) for most applications. The J type has a broad temperature range, good linearity, and relatively high signal output. A disadvantage is its low resistance to corrosion. Other types are chosen for specific situations. For example, N types (nickel—chromium—silicon/nickel—silicon—magnesium) are used as an alternative to Ks, due to their greater stability at high temperatures.
  - A *resistance temperature detector (RTD)* is a passive device which measures the change in the electrical resistance of a metal as a function of the temperature. Noble metals such as platinum or nickel are used because they do not oxidize and have a highly linear temperature—resistance relationship. RTDs require an external voltage to operate and make the measurement. This is called the excitation voltage which is used to make a bridge circuit measurement of the electrical resistance.
  - *Infrared (IR) sensors* can also be used to measure temperature. Bodies at higher temperature (>200 °C) emit significant IR radiation (heat waves). A photon detector captures the emitted radiation and converts it into a voltage which, by calibration, is displayed as temperature. Since the IR radiation is proportional to the fourth power of the absolute temperature, the IR probes show a highly nonlinear output

  signal versus temperature, but they have the benefit of making a noncontact measurement which is important when one does not want to disturb the melt flow or a film or final plastic product.

- *Pressure transducers* are also very common in plastics processing. While load cells are used in equipment to measure an applied force, process monitoring applications will typically utilize pressure transducers to measure hydraulic or melt pressures.
  - Pressure transducers using strain gauges are the most common type, particularly in extrusion. For direct melt contact, the sensing elements must be separated from the abrasive, possibly corrosive, and high temperature environment by a fluid-filled capillary. Thus, the actual strain gauge may be 40−50 cm away from the melt, resulting in a large and bulky device which does not fit well into some situations. Strain gauge pressure transducers have been widely used in injection molding to measure cavity melt pressure by installing them behind ejector pins.
  - Piezoelectric sensors have become widely adopted in injection molding, offering smaller profile and faster response times. These devices are based on the electrical property of some crystals that will develop an electrical charge when strained, with the output signal proportional to the applied pressure. These devices do not require an external excitation source and have a fast response time. Piezoelectric sensors produce a very low voltage output and do require amplification circuitry.
  - While the merits of each type have been debated, it has been demonstrated that data from both types correlate well with one another and that perhaps the most important distinguishing characteristics are their response times, relative costs, and robustness in a specific manufacturing environment [10].
- *Position transducers* are also very important in the plastics industry. Both linear and rotary displacement sensors are widely used. In injection molding, screw position for shot size and cushion must be very accurately measured. Mold open and close positions as well as ejector plate travel are also controlled with input from linear position sensors. Generally, it is recommended that linear position sensors provide an accuracy of better than 0.01%, a response time of less than 1 ms, and good vibration resistance [9].
  - *Rectilinear potentiometers* are resistive displacement sensors, based on the principle of measurement of the change in electrical resistance versus distance. A similar device called a *rotary potentiometer* translates the linear movement of the screw or mold into a rotary motion that changes the electrical resistance of the potentiometer. These devices require an excitation voltage which is applied to the resistor, and a sliding pickup arm divides the resistance linearly and gives a corresponding change in voltage. Resistive position sensors offer a proven and low cost solution and are very common on auxiliary equipment but are now less commonly used in critical areas on primary processing equipment, due to inherent limitations in accuracy compared to other available sensors.
  - *Linear variable differential transformers (LVDTs)* are an example of inductive displacement transducer devices, which are often used with plastics equipment when the distance to be monitored is not extremely high. The LVDT is comprised of a primary coil and two secondary coils. A moving iron core passes between the primary and secondary windings and the movement linearly changes the output of the transformer depending on the engaged electromagnetic field that the core intercepts.
  - *Magnetostrictive linear displacement transducers (MLDTs)* measure the time it takes for a sonic pulse to travel from a fixed source to a variable position. These newer devices are very accurate and are contact-less, offering the potential of long life [9].
  - *Optical encoders* are commonly used in the plastics industry, particularly the rotary version used to measure screw rotation. At the most basic level, a light source directs rays through a plane convex lens that focuses the light into a parallel beam. The light beam is split to produce a second beam of light 90° out of phase. Light from the original (A) and the second (B) channel passes through a "pulse disk" onto the photodiode array. The pulse disk turns, creating a light/dark pattern through the clear and opaque segments of the disk. The number of lines can be counted electronically. If a distance of 1 in. generates 1000 lines, the device can measure to a distance of 0.001 in.
  - Other position measurement devices utilize different electrical properties that can be used for position measurements, such as capacitance and magnetic field intensity (Hall effect).
- Thickness measurements are specific position measurements that relate to product thickness. Thickness of a sheet may be measured directly by a caliper sensor such as a laser caliper sensor or be determined indirectly by measuring the mass of the plastic. Mass measurement gauges are typically the preferred mode since they tend to be simpler in design than thickness measuring devices. Physical principles that are used in mass basis measurement are X-rays, beta, gamma, and IR radiation. IR light is particularly useful with clear applications. It has a wavelength longer than that of visible light and

its intensity is less than UV light, so it does not break the covalent bonds of the plastic molecules. Specific wavelengths of IR light can be used to target the functional group of the plastic at which the plastic will absorb. Film thickness can be calibrated versus the absorption or reflection of a particular wavelength. A great benefit is that in individual layers a multilayer film can be measured with IR interferometry. These multilayer films are increasingly important in packaging.

20.5 Data Acquisition Systems

Effective process monitoring requires the means to capture large amounts of data, often from several different types of transducers. With the advancements in microprocessors and computer processing, DAQ systems are now widely available at relatively low cost. While there are many types of systems, with some being more universal and some configured to target specific situations, there are common traits to all DAQ systems. Generally, a DAQ system consists of components that are integrated to:

- Receive signals from transducers (sensors)
- Condition signals for analog to digital (A/D) conversion, possibly providing isolation from unwanted signals, linearization, filtering, and amplification
- Convert signal to digital format for a computer
- Process, analyze, store, and display data as determined by software.
    - Acquiring meaningful data is the most important objective and it is important that the system capability be matched to the situation and the data requirements.
- The *resolution* of the system will be determined by the A/D converter's number of bits. For example, an 8-bit chip will provide a resolution of 256 (28) and a 12-bit chip provides a resolution of 4096 (212).
- The *sampling rate* of the system determines how accurately the data represent a rapidly changing input. If the system is rated with a 1 Hz sampling rate, the system is capable of 1000 scans per second or a 1 ms scan rate. Often DAQ systems will provide multiple channels, with one very high speed A/D converter shared between them. With these "multiplexed" devices the maximum scan rate must be divided by the number of channels. For example, if the DAQ device is rated at 100 kHz and has 16 channels, the actual scan rate available to each channel is 6.25 kHz. Generally the higher the sampling rate, the better the representation of the input from a changing process parameter; however, the sampling rate should be determined on the needs in the specific situation. For example, if a pressure transducer transmits an updated signal every 200 ms, there is no need to utilize a scan rate of much lower than that figure. The fastest scan rates also collect the largest amount of data, and there is no need to allocate memory space to unnecessary data.
    - The application software may be the most important component in any DAQ system (or closed-loop control system). There are systems available which have user interfaces which are designed to focus on specific processes and there are also a number of more generic systems which can be customized to meet specific needs. Of this group, several suppliers offer higher level programming tools and the technical support needed to make DAQ system development more accessible to engineers who are not experienced C or C++ programmers.

20.6 General Control Strategies: Extrusion Versus Injection Molding

- Temperature: There are many common characteristics of these two major manufacturing processes, such as the use of a heated screw and barrel to melt and move plastic to a point where it can be shaped. The output from the heater bands is managed with similar sensors and controls. However, even the control strategies for managing melt temperature for the two processes diverge, because with extrusion, the condition of the melt at the exit point from the barrel is generally considered to be the major determinant of product quality. While a uniform melt temperature is certainly important for injection molding, overall melt uniformity has not received the same degree of focus in injection molding control strategies. With extrusion, the maintenance of a constant temperature is so important that temperature controls such as *cascade controls* have been developed which use multiple TCs at different depths to detect a changing temperature more quickly and to predict the slope of the change and to interject a correction more quickly without overshoot of the temperature.
- Pressure: With extrusion, the main purpose of the drive system is to provide a steady supply of molten polymer to the die by maintaining a constant rate of screw rotation, in spite of variations in pressure, which result from viscosity changes due to different material lots or changes in temperature. One might monitor the amperage of the extruder's drive motor or pressure at the die to learn of changes in viscosity of the material and to provide a basis for adjusting the process to the changes. The objective of the drive mechanism in the injection molding machine is to deliver a precise dosage of molten material to the front of screw, which for every cycle will shift functions from a rotating melt

conveyance device to an injection ram. There is little or no interest in monitoring the amperage drawn by the motor to determine how hard it is working to prepare the next shot. Typically, a change in the injection pressure (the pressure required to maintain a specific ram speed) would be noted as an indicator of a change in material viscosity.

- Feed rates: With twin screw extrusion, much attention is paid to controlling the feed rate of the plastic to the machine, so as to minimize disruptions in the continuous stream of molten plastic to the die. With single screw extrusion and molding, gravity typically provides adequate control of the feeding process.
- Flow rates: With extrusion, the need for a constant flow rate to the die is so important that it has led to different approaches to the melting process, such as the development of the gear pump, a device that is positioned between the barrel endplate and the die. Its entire function is to deliver a constant melt stream to the die in spite of any changes within the barrel, regardless of the source of the change. Pressure variations in the barrel are absorbed in the gear pump which then delivers a constant flow rate at a constant pressure. There is no similar development in the molding area; however, the screw-fed plunger could be considered to be an analogous development, in that the objective is to better control the volume of each shot.
- Shaping: With both extrusion and injection molding, the melted plastic leaves the barrel of the machine and passes downstream into “shaping tools.” For the extruder, this would be the die and takeoff devices and for the injection molder, the mold. One common trait in this area is the very important objective of removing heat from the shaped plastic, so that the product can be removed from the machinery. In each case, water or air is provided for cooling and the process controls for the equipment would utilize similar common temperature control devices. In each case, coolant flow rate control is important. With each process, the rate of cooling designed into the process typically controls the maximum output possible, limiting the extruder output or the injection molding machines’ cycle time. The two processes differ greatly in how important characteristics of the product are integrated back into the process control system. With extrusion, the shape of the product is defined at the exit point of the die. The thickness, which is typically the critical control parameter, is determined by the opening of the die lips and the rate of the downstream takeoff equipment. With a constant output from the die, an increased takeoff speed results in a thinner product. If the die lips are opened, the product thickness is increased. In most extrusion processes the takeoff rolls provide the primary thickness control mechanism. With foam extrusion, die lip control is the most important factor. In each case, the measured product thickness is used as an input to determine the change in the process parameter, so product thickness is an integral part of the control loop. In injection molding, the main determinant of product quality has historically been considered to be the mold. The most important control function of the mold has historically been the cooling process, again with temperature control the most important control loop. It is generally agreed that the most important function of the molding machine relative to product quality is the delivery of a consistent amount of plastic to the mold, under consistent conditions. This has led to a focus on the development of controls with this objective in mind. As discussed elsewhere, the most important process control development of recent years is probably the adoption of servo valve and servo control velocity controls for injection. But even with these developments and with improved position, temperature, and pressure controls, most molding processes do not integrate real-time product variables into the control strategy. The major reasons for this situation are (1) product dimensions typically do not stabilize until hours and even days after molding, (2) injection occurs very quickly, and (3) the major process variables are all interrelated in a complex manner which is not broadly understood. Until fairly recently, most molders have felt that if the individual machine parameters can be stabilized with effective process control loops, there was no real need to integrate product data. In recent years, there has been a growing shift in thinking that real-time information from the cavity during the filling process could be used as an effective surrogate for product quality data. The focus has been on linking the cavity pressure and temperature to the part weight and dimensional results and then to the machine process parameters that control the mold filling process.

20.7 Process Control Applications Overview: Extrusion

In general, as extruded products have become more complex with more demanding polymers, multilayers, and overall thinner walls, control has become much more important. Each type of extrusion process has its own requirements, but there are several common control strategies. With extruders the single most important objective is to deliver a steady flow of material to the die. Temperature control and a consistent pressure are critical to avoid surging which results in a varying product and often reduced output. Therefore most extruders will have:

1. Temperature sensors on the barrel
2. Pressure transducers at the end of the extruder barrel pressure

3. Pressure transducer at barrel vents
4. Pressure transducer(s) in the die

There will be variations on this arrangement based on the particular situation; for instance, with foam extrusion, a pressure transducer would be placed before and after the entry point for the gas (physical foaming agent), to allow the operator to be sure that no gas-laden material moves backward in the barrel.

- Single screw extruder drive systems

While extrusion drive systems have evolved and can maintain speeds within 0.1%, the recent trend toward AC drives is being driven primarily by improvements in reliability and cost and not for better controls. The primary role of the drive system has remained the same, to maintain a constant speed. A constant speed is essential since any fluctuations in speed will result in throughput fluctuations and in changes to the melt temperature and pressure at the die. The main reason is that screw rotation speed causes frictional heating changing approximately with the square of the shear rate and this must be controlled or melt will overheat. Die melt pressure also increases with increasing screw speed that could possibly result in an extrusion instability known as surging. Surging is a phenomenon where the solid bed material in the feed throat area slips in the screw channel causing sudden drops in melt pressure at the die. This pressure then rebuilds itself slowly only to slip again when the pressure becomes too high. These disturbances of viscous heating and the surging may take hours to restabilize, so the time constants are too long to use screw speed as a final control element. Each extrusion process has its own maximum recommended die melt pressure. Rather than basing control loops solely on the source of the melt, the primary process control loops utilize downstream takeoff, die lip controls, and sizing units to control the dimensions of the cooled, stabilized product. Since the output of many extrusion processes, such as blown film and sheet, will ultimately be heat transfer limited, considerable effort is made in line design, with consideration of the base polymer(s) to be used, melt temperatures, capacity (lb or kg/h) sheet thickness or film bubble diameters, configuration, and temperature of the takeoff rolls. A PLC-based system is typically used to coordinate the material feed and blending system, the extruder itself, the takeoff system, winder, and/or stacker. SCADA technology (supervisory control and data acquisition) systems are often used to provide the human machine interface (HMI) to provide the means to monitor and control the process.

Common to most extrusion systems is the need to establish several important key control loops, with one loop set up to control variations in the machine direction (MD) and the other to control variation in the transverse direction (TD). Takeoff speed is used to control thickness in the MD while adjustments to the die lips are used to control transverse variations. In the early 1970s with blown film lines, the TD control was done manually where the operator adjusted die bolts to center the mandrel. Later, spiral mandrel dies gave better centering control and a segmented air ring further controlled TD variation. Air inflation of the film bubble controls the stretching in the TD. The nip rolls trap the air in the bubble and the film thickness and diameter stabilize unless there is a bubble break. The block diagram for the MD control loop for the blown film process is shown in Figure 20.5.

- Blown film systems: Early blown film systems introduced by LFE Corporation in the 1970s used a noncontact IR gauge to measure film thickness. A filter wheel allows the correct wavelength of light to hit the film. The light is split before it hits the film to provide a reference beam. The reflected light is compared to the reference beam to calculate the thickness of the film. The gauge is fixed at two possible locations: one is just above the frost line where the dimensions have stabilized. Originally, a rotating die was used, which slowly rotated about ¼ rpm so that a gauge scans around the bubble, providing the least DT. An alternate location was just before the collapsing nips but this location gave more DT and allowed more defective film to be produced in an upset. As bottom fed dies that rotate are difficult to maintain, later systems typically have a fixed spiral mandrel die and one rotates the nip rolls at the top of

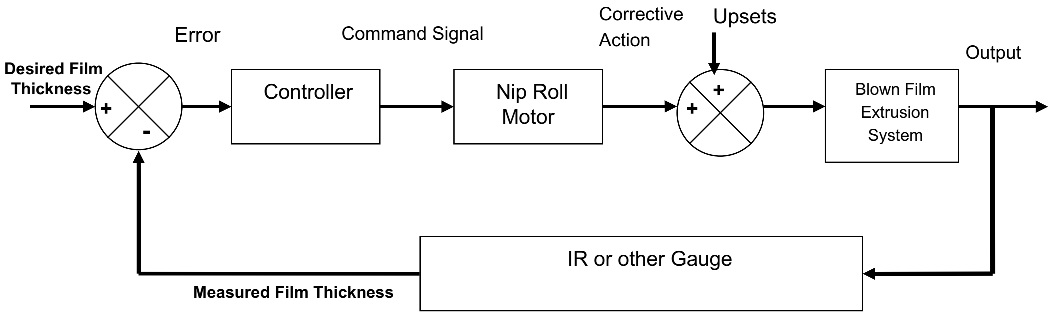


Figure 20.5 Block diagram for blown film MD thickness control.

the tower. A system by Gloucester Engineering is representative of the continuous advancements since the 1970s, with the introduction of internal bubble cooling, in addition to the traditional external bubble cooling, which increased throughput by 40%.

- A number of strategies have been developed on how to control the bubble diameter by controlling the airflow rate for internal cooling. Variable speed motors and variable vanes are both used, with the variable vane being the lower cost option. There are pros and cons to the two major methods. If a variable vane controls the flow rate on the supply side of the air, the choking of the air on the supply side causes a pressure drop and the air becomes heated, providing less effective heat transfer. If the vane is placed on the exhaust side, the filter which is also on exhaust side will clog up faster, with the contamination coming from out-gassed volatile plastics additives. Internal airflow via the vane control element can form a closed-loop for TD bubble control and also bubble diameter control. If a bubble break occurs, a control algorithm can program fast bubble reinflation. Noncontact gauges are preferred, particularly when running the newer metallocane tacky films. The film thickness is typically measured with beta or IR gauges. The gauges are mounted on top of the tower after the point where the bubble has collapsed. A "traverse nip" oscillates the collapsed film 360−720°. This allows the stationary thickness gauge to scan around the bubble pre- or postcollapse. A closed-loop set point control can be set up to increase or decrease the takeoff speed to control the MD thickness of the film.

Gloucester Engineering introduced control loops based on four ultrasonic gauges which are located at four corners of the blown film tower. The ultrasound bounces of the bubble and by a triangulation algorithm one can calculate the bubble diameter and whether the bubble is centered and circular. This system, based on Polaroid's "autofocus" technology, measures the distances from the gauges to the bubble and by triangulation, the bubble diameter and its center is constantly calculated. These sensors also will detect a break in the bubble and an algorithm calls for rapid reinflation of the bubble. The closed-loop control is set up to control the bubble diameter, where the blower motor is used to control the airflow rate.

- Web processes: Processes such as chill roll film or sheet extrusion, extrusion coating of paper, foils, or fabric, and lamination are all web processes. Thickness is typically the critical quality attribute, and the primary means of control is the control of the die gap, where each die bolt is adjusted by heating the die bolt with a cartridge heater to cause a smaller gap. Conversely, if sheet is too thin at a given die bolt location, the heater is turned off and a solenoid air valve blows air onto the bolt for cooling to contract the bolt and open the gap. The sheet thickness can be measured by various thickness gauges, such as the air cushion capacitance sensor and the laser caliper sensor. These devices locate the two surfaces and determine the distance between them. Both designs are fairly complex and they must be located on both sides of the sheet. Mass measuring devices, such as radiation gauges, are generally preferred. Gamma ray transmission gauges and beta transmission gauges work similarly in that both deliver energy through the sheet. The amount of energy that is received on the other side of the sheet is used to determine the sheet thickness. In this case, a detector is used to measure the radiation that has passed through the web. The real density (mass/area) determines how many particles pass. A different mode of measurement uses a back splatter gauge. An emitter and detector of the gamma or beta particles are mounted on the same side of the web. As the aerial density increases more particles are reflected (back scattered) to be measured by the detector. Gamma ray gauges emit very high energy atomic particles and beta gauges emit lower energy particles. X-ray gauges use high energy electrons and do not require government licensing, but they are sensitive to the composition of the plastic and are affected by additives. Beta particle transmission gauges are less sensitive to the chemical composition of the sheet but must be licensed and they must also be frequently calibrated due to the short half-life of the isotopes used. Gamma backscatter gauges are commonly used with extrusion processes. These gauges measure the amount of the gamma particles that are bounced back off the sheet; less radiation coming back means a thinner sheet. One major advantage is that the gauge is located on only one side of the sheet.
- Extrusion coating and laminating applications: In these applications, thicknesses are often determined by doing same spot measurement. The thickness of the substrate is measured first. The computer stores the thickness value using a coordinate system. After coating the same spot is measured again; an algorithm calculates the total thickness and the thickness of the coating layer.
- Pipe extrusion and ultrasonic gauging: Ultrasonic gauges are typically used to measure wall thickness, typically done through water to avoid exposing the transducer to the high temperature. The sound transmission is also much better through water which is particularly important for small bore tubing. Ultrasonic gauging is similar to sonar in that the time for sound to reflect from the inside and outside walls and return measures the distances and the resultant thickness. If four transducers are placed at locations 90° apart around

the perimeter, triangulation can be used to calculate the outside diameter (OD), inside diameter (ID) wall thickness, and the concentricity. A closed-loop is set up to increase or decrease the puller speed to regulate the MD wall thickness. Concentricity can be controlled in an open-loop fashion with a self-centering mandrel in the die or by having an operator adjust the die bolts in the center of the mandrel.

For very large diameter pipes, the pipe is cooled by water spray and an ultrasonic gauge may be traversing the perimeter. Water is pumped to act as a coupling fluid between the gauge and the pipe wall.

For very thin or small diameter medical tubing, ultrasonic gauges reach a practical limit and in those instances, laser and light gauges become important. Laser beams, which use coherent light and diffuse less in air, are more accurate. A limitation of optical gauges is the inability to measure the inside diameter.

Medical tubing can be quite complex and typically requires a very stable output, with precise alignment of the extruder, cooling water bath and takeoff system. In many cases, a gear pump is used to pressurize the melt going to the die to further stabilize the output and reduce surging of the extruder. The combination of the extruder and the gear pump leads to a higher order control system which is more complicated but is possible with microprocessor control. Medical tubing processors (e.g., Harrell) [11] have developed algorithms that predict the mass output and wall thickness for multilumen medical catheters. Programmed start and stop sequences are needed for safety and equipment protection. A die rupture disc must be installed to protect operators and equipment.

- Blow molding parison programming: In extrusion blow molding bottles and containers of complex geometry are produced. To compensate for the variation in bottle geometry and also to compensate for parison droop due to gravity in the case of large bottles, the molten parison is programmed to change its wall thickness as the length of the parison increases. The parison is a molten tube of plastic that emerges from the die head. Parison wall thickness can be programmed so that the bottle wall thickness stays uniform for complex shapes for containers up to 55-gal capacity.

20.8 Process Control Applications Overview: Injection Molding

Injection molding is based on injecting molten plastic into a mold cavity where the material cools to a point where the part can be ejected. The dimensions and to some extent the properties of the molded part depend on the amount of plastic that has been forced into the cavity and the pressure and thermal history that the part experiences while in the mold.

It is generally accepted that the overall control objective of injection molding is to deliver a consistent amount of plastic to each cavity with every shot. Shot size is one of the three primary process areas to be managed in injection molding, along with, injection velocity and cavity packing characteristics. The earliest screw-based injection molding machines for thermoplastics followed the thermoset process with a transfer plunger, incorporating an extrusion screw that delivered a pre-set set shot size to a transfer plunger. This plunger-based injection process provides a very consistent shot size and the concept has been reintroduced by several machinery makers, with particular focus on molding small and very precise products. Reciprocating screw injection molding machines, developed primarily for speed, rely on a check ring design to collect and separate the next shot at the front of the screw tip. The timing and completeness of the closing of the shut off ring determines the next shot size. This design introduces a degree of inconsistency that has affected the ongoing development of controls for the molding process. The possible variation in available shot volume, along with the need to adjust for other factors that can affect melt viscosity, has led to processors basing control strategies on the actual experience of the polymer in the mold, since some of those factors, such as molecular weight of the polymer or a variation in additives package or the sizes and exact percentage of a regrind mix are beyond the control of the processor.

With consistent part dimensions typically being the major quality objective, the management of shrinkage becomes a primary focus. The objective is to develop a process with a consistent shrinkage, without introducing excessive molded-in stresses into the molded part. There are two ways to compensate for shrinkage that occurs inside the mold and after ejection from the mold. The first way is to make the cavity larger to compensate for the inevitable shrinkage, utilizing shrinkage rates that are experimentally determined for each resin. A second way is to force additional melt into the cavity, after the initial filling, to compress the melt and compensate for some of the shrinkage. This is accomplished by using a melt cushion. The majority of the plastic, for example 95%, is delivered to the cavity by the screw/check ring combination acting as a ram, utilizing velocity control. The remaining plastic is delivered with a pressure-based control loop.

The exact shot size delivered to that point will have been determined by the “shot size.” This starting position is accurately controlled by a linear position transducer. The screw will have arrived at that preinjection point by turning the screw at a set RPM and under back pressure which the operator establishes as control set points.

For the injection step, two control loops are typically used. The screw will first travel until a transfer point is reached where control switches from ram velocity control to pressure control. Methods to switch from velocity control to pressure control can use the following modes: (1) time, (2) screw position, (3) hydraulic pressure, (4) cavity melt pressure, or (5) other cavity event detectors. Time is generally considered to be the worst method since it does not relate to what is happening in the cavity. Monitoring cavity melt pressure has generally been accepted as the best method but new transducers such as fast response TCs are also gaining acceptance.

The heart of the control system for the past 30 years has been a fast acting flow divider servo valve [3]. However, starting in the late 1990s all-electric machines have been introduced that show great benefit for energy savings. In these machines servo motors have replaced the servo valves. Servo control maintains a constant ram speed regardless of the required pressure (to an operator established pressure limit). The ram speeds that have been established may be a constant speed or be set to a profile, with different speeds set for different potions of the linear travel. The objective is to control the velocity of the melt front and the shear rate during the filling step. The velocity may be slowed at the beginning as melt goes through the gate to prevent jetting (squirting of the melt, like a worm) after which the velocity is typically increased, which increases the shear rate and reduces the melt viscosity so that the cavity can be filled with a reasonable pressure drop. Toward the end of fill the velocity is again decreased to prevent any flashing of the mold and to assure a smooth transition from fill to pack to hold. In most commercial machines 5–10 or even 20 velocity settings can be programmed over the screw travel distance.

Velocity control is based on utilizing two transducers to calculate the ram velocity. A position transducer such as a rectilinear potentiometer measures the ram position while a digital clock based on an oscillating quartz crystal keeps the interval time and the microprocessor calculates velocity as distance divided by time. The calculated velocity is compared against the servo input velocity to generate an error signal on which the controller acts to make a correction.

Then, at the linear set point usually called the transfer point, the molding controller transfers from velocity control to pressure-based control. Here, the servo valve is used to maintain a constant pressure as has been established as a set point by the operator. This is the segment of the filling process where the last portion, typically 5% or less, of molten plastic is forced into the cavity as the initially delivered material shrinks. Plastic will continue to enter the cavity until the gate freezes off, usually in 1–5 seconds. The screw then stops moving forward. The difference between the stop position and the zero screw position is called the cushion. This is an uncontrolled process parameter that is a result of other controlled parameters. Cushion is often monitored as an indicator of the consistency of the process. A changing cushion is often an indicator of a wearing or inconsistent check ring function. The operator will experiment with pressure levels and the time to hold that pressure level to determine the most effective pack pressure and hold time. For cold or hot runners with thermal gate control, a gate freeze-off study is typically done to determine when material will no longer pass through the gate. In the case of hot runner valve gates a similar study is done to determine what the most effective pack and hold set points are. Note that since plastics are a bit compressible, it is certainly possible to over-pack a cavity. During the cooling portion of the cycle, the plastic continues to shrink and the pressure in the cavity decays to 1 atm at which point the part actually shrinks away from the cavity wall.

Essentially, all molding machine controllers provide for the setting of the transfer point (switchover from velocity control to pressure-based control) based on the linear position of the screw. This control strategy is adequate for many molding processes and is the most common method used. However, this control model also has major limitations in that the pressure feedback that controls the process is based on what the screw (acting as a ram) experiences, measured by monitoring hydraulic pressure or with a load cell and not what the polymer melt experiences in the mold.

As product designs, such as CDs and DVDs, challenged the limits of the injection molding process, the need for cavity-based control has been more recognized and process development methodologies have become more sophisticated. One major shift in control strategies that has resulted is the increasing use of cavity sensors. One application of cavity sensors is to use them to provide the set point for the transfer from velocity control to pressure control. While a detailed study is beyond the scope of this section, the basic concept is to trigger the transfer point based on either a particular level of pressure at a given location in the mold or with the thermal confirmation of the location of the melt front in the mold. The melt pressure transducer or thermal sensor is placed in the cavity, preferably close to the end of fill. For the pressure transducer, the melt pressure is monitored and compared against the set point and the transfer to pressure control is initiated. Another control model would be to monitor the actual cavity pressure and to maintain a given level of applied pressure until the melt pressure actually begins to drop in the cavity as the part cools and the gate has frozen. A number of different pressure transducers have been used for melt pressure. The early gauges were strain gauges that were mounted behind an ejector pin or a dummy pin. Later, piezoelectric transducers were introduced that show better dynamic response which is required in injection molding. These sensors are being used in the traditional position behind an ejector pin and also indirectly in the mold cavity. Today one finds most transducers in injection molding are piezoelectric while for extrusion applications one finds the strain gauge type.

An alternative approach to monitoring with cavity sensors is to use temperature sensors located in the cavity to monitor the location of the melt front relative to time. In this case, the control loop that manages the transfer point is based on position of the melt front [8].

With all transfer point control strategies, the machine operator establishes the final process adjustments to make the part dimensions come out correctly. In the case of the cavity-based sensor input providing the transfer point control, subtle changes in material viscosity or machine conditions can be compensated for with equally subtle changes in the transfer point.

- Temperature in hot runners: Hot runner systems have many advantages such as smaller shot sizes, more choices for gate locations, shorter cycle times, lower injection pressures, lower clamping forces, lower labor costs due to automation (self-degating and parts handling), and overall better part quality. The melt temperature is controlled all the way to the gate whereas in a cold runner system the melt temperature control stops at the nozzle tip. A balance of fill analysis is a measure of process consistency for multicavity tooling which to a large degree reflects the melt temperature variation or lack thereof. In a multicavity cold runner system the balance of fill is considered adequate if it is within 10% for a 16 cavity tool. In the case of a hot runner system a balance of fill within less than 2% can be achieved. To accomplish this melt temperature is controlled more closely. One approach is to use PID^2 controller. Here one measures not only the first derivative of the error but also the second derivative, which tells whether the error is at a maximum or minimum and whether the error is increasing or decreasing with time. This allows for closer control. A second method of control is the use of heat pipes which run parallel to the hot runner melt channel and keep it at a more uniform and constant temperature. This system is used by Synventive® hot runner systems. The heat pipe is a closed tube with a working fluid (water) and a wick inside. At a hot spot next to the tube the water evaporates to steam and at a cold spot the steam condenses. The wick transports the liquid water back to the hot spot where it was depleted. Also, the steam travels due to a minor pressure difference to the cold spot where condensation slightly lowers the pressure. For a closed tube the pressure and temperature are not thermodynamically independent of each other and a change in one fixes the value of the other according to the Gibbs' phase rule from thermodynamics. Heat pipes in combination with titanium load washers which form dead air gaps inside the hot runner manifold allow for good insulation to control heat losses. Titanium is a very strong lightweight metal with much lower thermal conductivity versus steel. In addition, the outside of the hot runner manifold is clad with an insulation sheet at the place where the manifold contacts the stationary platen which prevents heat losses into the stationary platen that could damage the platen and molding machine.

20.9 Process Development Tools

- Design of experiments in injection molding

As noted in the introduction, while 97% quality output and 5% scrap rates were acceptable in the early 1970s, this defect rate of 30,000 parts in a million is far from today's benchmark of the six sigma quality level, which relates to 99.999998% quality or 3.4 ppm defects. These levels were not possible in any industry without the use of SPC, which has helped to redefine quality. As stated earlier, however, SPC alone cannot produce higher quality products. Key process parameters which are linked to important product parameters need to be understood and, if possible, controlled. A robust process is defined as one where one still makes good product even as process conditions, resin properties, and the environment change. To link robust process controls to the product quality requires a well-developed understanding of the process. In injection molding, virtually every part, mold, material, and machine combination is unique. The large number of processing variables appears to affect the product outcomes independently, but in fact they often act interdependently. The non-Newtonian, viscoelastic behavior of plastics ensures that these cause and effect relationships are typically nonlinear and complex. In short, the process−product relationships are very difficult to understand completely.

Designed experiments are statistical tools that were developed and first applied to industry in the 1940s to help sort out complex relationships and to make them more manageable. A designed experiment (DOE) is run to determine which process variables have the greatest effect on the quality variables of interest [12]. Then the SPC control plan is implemented, with a focus on these process variables. This leads to a molding area diagram (MAD) that delineates the process boundaries. The goal is to find the process settings where the machine produces good parts even as the conditions beyond our control change. Taguchi called these uncontrolled factors "noise." As a first approximation to determine the important factors (variables), Taguchi proposed a series of experiments in which he deemed interactions between the factors to be unimportant. This is accomplished mathematically by choosing special mathematical arrays (matrices) in which the interacting terms cancel out. These are called square (orthogonal) arrays. For example, with traditional injection molding the following variables and ranges have been demonstrated to be important factors:

Melt temperature (±15 to 25 °F from nominal)

Injection speed (fill time) (±approximately 30% from nominal)

Packing pressure (±approximately 100 psi hydraulic pressure from nominal)

Mold temperature (±approximately 10 to 20 °F from nominal)

For each variable a low and a high setting is chosen. The desired result of the DOE is the "response." The response is measured for each set of conditions and an "ANOVA" (analysis of variance) is calculated. This tells the importance of each factor and how it influences the response. Of course, other process parameters and different ranges may prove to be more effective in different situations.

The DOE yields the following benefits:

1. Identify the process variables that have the most effect on part quality and part dimensions.
2. Process adjustments can be made to assure consistent part quality.
3. One can use the data as a guide to help establish the optimum process conditions for the production settings.
4. One can identify how "robust" the process is to process disturbances.

The goal of the DOE is to design a product, mold, and process that is least influenced by the many sources of variation which are not controlled. Similar DOEs can be run for all major plastics processes.

- Statistical Process Control (SPC)

After the DOE, SPC is implemented to the following:

- Observe and record the patterns of process variation
- Make adjustments to the process before defective parts are produced
- Use statistics to determine acceptable limits of variation[12]

Thirty years ago the industry controlled the molding process to ±3 sigma limits. Today the industry strives to control to ±6 sigma limits to produce fewer than three defective parts in a million. How close one is toward that goal is determined by calculating the CP (process potential) and CPk (process capability). CP calculates the ratio of the process specifications against the estimated process variation as shown by the equation below.

$$C_p = (\mathrm{USL} - \mathrm{LSL})/6\,\sigma$$

where σ is the estimated process standard deviation.

Ratios greater than 1.0 are favorable but the mean must be centered between the specification limits. Next, one calculates the CPk which determines if the process is centered.

$$\begin{aligned}\mathrm{Cpk\ (lower)} &= (\mu - \mathrm{LSL})/3\,\sigma \text{ and } \mathrm{Cpk(upper)}\\ &= (\mathrm{USL} - \mu)/3\,\sigma\end{aligned}$$

when CPk (lower) = CPk (upper) the process is centered. The minimum of the two CPk values is used. CPk values greater than 1.0 are favorable in the sense that one can control to ±3 sigma limits and as CPk approaches 2.0 one approaches control to ±6 sigma limits. This desire to control to ±6 sigma limits does not happen by itself. A painstaking dedicated task called continuous improvement (Kaizan) is used to improve the product design, the mold design, the process control, the raw material supply, and the workforce training to approach CPk2.

- Use of advanced statistical tools

SPC has become an effective tool for injection molding, with early application limited to monitoring product measurements but more recently being applied to multiple process parameters. Multivariate analysis (MVA) is an extension of SPC techniques used to deal with large data sets [13−15]. These tools take advantage of modern computing capabilities to analyze multiple product and process variables simultaneously. It is telling that even with the most advanced computers and machine controls, it is virtually impossible to monitor all the process variables and their interrelationships. Therefore, just as in effective SPC-based controls, the selection of the most important variables, called the key process variables (KPV), is extremely important. A multivariate model of a known acceptable process window is developed, usually with DOE techniques. Then a multivariate comparison and analysis is performed on each cycle against the known model and parts are accepted or rejected based on the comparison to the model. While still in early development, this open-loop approach, along with modern fast response sensors, has promise to provide quality improvements based on early fault detection. MKS Instruments® has offered a commercial system based on MVA. The system acquires machine parameter data such as injection pressure, ram velocity temperatures, and screw position for each shot and the variables are compared in real time to a historical model that represents ideal processing conditions. When the various conditions are all within their desired ranges, all molded parts should be good. If the process drifts out of statistical control, MVA indicates which variables are out of tolerance and can rank the variables by order of significance to the problem.

Another process monitoring technique which is based on a statistical method called "correlation technology (CT)," has been offered commercially by Algoryx [16]. CT is based on the idea that although the relationships between the causes (machine settings) and effects (dimensions) may be too difficult to discern, the relationships between physical dimensions of the finished parts should always be related and consistent within a normal process window. The technique is based on the use of proprietary algorithms to characterize the dimensional relationships and to identify a lead "predictor dimension."

20.10 Conclusions

While new techniques continue to be studied and tested, there is a general acceptance that to be a successful processor over the long term one needs to understand the process as well as one can develop and execute an effective monitoring and control strategy. To survive and flourish in the plastics industry manufacturers simply cannot afford to rely on a black art approach to the plastic manufacturing processes.

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21 Polymer Stabilization

Pieter Gijsman
DSM Research, P.O. Box 18, 6160 MD Geleen, The Netherlands

21.1 Introduction

There are many plastics available that differentiate from each other by molecular parameters as, for example, (co-) monomer composition, molecular weight, molecular weight distribution, chain branching and end groups, added fillers (e.g., glass, (nano) clay, talcum), pigments, and other inherent properties improving additives. All these factors are, during polymerization and processing, well controlled to produce materials with the desired properties. However, once these plastics are exposed to shear stress, heat, light, air, water, radiation, or mechanical loading, chemical reactions can be initiated that lead to changes in molecular weight and chemical composition. In practice this might result in an undesired change (degradation) in appearance (e.g., gloss, texture, and color) and mechanical properties (e.g., tensile, flexural, or impact strength). The terminologies used to describe the type of degradation are related to the environment to which the plastic is exposed.

During processing, thermoplastic polymers are exposed to harsh environments. Temperatures are relatively high (above the melting or glass transition temperature of the polymer), in many cases a lot of shear is involved and although the majority of processing equipment is closed, oxygen and water can play an important role too.

Although the conditions plastics are exposed to, in their applications, are less harsh than during processing, the times they are exposed to these conditions are much longer. Depending on its application requirements of life times vary from months to hundreds of years (Table 21.1), causing that in-service degradation of plastics is important too. The type of in-service degradation also depends on the environment to which the plastic is exposed.

For outdoor applications, sunlight plays an important role. This type of degradation is defined as UV degradation. Important plastic applications that suffer from UV degradation can be found in cars, for example, polypropylene (PP) bumpers and dashboards, polyamide (PA) or polyester (PES) mirror housings, and rubber window sealings; in the building industry, for example, polyvinylchloride (PVC) window frames, polycarbonate (PC) roofing, and PP stadium seats; in agricultural applications plastics are used as greenhouse cover or as ground cover to increase the growing season; and in many other applications such as bottle crates, containers, and robes.

Table 21.1 Life time requirement for several application areas

Application area	Life time requirement
Packaging	1 year
Automotive	15–20 years
Building	50 years
Civil Engineering	“Eternity” (200 years)

If sunlight does not play an important role, such as in under the hood applications and in geotextiles, plastics degrade too. In this case the degradation is a result of long-term heat aging (LTHA). This type of degradation is called thermooxidative degradation.

To make it possible to process plastics and to make them useful for the above-mentioned applications, most plastics need to be protected. This can be done by adding stabilizers of different types, which is the subject of this chapter. The type of stabilizer necessary highly depends on the environment against which the polymer has to be protected. The definitions used to describe the different types of stabilizers are derived from the environment they have to be protected against (e.g., processing stabilizers, UV stabilizers, and long-term heat stabilizers) as well from their function (e.g., antioxidants against oxidation and UV absorbers to absorb the harmful radiation of the sunlight).

The performance of stabilizers is not only determined by its effectiveness to protect the polymer against degradation, but also by its physical properties, color, discoloration, interactions with other additives, chemical resistance, dosability, toxicity, food approval, and price.

In this chapter an overview is given of the most important factors that determine the use of stabilizers, their mechanism of action, as well as the influence of other factors on the choice of stabilizers. As stabilizers prevent degradation of plastics, it is inevitable to give a brief overview on the degradation of polymers before discussing the mechanism of action of stabilizers.

21.2 Degradation Chemistry

In the degradation of polymers during processing as well as in service, several mechanisms play a role. The most important degradation mechanisms are shown in Table 21.2.

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Table 21.2 Most important plastic degradation mechanisms

Degradation type	Main rate determining parameters
Thermal	Temperature
Thermo-oxidative	Temperature and oxygen
Photolysis	Light
Photo-oxidation	Light, Oxygen and Temperature
Hydrolysis	Water and Temperature

It has been shown that in an environment without oxygen, polyolefins hardly degrade [1—3]. In an inert atmosphere, PE and PP start to decompose above 350 °C [4,5]. However, in their applications the plastics are normally in contact with air. Oxygen in the air leads to chemical reactions and degradation of plastics. For many polymers it is shown that the observed loss in properties correlates well with their reaction rate with oxygen [6,7]. For polyolefins oxidative degradation is important not only in their application, but also during processing. Although normally plastics are processed in closed processing equipment that excludes oxygen, a study by Epacher et al. [8] showed that the oxygen content of polyethylene that is fed to, for example, an extruder is high enough to cause oxidative degradation. For polymers with lower oxygen content (e.g., PAs and PES), oxidative degradation during processing is less important. Degradation of these polymers during processing is a thermal process. Photolysis is a chemical reaction in which absorbed light directly leads to degradation of the polymer. It was shown that the outdoor degradation of PBT is due to this reaction [9,10]. However, for the majority of the plastics, photooxidation (due to light and oxygen) is the most important outdoor degradation mechanism. Hydrolysis is a reaction with water from the environment; this degradation mechanism plays an important role in polycondensates (e.g., PAs, PES, and PCs), which causes that these materials have to be carefully dried before processing. Other factors that can have an influence on degradation are air pollutants as, for example, singlet oxygen, ozone, and NOx.

21.2.1 Thermal Degradation

Polymers can degrade due to exposure to high temperatures. For a number of polymers processing temperature can be that high that thermal degradation can take place. However, this is not the case for polyolefins [4,5]. In an inert atmosphere these polymers have to be exposed to temperatures far above their processing temperature to get significant degradation. For PAs and PES, thermal degradation during processing can be relevant, although in most cases the amount of degradation is that limited that it is not important. PES based on terephthalic acid and an aliphatic alcohol can show thermal degradation. In this case the ester linkage is transformed in an acid and an olefinic end group [11—13]. During processing, adipic acid-based PAs can give a chain cleavage reaction leading to primary amines and substituted cyclopentanone end groups [14—16].

For chlorine containing polymers, as PVC, thermal degradation during processing is important. In this case HCl is split off the chain, which catalyzes further decomposition [17—21].

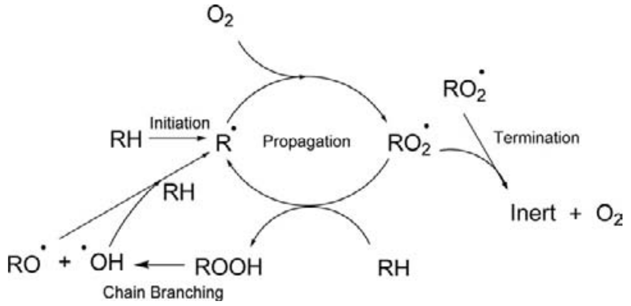
21.2.2 Thermooxidative Degradation

The thermooxidative degradation of many plastics can be described with a mechanism developed by Bolland and Gee [22,23] to explain the thermal oxidation of rubbers. Several polymer-specific variations on this mechanism have been proposed [24—33]. An example of this thermooxidative degradation mechanism is shown in Scheme 21.1.

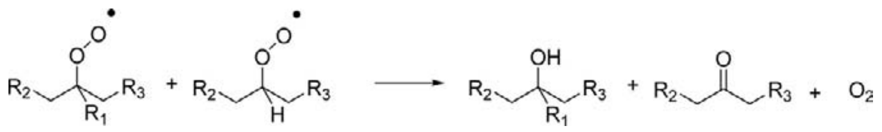
In the first stage, the initiation reaction, free radicals are generated. It is assumed that these radicals are formed thermally or through the combined action of heat and mechanical stress, although this reaction has not been fully clarified yet. The second stage is the propagation reaction. This reaction has been studied in more detail [34—43]. The rate of the reaction of oxygen with alkyl radicals is very high; therefore, the rate of the propagation is largely determined by the ease of hydrogen abstraction in the second step of the propagation. Polymers having a lower carbon—hydrogen bond strength form more stable radicals and consequently these substrates are more oxidizable. The propagation reaction is a repeating reaction—the average number of propagation cycles (kinetic chain length) is polymer dependent. For polyolefins it has been reported to vary between 800 and 1.75×10^4 [39].

The autoacceleration of oxidation is ascribed to hydroperoxide decomposition reactions described in the chain branching reaction. The hydroperoxides formed in the propagation reaction decompose to form radicals, leading to an increase in the oxidation rate. The decomposition of hydroperoxides can be described by several mechanisms [7,44—49].

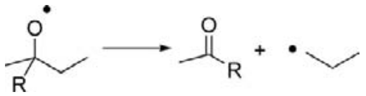
Termination reactions are bimolecular. In the presence of sufficient air, which normally is the case during long-term degradation of polymers, only the reaction of two peroxy



Scheme 21.1 General proposed autooxidation mechanism for polymers (R = polymer chain, H = most labile hydrogen).



Scheme 21.2 Termination according to the Russel mechanism.



Scheme 21.3 β-Scission reaction of alkoxy radicals.

radicals has to be considered [1]. The exact reaction depends on the type of peroxy radical present. For tertiary peroxy radicals (as present in PP) the termination reaction is expected to lead to dialkyl peroxides and oxygen [24], although oxidation experiments of PP in mixtures of $^{32}O_2$ and $^{36}O_2$ did not result in $^{34}O_2$, which shows that the importance of this termination reaction is limited [50]. Secondary peroxy radicals (as formed in PE) terminate according to the Russell mechanism to an alcohol and a ketone (Scheme 21.2) [51]. During processing the amount of oxygen available is limited implying that reactions between other radicals than peroxy radicals can cause termination too.

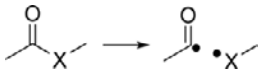
The most important side reaction is the β-scission reaction of alkoxy radicals (Scheme 21.3). This reaction causes chain cleavage resulting in a decrease in mechanical properties.

21.2.3 Photolysis

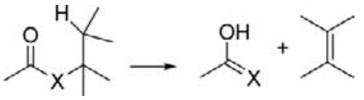
If a polymer contains structures that can absorb terrestrial sunlight wavelengths (>290−300 nm), which leads to chemistry causing changes in molecular structure, photolysis can be an important degradation mechanism. Norrish I and II of carbonyl, ester, or amide containing polymers (e.g., oxidized PE, PES, and PAs) and the photo-Fries reaction in bisphenol A polycarbonate (BPA-PC) are well-known photolytic reactions [52]. These reactions are shown in Schemes 21.4−21.6.

21.2.4 Photooxidation

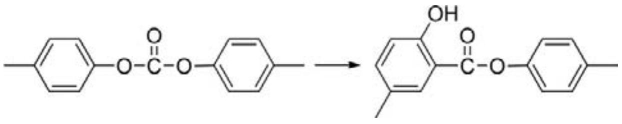
There are many similarities between the above-mentioned thermooxidation (Scheme 21.1) and the photooxidation mechanisms. A difference can be found in the initiation reaction. In photooxidation, initiation reactions are a result of photolytic reactions. If the polymer contains carbonylic groups the Norrish I reaction (Scheme 21.4) can be the initiating reaction. In the case of polyolefins it is postulated that due to processing or storage formed hydroperoxides or ketones initiated the photooxidation [53,54]. However, for well-stabilized polyolefins initiation by charge transfer complexes between the polymer and the oxygen was shown to be important [55,56]. For BPA-PC the photo-Fries reaction (Scheme 21.6) was postulated as an oxidation initiation reaction [57,58], but it was shown that if this polymer is irradiated with terrestrial sunlight wavelengths (>290−300 nm) this reaction does not lead to the initiation of the oxidation of BPA-PC. It was shown that other initiation reactions are more important [59]. Another difference between thermo- and photooxidation is the decomposition rate of hydroperoxides [53], which is catalyzed by UV light.



Scheme 21.4 Norrish I reaction of carbonyl (X=CH2), ester (X=O), or amide (X=NH) containing polymers.



Scheme 21.5 Norrish II reaction of carbonyl (X=CH2), ester (X=O), or amide (X=NH) containing polymers.



Scheme 21.6 Photo-Fries rearrangement reaction in BPA-PC [52].

21.2.5 Hydrolysis

For polycondensates hydrolysis can be an important degradation mechanism too. Especially during processing polycondensates can easily hydrolyze, which causes that the majority of the polycondensates are carefully dried before processing. In use hydrolysis of polycondensates with water from the environment can be a degradation mechanism too. Especially for aliphatic PES this is a well-known degradation mechanism [60−62].

21.2.6 Other Degradation Mechanisms

It was postulated that the initiation of the oxidation might be due to tropospheric ozone [63], but this influence was not found when stabilized PP samples were subjected to tropospheric concentrations of ozone [64]. In the 1970s efforts were made to relate photooxidation of polymers to singlet oxygen [65]; however, later this reaction was only seen as important when singlet oxygen sensitizing molecules (e.g., pigments) are present, because the natural abundant singlet oxygen concentrations are too small to play an important role [66,67]. Other gaseous pollutants that can influence the stability are NOx and acidic or acid forming species. NOx can react with PAs, which can cause degradation [68,69], but the most well-known reaction of NOx is its reaction with phenolic antioxidants (see Section 21.3.1). Acids can induce hydrolysis of polycondensates but can also deactivate hindered amine light stabilizers (HA(L)S) (see Section 21.3.3).

21.3 Stabilizers

As shown above polymers degrade as a result of different chemical reactions. If the degradation is accelerated by chemicals that are present or that are formed during degradation, it is possible to reduce the degradation rate by adding substances (additives) to the polymer that reduce this catalytic effect or that prevent the formation of accelerating species. These substances are called stabilizers. There are many different stabilizers; their use and activity depend on the circumstances in which they are applied.

Primary antioxidants are radical scavengers such as phenolic antioxidants and aromatic amines. They act by interrupting in the oxidative degradation cycle (see Scheme 21.1) by scavenging radicals. Their main use is as processing or long-term heat stabilizer.

Secondary antioxidants act against oxidative degradation by decomposing hydroperoxide. Important classes of secondary antioxidants are phosphites and thioethers. Against degradation during processing, mainly phosphites are used, while as long-term heat stabilizer thioethers as well as phosphites are used—which one is most effective depends on the polymer in which they are used.

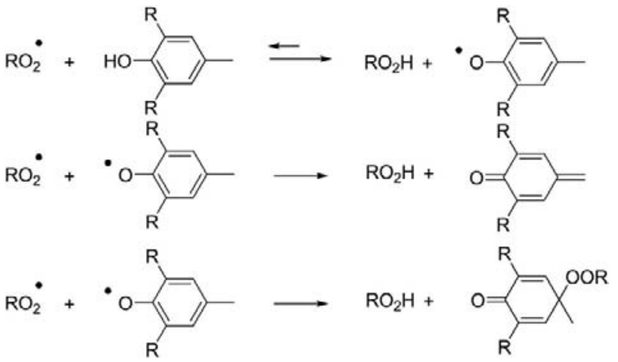
HA(L)S were originally developed as light stabilizers and can act in different ways against outdoor degradation; however, the same molecules are more recently introduced as long-term heat stabilizers [70–74]. This caused that their abbreviation changed from HALS into HAS.

Other examples of stabilizers that can be used against outdoor degradation are UV absorbers and quenchers.

In the following the mechanism of action of the major classes of stabilizers is described. In Appendix 1 an overview of the chemical structures of in-use stabilizers is given.

21.3.1 Primary Antioxidants (For Commercial Examples, See Appendix 1)

The most important radical scavengers are the phenolic antioxidants. They convert peroxy radicals into hydroperoxides and are themselves converted to phenoxy radicals. The phenoxy radical can in different ways react with another peroxy radical resulting in nonradical products (Scheme 21.7). However, phenoxy radicals formed are also able to abstract a hydrogen from the polymer chain and in this way initiate a new oxidation cycle. The majority of the phenolic antioxidants contain two tertiary butyl groups on the 2 and 6 positions; these groups are able to shield the formed phenoxy radical (sterical hindrance) and prevent initiation of a new oxidation cycle. However, introducing sterical hindrance also causes a decrease in radical scavenging rate. Reducing the sterical hindrance results in an increased radical scavenger activity, but the formed phenoxy radicals can initiate new oxidation cycles. The ratio between the increased radical scavenging rate and the initiation rate will determine the effectivity of an antioxidant.

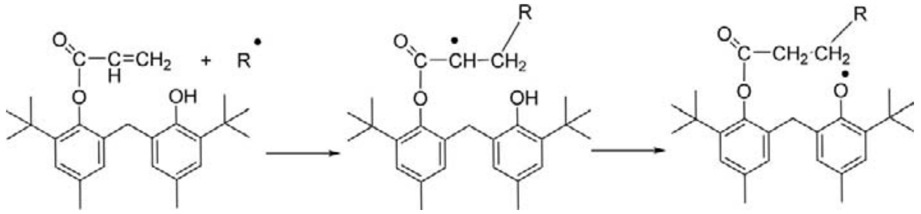


Scheme 21.7 Reactions of a phenolic antioxidant with peroxy radicals.

Although phenolic antioxidants mainly react with peroxy radicals, in oxygen-deficient conditions (like processing) the lifetime of alkyl radicals can be long enough to be scavenged by very reactive phenolic antioxidants. In this case less sterical hindrance can lead to higher stability. However, in oxygen-rich conditions (LTHA) the lifetime of alkyl radicals is shortened enormously, which makes that alkyl radical scavenging becomes less important. In this case the initiation reaction by phenoxy radicals can become important and less hindered antioxidants perform worse. Vitamin E is less sterical hindered than the majority of the phenolic antioxidants, which causes that vitamin E is under oxygen-deficient conditions (processing conditions) more effective than more hindered phenolic antioxidants [75], while vitamin E is much less effective as long-term heat stabilizer (oxygen-rich conditions). Besides the sterical hindrance the higher activity of vitamin E is also subscribed to the oxygen substituent para to the OH [76].

Another way to make phenolic antioxidants reactive toward alkyl radicals is to introduce a more reactive group. It is shown that phenolic antioxidants with an unsaturated side chain can scavenge alkyl radicals [77]. A phenolic antioxidant containing such a moiety was developed by Yachigo et al. (Sumitomo Chemicals) [78,79]. For its mechanism, see Scheme 21.8.

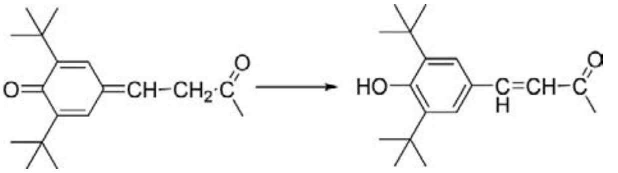
Scheme 21.8 Alkyl radical scavenging involving intramolecular hydrogen shift.



In doing their job phenolic antioxidants are converted; each phenolic group can scavenge at least two radicals (see Scheme 21.7). However, the chemistry is not finished after the formation of quinones. These molecules are still reactive and can undergo several side reactions. For propionate-based phenolic antioxidants the quinone can rearrange and form a phenolic antioxidant back (Scheme 21.9), which causes that each phenolic group can react with at least four radicals.

Phenolic antioxidants exhibit a weak absorption tail extending well above 300 nm, which causes that when they are irradiated with terrestrial sunlight wavelengths they are easily transformed [80]. As a result phenolic antioxidants are not very effective UV stabilizers. However, alkyl substituted *p*-hydroxybenzoates (e.g., UVA-BZ-1) exhibit little, if any, absorption of terrestrial sunlight wavelengths. On this basis, it is expected to be more photostable than phenolic antioxidants under sunlight exposure conditions, which causes that they are ultraviolet stable radical scavengers. These UV stabilizers were shown to be effective in PE and PP [81], particularly in the presence of pigments [82].

In doing their job, phenolic antioxidants can also be transformed into conjugated quinoidal products that are highly colored [83,84]. The formation of stilbenequinone in polymers stabilized with BHT is most investigated. Propionate-based phenolic antioxidants have a lower tendency to discolor due to the rearrangement reaction shown in Scheme 21.9. However, further reactions of the formed cinnamate can lead to highly colored products too [84,85]. Phenolic antioxidants in which the phenolic group is attached to an isocyanurate ring have a lower tendency to discolor, which is ascribed to hindered movement of the phenolic groups resulting in hampering of dimer formation and thus discoloration [85].



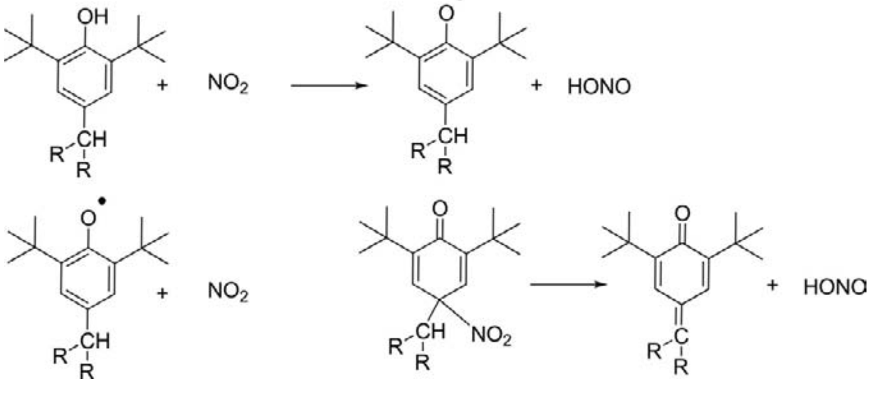
Scheme 21.9 Rearrangement of a quinone to a cinnamate.

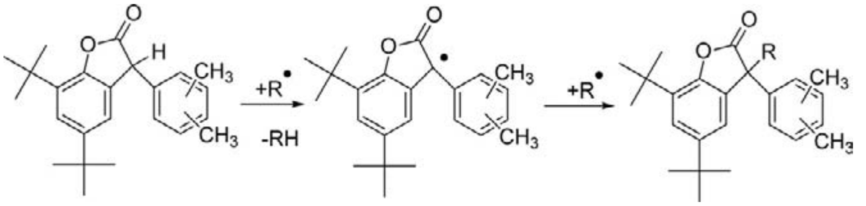
Another potential discoloring reaction of phenolic antioxidants is their reaction with NOx from the air, which is known as gas fading. NOx from the atmosphere can, even at very low concentrations, convert phenolic antioxidants to quinone methides (for mechanism, see Scheme 21.10), which easily lead to discoloration. The discoloration due to gas fading is phenolic antioxidant type dependent, although all phenolic antioxidants are suffering from it. According to Yatchigo [86] the discoloration of not fully hindered phenolic antioxidants is less than that of fully hindered phenolic antioxidants.

Due to the direct substitution of the carboxylic acid group onto the phenyl ring alkyl substituted *p*-hydroxybenzoates are resistant to dimerization and subsequent yellowing [87−89,141].

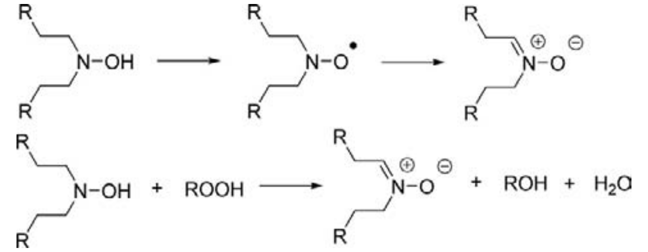
Secondary aromatic amines are very reactive antioxidants [90−93] and, as with the phenolic antioxidants, the primary radical can react with radicals, leading to various decomposition products. The main drawback of this type of antioxidant is that many of these decomposition products are colored. For this reason their application is mainly limited to carbon black-filled polymers.

Scheme 21.10 Reaction of NO_2 leading to quinone methide.





Scheme 21.11 Mechanism of action of benzofuranones.



Scheme 21.12 Free radical scavenging and hydroperoxide decomposition mechanism of hydroxylamines.

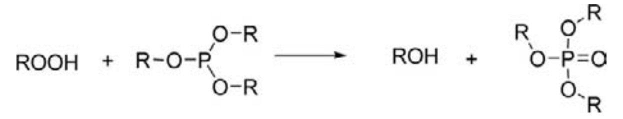
The latest developments in radical scavenging are the benzofuranones and the hydroxylamines [94]. The benzofuranones are able to scavenge alkyl radicals according to the mechanism as depicted in Scheme 21.11. It was shown that the place of the methyl substituents has an effect on the activity of the benzofuranones [95].

Hydroxylamines, besides acting as alkyl radical scavenger, can also act as hydroperoxide decomposer (Scheme 21.12) [94]. As alkyl radical chemistry is most important under oxygen-deficient conditions and at high temperatures, these stabilizer types are used only as processing stabilizer—they are not effective as long-term heat stabilizers.

21.3.2 Secondary Antioxidants (For Commercial Examples, See Appendix 1)

The most important secondary antioxidants are the trivalent phosphorous compounds and the thioethers. According to the definition, they act by reducing hydroperoxides. The trivalent phosphorous compounds can be used as processing as well as long-term heat stabilizers although the latest function is highly polymer dependent. In polyolefins, phosphites are hardly effective as long-term heat stabilizers. Only aromatic phosphites that can form phenolic antioxidants by hydrolysis show some effectivity in polyolefins [96]. For other polymers it was shown that phosphites contribute to the long-term heat stability [24,25].

The most accepted mechanism of action of these phosphor-containing stabilizers is their ability to reduce hydroperoxides to alcohols as shown in Scheme 21.13. However, this mechanism has been mentioned to be improbable for stabilization during processing as at processing temperatures the decomposition rate of hydroperoxides is high [97].



Scheme 21.13 Decomposition of hydroperoxides by trivalent phosphites (R3=O−R4) or phosphonites.

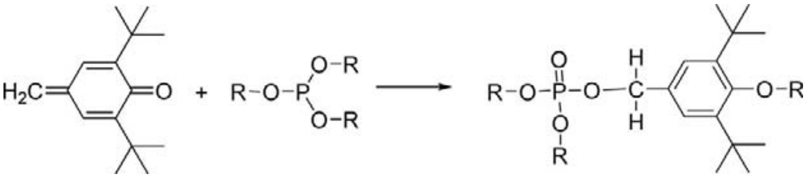
There is some evidence that these phosphor-containing antioxidants can scavenge radicals too [98,99]; however, this reaction is of importance only when there are no other radical scavengers present. Another mechanism postulated that explains the effectivity of phosphites as processing stabilizer is a direct reaction of the phosphite with oxygen resulting in a reduction of the concentration of oxygen and thus a decrease in degradation rate during processing [97].

In the presence of water, phosphites can hydrolyze and form phosphoric acid derivatives and alcohols [96]. The hydrolysis rate depends on the structure and physical form of the phosphite [100]. Its stability increases when R is changed from aliphatic to aromatic to sterically hindered aromatic. The effect of the hydrolysis on the effectivity as a stabilizer is limited, but decomposition products can have an influence on organoleptic properties. A major problem occurs when the stabilizer is hydrolyzed before it is added to the polymer as hydrolysis leads to stickiness and decrease of the flow properties, which can lead to dosing problems. These problems can be overcome when the phosphite is handled with care.

If degradation leads to discoloration, this can be reduced by adding phosphites. There are several mechanisms postulated to explain this fact.

- In polyolefins the main sources of discoloration is the phenolic antioxidant, replacing it (partly) by nondiscoloring antioxidants, as phosphites, will result in a decrease of discoloration, although this can lead to a stability decrease.
- It is well known that polymerization catalyst residues can induce the degradation of polymers, which can result in a faster conversion of present phenolic antioxidants and thus to discoloration. A possible mechanism of action of phosphites is that they form a complex with these metal ions and reduce their negative influence. This can lead to a slower conversion of the phenolic antioxidant and thus reduction of the formation of their yellow conversion products.

Scheme 21.14 Reaction of phosphites with quinone methide.



- Another postulated mechanism of action of phosphites as color suppressant is a reaction between the phosphite and a yellow chromophore leading to noncolored product as explained in Scheme 21.14.

Another class of stabilizers that is able to reduce hydroperoxides is the thioethers. These stabilizers act mainly as long-term heat stabilizers. In combination with phenolic antioxidants they have a big influence on the long-term heat stability of polyolefins [101] (Table 21.3).

One of the reasons that thioethers are effective stabilizers is that their oxidation products act as long-term heat stabilizers [102—104]. They can be even more effective hydroperoxide decomposers than the original compounds [105]. A proposed mechanism of action of thioethers is shown in Scheme 21.15 [106].

Experimentally it was shown that at 75 °C and 85 °C stabilizers based on two adjacent sulfur atoms are more effective than those based on sulfur stabilizers containing an alkoxy-carbonyl group in the beta position [107]. This higher effectiveness of the disulfides was ascribed to the formation of thiosulfinates, which was considered to be the key step in the hydroperoxide deactivation mechanism.

21.3.3 HA(L)S (For Commercial Examples, See Appendix 1)

After the introduction of the first HA(L)S in the 1970s, this class of light stabilizers rapidly became the most important UV stabilizer for the majority of plastics. Without the discovery of HA(L)S, the outdoor applicability of many polymers would be limited. So, the use of PP in automotive application without the use of HA(L)S would be impossible. Although HA(L)S stabilizers were developed as UV stabilizer they are more and more used as long-term heat stabilizers too [74,108]. Especially where phenolic antioxidants cannot be used due to their discoloration, HA(L)S is used to protect the polymer against long-term heat degradation [73].

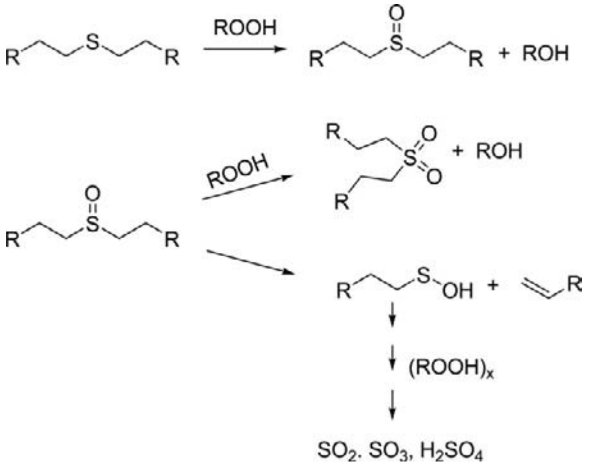
Since the discovery of HA(L)S, a lot of research was done on their mechanism of action and many different mechanisms were proposed.

Many of these mechanisms are based on radical scavenging in which a nitroxide plays a key role. In the first reaction the amine is converted into a nitroxyl radical. For this reaction several mechanisms are proposed. Sedlar et al. [109] proposed a reaction of a hydroperoxide with the amine to form an alkoxyamine, which reacts with a peroxy radical to form a nitroxide. Carlsson et al. [110] published a mechanism involving an aminyl radical which is oxidized to a nitroxide. Geuskens and Nedelkos [111] suggested that the reaction of an amine with a peroxy radical leads to the nitroxide and an alcohol. Toda et al. [112] and Felder [113] suggested that the formation of the nitroxide is related to the oxidation of aldehydes that are formed by oxidation. Toda et al. [112] assumed that the nitroxide is formed by a reaction of a peracid with the amine and Felder [113] suggested a reaction between an acylperoxy radical and the amine to form the nitroxide and an acid.

Zahradnickova et al. [114] showed that the nitroxide indeed is formed by the reaction of the amine with oxidized PP containing peracids. Most recently it is suggested that the nitroxide is formed from its charge transfer complex with oxygen [115].

Table 21.3 Influence of a phenolic antioxidant, thioethers and a phosphite on the long-term heat stability of 1 mm thick compression molded PP [101]

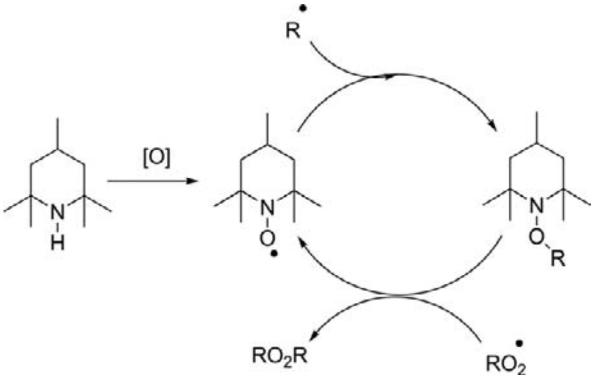
PAO	S-M03	P-M03	Embrittlement time (hrs)			
	%	%	80°C	100°C	135°C	150°C
0.05% PAO-1	-		15700	6900	90	<24
0.05% PAO-1	0.15		32000	12100	540	190
0.05% PAO-5	-		25000	2300	90	<24
0.05% PAO-5	0.15		67100	17900	1000	290
0.05% PAO-2	-		25000	8100	670	97
0.05% PAO-2		0.05	25000	8100	650	105
0.05% PAO-2	0.15		35000	12200	1950	550



Scheme 21.15 Mechanism of action of thioethers.

Nitroxides are good radical scavengers that can react with alkyl radicals and form an amino ether. These amino ethers are able to react with radicals and form the nitroxide back. According to the Denisov cycle (see Scheme 21.16) as a result the stabilizer is not consumed. There are many variations on the Denisov cycle suggested, but all of them are based on the regeneration of the nitroxide. According to Bolsman [116] the cyclic mechanism that is responsible for the catalytic scavenging of tertiary alkyl and peroxy radicals involves the formation of a hydroxylamine from the alkyloxyamine. From a very thorough study Step et al. [117,118] concluded that peracyl radicals play a key role in the nitroxide regeneration mechanism.

Although the radical scavenging mechanism of HA(L)S is the most accepted, several other stabilization mechanisms were postulated too. It is well known [119] that transition metals can initiate the photooxidation of polymers. Fairgrieve and McCallum [120] showed that HA(L)S is capable in complexing transition metals. They postulated that the mechanism of action of HA(L)S is related to this complexation, which could prevent the decomposition of hydroperoxides into initiating radicals. The most recent mechanism of action of HA(L)S postulated is by the quenching initiating polymer oxygen CTCs [55,56,121].



Scheme 21.16 Mechanism of action of HA(L)S according to the Denisov cycle.

As a result of their chemical structure the majority of the HA(L)S stabilizers are basic [122−124], which causes that they can form ammonium salts with acidic compounds. These salts cannot form a nitroxide and as a result are not active as stabilizers [125]. Carlsson et al. [126] showed that HCl, HBr, and HNO_3 have a large negative effect on the effectivity of HA(L)S. For combinations of thioethers and HA(L)S antagonistic effects were found [127], which was ascribed to the prevention of the formation of the nitroxide too [128,129]. Other species that can deactivate HA(L)S are halogenated flame retardants [130,131] and insecticides or pesticides [132−134]. As a result of all these potential negative effects less basic HA(L)S types were developed. One of the major developments was the substitution of the NH HA(L)S derivatives by their much less basic *N*-oxyl (NOR) analog [122].

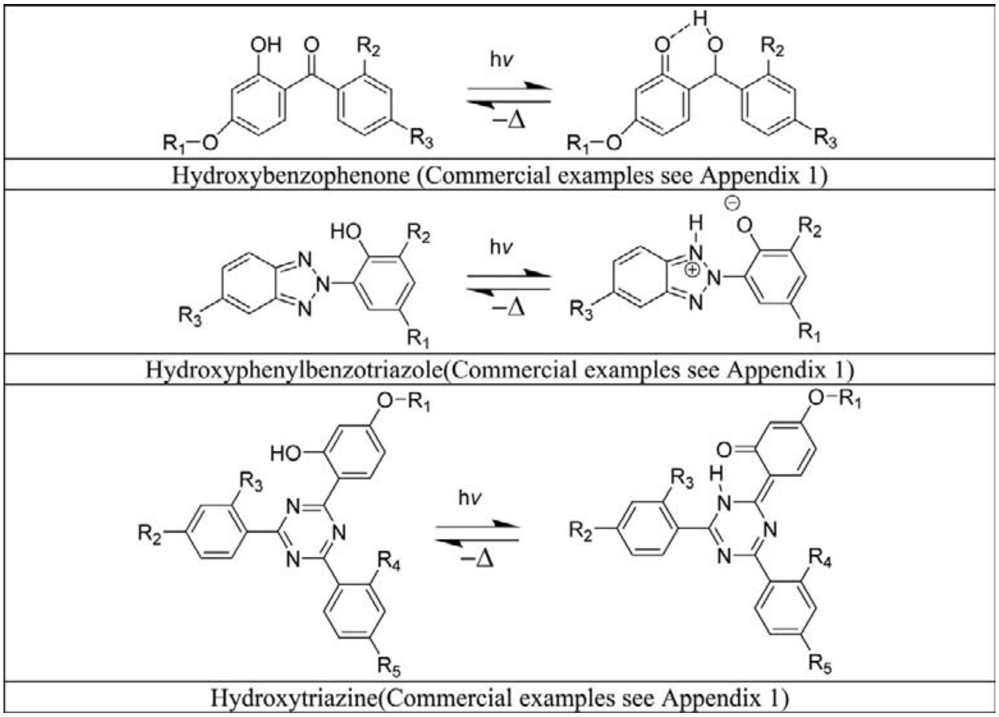
21.3.4 UV Absorbers (UVAs) (For Commercial Examples, See Appendix 1)

Sunlight degradation of polymers can be reduced by adding substances that absorb the harmful UV light more effectively than the polymer and transform the excess of energy to heat or less harmful radiation. This can be done with dyes, pigments (colored) and UVAs (noncolored). As pigments and dyes are colored, their applicability as a stabilizer is limited. Organic UVAs are generally not (or very limited) colored, which makes their applicability much broader. To be effective as a UV stabilizer, UVAs must strongly absorb, for polymers, harmful UV light; they have to be able to transfer the absorbed light in harmless energy and they have to be active during the service life of the polymer.

UVAs in use are hydroxybenzophenones, hydroxyphenylbenzotriazoles, hydroxytriazines, oxalanilides, phenyl esters, benzooxazinones, cyanoacrylates, formamidines, and benzylidene malonates. The UV absorption characteristics of these classes of UVAs are shown in several publications [54,135−137]. The most important classes are the hydroxybenzophenones, hydroxyphenylbenzotriazoles, and hydroxytriazines; for these three classes the absorption of the UV light leads to a proton shift (see Scheme 21.17).

According to Lambert−Beer's law light absorption is a function of the extinction coefficient of the absorber, its concentration, and the path length. As a result the effect of UVAs to protect thin articles or against surface degradation is limited [138].

For effective UVAs the transformation of the absorbed UV light to harmless energy has to be very efficient; even if the quantum yield for destruction is only 10^{-6} about 30% of the UV stabilizer is deactivated within 1 year of Florida exposure [139]. However, photolysis is not the only way UVAs degrade. Especially in easily degrading polymers, radicals



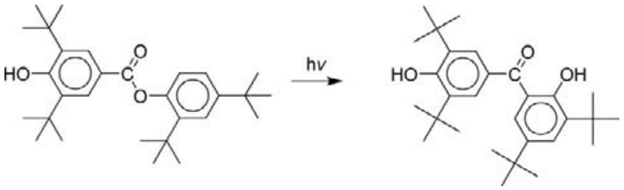
Scheme 21.17 UV absorption mechanism of hydroxybenzophenones, hydroxybenzotriazoles, and hydroxytriazines.

that are produced by the polymer matrix can attack the UVA, leading to inactive decomposition products. In a polymethylmethacrylate (PMMA) matrix it was shown that the hydroxytriazines are the most photostable UVAs [140].

Phenyl-substituted *p*-hydroxybenzoates do not absorb enough sunlight wavelengths to prevent UV degradation, but they are precursors for 2-hydroxybenzophenones, which are formed through a photo-Fries rearrangement (Scheme 21.18) [141]. Recently, a PC PES copolymer was developed that contains moieties that through this photo-Fries rearrangement forms 2-hydroxybenzophenone moieties, which act as a UV shield and prevent the polymer from degradation [138,142].

21.3.5 Quenchers (For Commercial Examples, See Appendix 1)

Photodegradation is a result of the absorption of UV light that leads to molecules in the excited states, which undergo reaction. When molecules are present that take over the energy from the excited polymer and release this energy in a harmless form, an increased stability can be expected. Although there is no consensus on the mechanism of action of nickel chelates, they are the most well-known quenchers. It was shown that nickel (Ni(II)) chelates are able to quench in liquids different triplet excited states [143−146], although it could not be proven to be the UV stabilization mechanism [147]. As a result several other possible UV stabilization mechanisms of nickel chelates were proposed [148−154]. As mentioned before a possible mechanism of action of HA(L)S is quenching of excited polymer oxygen charge transfer complexes. Other possible excited charge transfer complex (CTC) quenchers are amines with a nitrogen in a bridgehead position that cannot form a C=N bond, such as bridged amines. Adding these types of stabilizers to PP led to an increase of the UV stability with a factor of 2−3 [115].



Scheme 21.18 Photo-Fries reaction of phenyl-substituted *p*-hydroxybenzoates.

21.4 Performance of Stabilizers

21.4.1 Processing Stability

During melt processing degradation can be due to thermal, thermooxidative, or hydrolytic degradation processes. If hydrolysis is an important degradation mechanism the best remedy is to dry the polymer carefully before processing. Stabilization against thermal degradation is possible only if this process is catalyzed as is the case of PVC. Against thermooxidative degradation antioxidants can be applied. In the following, the stabilization of different polymers against degradation during processing will be discussed.

As a result of thermal degradation PVC rapidly dehydrochlorinates at processing temperature, which results in the formation of corrosive HCl and discoloration of the polymer. This degradation can be reduced by using stabilizers such as synergistic mixtures of metal soaps [155,156] with costabilizers such as phosphates [157], diketones [158], polyols [159], amines, [160] and epoxides [161,162]. A proper balance between color stabilization and HCl scavenging capacity can be obtained by applying synergistic mixtures of synthetic hydrotalcites, metal soaps, and metal acetylacetonates [163].

Polyolefins only show thermal degradation far above their normal processing temperature. For these polymers degradation during processing is a result of thermooxidative processes [164], which results in molecular weight changes and discoloration. To reduce degradation during processing primary as well as secondary antioxidants can be used. Phenolic antioxidant provides melt processing stability as a hydrogen atom donor and the phosphorus-based melt processing stabilizer functions as a hydroperoxide decomposer during the melt compounding step. These chemistries work together synergistically to reduce degradation of the polymer [165]. The effectiveness of stabilizers in polyolefins can be determined by measuring molecular weight and color changes as a function of times the polymer is processed [166].

In Figure 21.1 the molecular weight and color changes of PP as a function of times the polymer is processed are shown. Adding PAO-2 leads to a smaller increase of the melt flow ratio (MFR); the addition of phosphites leads to a larger decrease of the MFR increase. However, the smallest increase in color was found for the unstabilized PP and the largest with the PAO-2 only containing polymer, while the discoloration of the phenolic and phosphite containing samples is in between both. This discoloration can be ascribed to transformation products of the phenolic antioxidant.

For high-density polyethylene (HDPE), linear low-density polyethylene (LLDPE), and PP combinations of phenolic antioxidants and phosphites lead to a synergistic protection of the polymer. For HDPE and LLDPE an increased amount of phosphite provided increased processing stability at constant phenol concentration. A 4:1 ratio of phosphite to phenol exhibited the best performance, while the most efficient ratio for protecting melt flow of the PP was found when a 2:1 ratio of phosphite to phenol was added [167]. According to Parrondo molecular weight changes can best be reduced with phenolic antioxidants, while phosphites prevent discoloration [168].

A comparison between the effectivity of several phosphorous antioxidants as processing stabilizer for PE and PP is given in Costanzi et al [169]. A thorough study on the effect of different phosphorous compounds on the melt stability of Phillips type HDPE was made by Kriston et al [170,171].

For PP it was found that vitamin E is more effective as melt stabilizer than PAO-2, although vitamin E led to larger discoloration than PAO-2. This discoloration could be reduced drastically by incorporation of a phosphite (P-3) [172].

Adding benzofuranones to binary blends of phenolic antioxidants and phosphites leads to an increase of the processing stability [173,174]. If discoloration due to the presence of phenolic antioxidants is a problem, combinations of a benzofuranone (BP-1) or alternatively a hydroxylamine (HA-1) and a phosphite can be used as a processing stabilizer [175].

In contrast to phosphites, thioethers do not contribute to the processing stability of polyolefins [106,166] and although HA(L)S stabilizers are radical scavengers too, they do not act at high temperatures and therefore do not act as processing stabilizer [164,176].

21.4.2 Long-Term Heat Stability

Although in the application, temperatures are lower than during processing, the oxygen concentrations are much

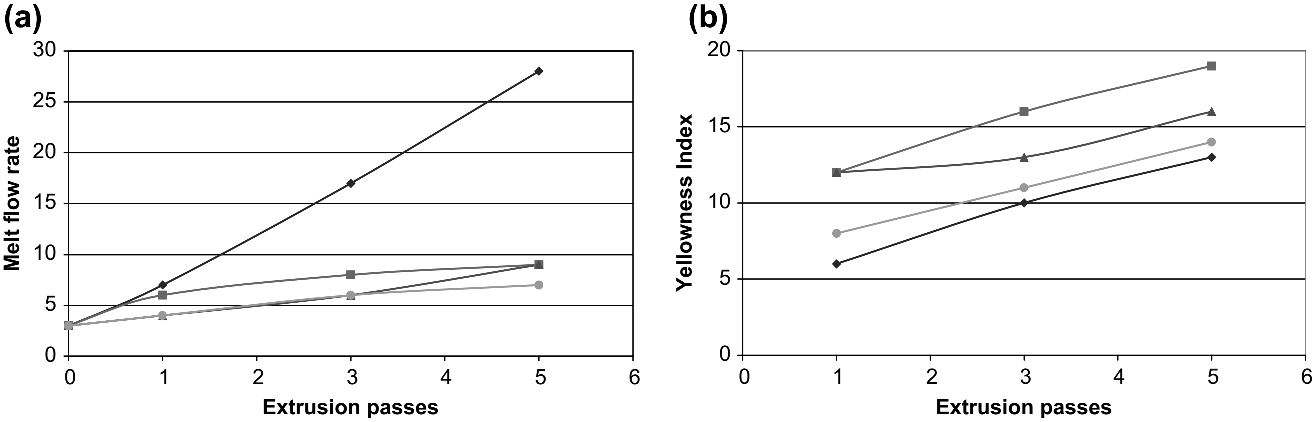


Figure 21.1 Influence of phenolic antioxidant and phosphites on the changes of the MFR (a) and color (b) of PP as a function of times processed at 260 °C (Unstabilized (□) 0.1% PAO-2 (■),0.1% PAO-2 + 0.05% P-1 (▲),0.1% PAO-2 + 0.05% P-2 (●) (From Klemchuk and Horng [166]).

higher and the aging times much longer, which causes that in use polymers can degrade too. Especially oxidation reactions as shown in Scheme 21.1 cause that plastics fail in their application. To reduce the oxidation rate of polymers primary as well as combinations of primary and secondary antioxidants are applied. In contrast to preventing degradation during processing phosphites are not very effective in polyolefins, thioethers perform much better (Table 21.3), although they need to be applied in combination with a phenolic antioxidant [177,178]. In those cases that phosphites do contribute to the long-term heat stability this is ascribed to the formation of phenolic components by hydrolysis of the phosphites or to a reduced conversion of the phenolic antioxidant during processing [106,179]. From Table 21.3 it is also clear that the aging temperature determines which phenolic antioxidant performs best, which also is shown in Glass and Valange [180]. At 150 °C PAO-2 in combination with S-1 performs by far the best, while at 80 °C the combination of PAO-5 with S-1 is the best. It was also shown that synergism of PAO-3 with thiopropionates is larger than that of PAO-2. This was attributed to a difference in sterical hindrance of the phenolic groups [181]. Another half hindered phenolic antioxidant (PAO-4) showed a large synergism with a sulfur-containing secondary antioxidant [85,182].

One of the reasons that sulfur-containing antioxidants are effective stabilizers lies in the fact that oxidation products of these stabilizers act as long-term heat stabilizers too [102−104], which can be even more effective hydroperoxide decomposers than the original compound [105].

The use of benzofuranones or hydroxylamines makes it possible to protect polymer against degradation during processing without the use of phenolic antioxidants. However, the benzofuranones as well as the hydroxylamines do not contribute to the long-term heat stability, which causes that in many cases alternative long-term heat stabilizers have to be used. HA(L)S were developed as UV stabilizers, but it was found that they act as long-term heat stabilizers too, although the way they reduce the degradation rate is different than that of phenolic antioxidants. Phenolic antioxidants are consumed in doing their job, causing that after an induction time, a sudden drop of the mechanical properties is observed, while in the presence of HA(L)S stabilizers a more steady decline in the mechanical properties is found (for a schematic presentation, see Figure 21.2) [108,183]. For PP this difference was ascribed to from Scheme 21.1 deviating oxidation mechanism and a difference in mechanism of action of phenolic antioxidants and HA(L)S. For more details, see Gijsman and Gitton [73] and Gijsman [184].

Depending on the aging condition (temperature) and failure criterion HA(L)S can even outperform phenolic antioxidant [185]. In low-density polyethylene (LDPE), HA(L)S acts as a long-term heat stabilizer too, but this polymer at 100 °C PAO-2 is still much more effective than several HA(L)S types [186].

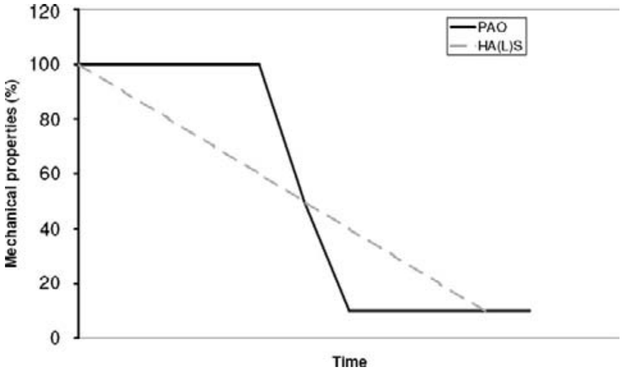


Figure 21.2 Schematic presentation of the influence of phenolic antioxidants and HA(L)S on the decline of the mechanical properties [183].

21.4.3 UV Stability

Due to the influence of sunlight polymers degrade. The most used stabilizers to reduce this type of degradation are the UV absorbers and HA(L)S stabilizers; although for the majority of polymers HA(L)S stabilizers are the most effective.

In many cases synergistic combinations of a UV absorber and a HA(L)S are applied [72,81,187−190]. For LLDPE the addition of UV stabilizers leads to a tremendous increase of the stability during outdoor weathering (Florida). The addition of a combination of a Nickel quencher (Ni-1) and a UVA (UVA-BP-1) leads to a six times larger lifetime. The additions of a HMW-HALS (HMW-HALS-2) leads even to a larger (>10 times) increase in the lifetime [191]. In PP it was shown that HA(L)S is about 5−10 times more effective than UV absorbers [192,193]. In polystyrene HA(L)S is more effective than a UV absorber, but their combination results in an synergism [194,195]. This is the case for ABS too [196]. Although HA(L)S performs better in PA66 than UV absorbers, the differences in this polymer are smaller [197].

Kurumada et al. [188] investigated the synergism of a HA(L)S (LMW-HA(L)S-1) and two UVAs (UVA-BZT-1 and UVA-BZT-6) in PP, HDPE, ABS, and PS. A large synergism was observed in PP, HDPE, and ABS resin. A moderate synergistic effect was obtained in polystyrene.

Due to their basicity, HA(L)S stabilizers cannot be applied in BPA-PC; as a result other stabilizers have to be used. A comparison of the effectivity of several UV absorbers to reduce the discoloration of BPA-PC as a function of weathering time is shown in Diepens and Gijsman [198].

Phenolic antioxidants that are used to protect polyolefins for degradation during processing, and HA(L)S stabilizers can show synergisms as well as antagonisms [199−201]. The largest synergism was observed for combinations with PAO-1 [200,201].

21.5 Other Factors Determining the Choice of Stabilizers

Besides the performance there are many other factors that determine the choice for a stabilizer system. As stabilizers have to protect polymers for long times, it is important that these stabilizers stay in a polymer over the lifetime, which is related to several stabilizer-related physical factors. Stabilizers are normally added in mixtures or together with other additives; possible interaction between these additives might have an influence on the performance of stabilizers. Reactions with other chemicals from the environment of the plastic can lead to a deactivation of the stabilizer and a reduced lifetime. In many cases another requirement for stabilizers is that they are not colored or discolored. If polymers are used that can come into contact with food, an indirect food contact approval is required. As stabilizers have to be added to a polymer there are requirements for toxicity (which is not equivalent to indirect food contact approval) and dosability. A number of these requirements are discussed in the following.

21.5.1 Physical Factors

Besides chemical factors, physical factors determine the choice of stabilizers too [202]. When stabilizers are present above their solubility limit they show a tendency to diffuse to the surface. For stabilizers with a low volatility, in many cases this will result in a white powder on the surface of the stabilizer (blooming). Stabilizers with a high volatility will evaporate from the surface. The driving force for stabilizers to migrate to the surface is their solubility; however, the rate is related to the diffusion coefficient. Blooming mainly appears under use conditions (at relative low temperatures), because the solubility at these low temperatures is much lower than at processing conditions. However, not all stabilizers that are present above their solubility limit will show blooming. Stabilizers with a low diffusion coefficient will, even when they are present in concentrations far above their solubility limit, not show blooming during their service life.

Especially for thin articles evaporation of the stabilizer can be the mechanism causing service life failure. For this reason, for thin articles generally relatively high molecular weight stabilizers perform better than their lower molecular weight analogs. For thicker articles this can be different: in this case the low molecular weight stabilizers performs in many cases better than their high molecular weight versions [203]. This is attributed to a reservoir effect for the stabilizer in the bulk of the material [203].

21.5.2 Interactions with Other Additives

Besides stabilizers there are many other additives in use that improve the properties of polymers. However, additives can interact with each other which can lead to a decrease in stability. Examples of additives that can show a negative interaction with stabilizers are anticorrosives, flame retardants, and reinforcing agents.

In polyolefins antiacids (as metal stearates) are used to prevent corrosion. These metal stearates have an influence on the processing and long-term stability. Calcium lactate was shown to contribute to the processing stability of PP [204]. The presence of peroxide impurities and metal oxide residues in metal stearates has been shown to be the reason for antagonisms between metal stearates with hindered phenolic and phosphite type stabilizers [205,206].

HA(L)S stabilizers were shown to be the most-effective UV stabilizers for the majority of all polymers. However, the effectivity of these stabilizers in polymer systems containing brominated flame retardants is limited. This is attributed to the generation of acidic products during processing or UV exposure, which transform HA(L)S stabilizers into their inactive salt. Several UV stabilization strategies were developed to reduce this problem [130,131, 207–209].

Talc is used to increase the heat deflection temperature (HDT) and stiffness of plastics, but talc can also adsorb stabilizers on its surface and thus reduce the service lifetime of the plastic [210,211]. This negative effect can be reduced by applying more stabilizers or by adding modifiers with higher affinity for talc to coat the talc surface [212–214]. Some modifiers lead to a synergistic effect [215].

The addition of nanosized fillers can result in the improvement of thermomechanical, transparency, and film barrier properties. However, it was shown that nanoclay reduces the efficiency of the light stabilizers, which was ascribed to adsorption of the stabilizers onto the hydrophilic nanoplatelets [216]. If the nanoparticles contain Fe impurities, these can accelerate the photodegradation; however, this negative effect can be reduced by applying metal deactivators [217].

Besides interaction between stabilizers with other additives, different types of stabilizers can react with each other too. It is known that combinations of HA(L)S and sulfur-containing stabilizers can show an antagonism [127]. This antagonism was ascribed to a reduced nitroxide formation rate due to the decomposition of present hydroperoxides by the S-containing compound [128] or to the formation of a salt between an acidic decomposition product of the S-containing compound and the basic HA(L)S that is not able to form the stabilizing nitroxide [129]. Although, according to Luci et al. [218] the stabilizing reaction product is the nitroxide that is deactivated by a reaction with radicals formed on the S-containing stabilizer.

21.5.3 Chemical Resistance Stabilizers

Besides with additives being present in the polymer stabilizers can also interact with chemicals from the surrounding atmosphere. So can phenolic antioxidants be oxidized by chlorine species, even at low concentrations as used in tap water to avoid the spreading of infection [219]. This results in a decrease of the stability of polymers in contact with chlorine containing water.

Another well-known interaction between a stabilizer and chemicals from the environment is the deactivation of HA(L)S stabilizers by insecticides and pesticides [132−134].

21.5.4 Color and Discoloration

It is obvious that the addition of colored stabilizers leads to a colored polymer. Many aromatic amines are colored, which limits their applicability enormously. As a result they are mainly (only) applied in black colored plastics.

Discoloration of polymers is in most cases due to the presence of phenolic antioxidants, which can be transformed in yellow products. These mechanisms are described above.

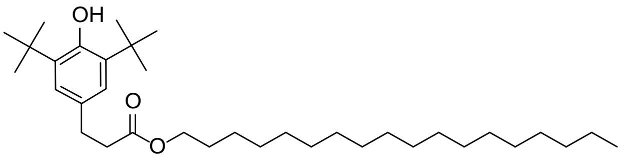
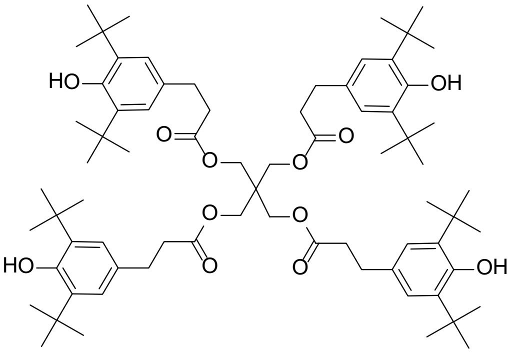
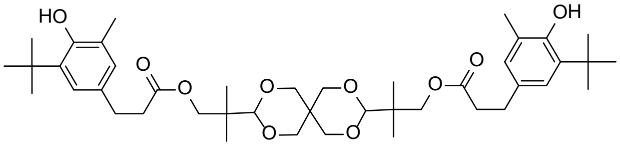
21.5.5 Toxicity and Dosability

To prevent degradation in many cases combinations of small amounts of stabilizers are used. Accurate addition of small amounts to large-scale commercial processes is difficult. Difficulties arise from large ratio imbalances, dust nuisances, and safety hazards of additive powders. As a result different physical forms of the pure stabilizers as well as of blends were developed [220−222]. Hydrolysis of phosphites can lead to lump formation which will cause dosability problems. The rate of hydrolysis of a high-performance phosphite can be drastically reduced by altering the physical form of the additive package [96].

21.5.6 Indirect Food Contact Approval

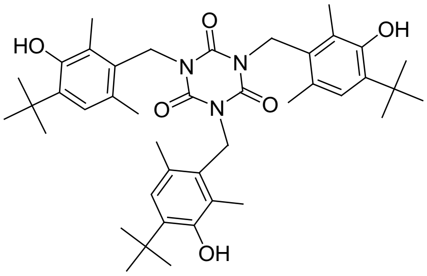
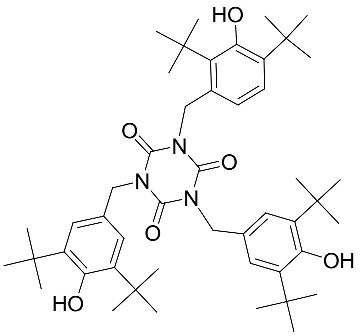
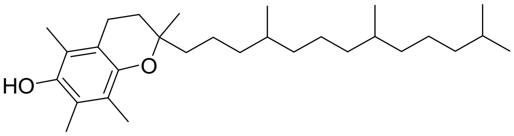
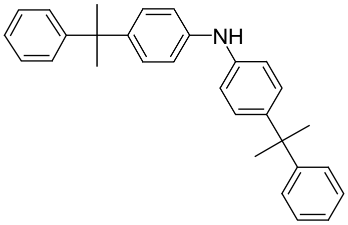
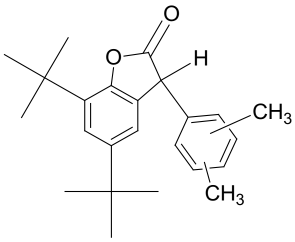
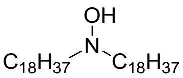
As components of polymers that come into contact with food may transfer to the food, the use of stabilizers for food contact applications is regulated [223]. A wide range of stabilizers are available that have been designated as food contact compliant [224,225].

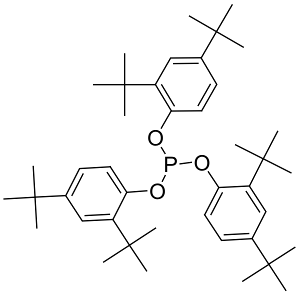
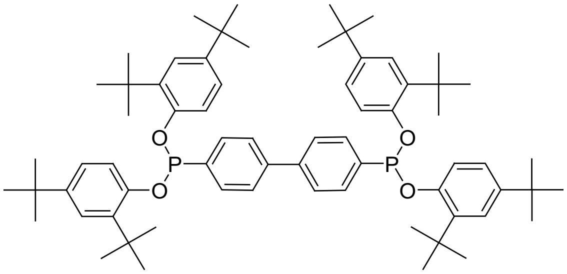
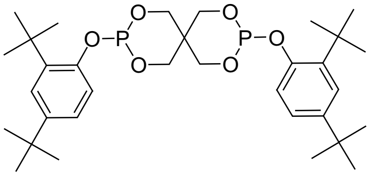
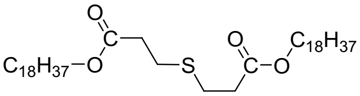
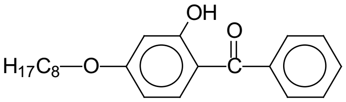
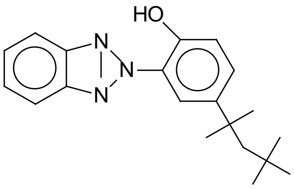
Appendix 1 Chemical structure, CAS number, and several trade names of several stabilizers

PAO-1 (2082-79-3)		ADKSTAB AO-50 Anox PP18 Dovernox 76 Irganox 1076
PAO-2 (6683-19-8)		ADKSTAB AO60 Anox 20 Dovernox 10 Hostanox O10 Irganox 1010
PAO-3 (90498-90-1)		ADKSTAB AO-80 Sumilizer GA80

(Continued)

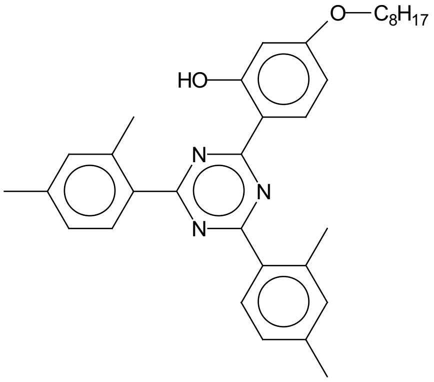
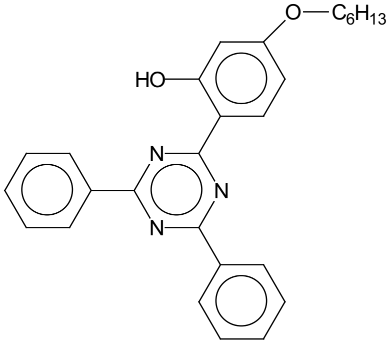
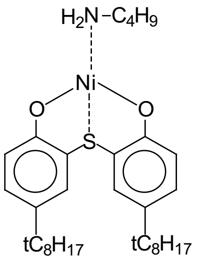
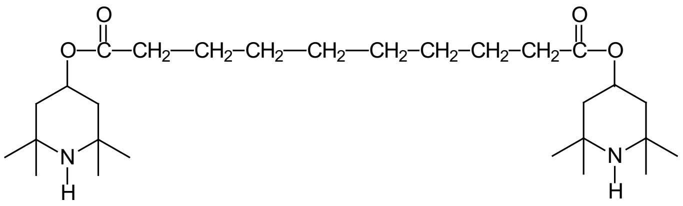
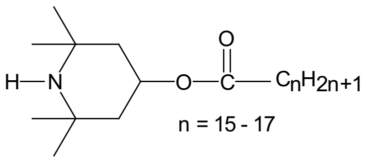
Appendix 1—cont'd

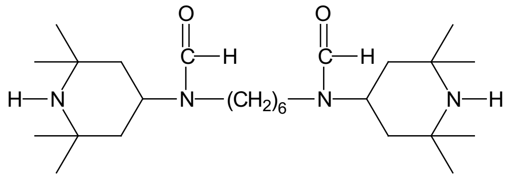
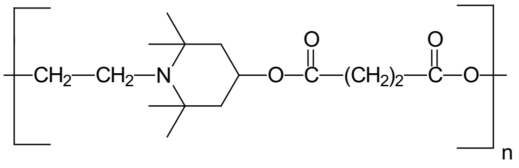
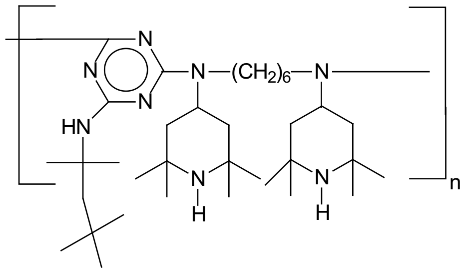
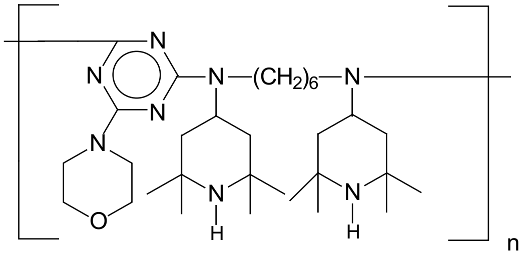
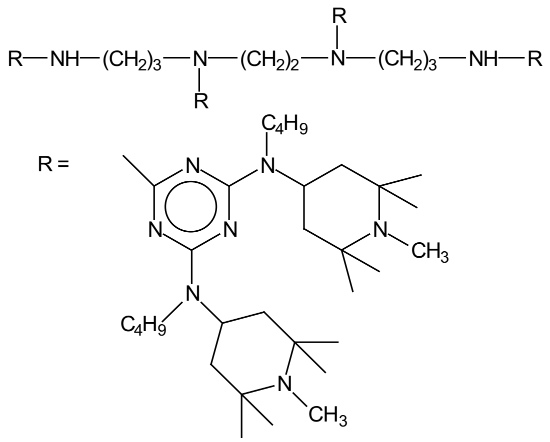
PAO-4 (40601-76-1)		Cyanox 1790 Irganox 3790 Lowinox 1790
PAO-5 (27676-62-6)		ADKSTAB AO-20 Alvinox FB Cyanox 1741 Dovernox 3114 Irganox 3114
Vitamin E (10191-41-0)		Irganox E201 Ronotec 201
AA-1 (10081-67-1)		Dusantox 86 Naugard 445 Nonflex DCD
BF-1 (181314-48-7)		HP-136
HA-1 (143925-92-2)	 $(C_{18}H_{37})_2N{-}OH$	Fiberstab FS-042 Irgastab FS042

P-1 (31570-04-4)		ADKSTAB 2112 Alkanox 240 Alvinox P Doverphos S480 Hostanox PAR24 Irgafos 168
P-2 (38613-77-3)		Alkanox 24-44 Irgafos PEPQ Sandostab PEPQ
P-3 (26741-53-7)		Alkanox P-24 Irgafos 126 Ultranox 626
S-1 (693-36-7)		Cyanox STDP Hostanox SE4 Irganox PS802
UVA-BP-1 (1843-05-6)		Chimassorb 81 Cyasorb UV531 Uvasorb 3C
UVA-BZT-1		Cyasorb UV5411 Lowilite 29 Sumisorb 709 Tinuvin 329

(Continued)

Appendix 1—cont'd

UVA-HTZ-1 (2725-22-6)		Cyasorb UV1164
UVA-HTZ-2 (147315-50-2)		Tinuvin 1577
Ni-1 (14516-71-3)		Cyasorb UV1084 Lowilite Q84 Uvasorb NI
LMW-HA(L)S-1 (52829-07-9		ADKSTAB LA-77 Lowilite 77 Sanol LS770 Tinuvin 770 Uvasorb HA77
LMW-HA(L)S-2 (24860-22-8)		Cyasorb UV3853 Dastib 845

LMW-HA(L)S-3 (124172-53-8)		Uvinul 4050H
HMW-HA(L)S-1 (65447-77-0)		Cyasorb UV-3622 Lowilite 62 Tinuvin 622
HMW-HA(L)S-2 (71878-19-8 or 70624-18-9)		Chimassorb 944 Lowilite 94
HMW-HA(L)S-3 (82451-48-7)		Cyasorb 3346
HMW-HA(L)S-4 (106990-43-6)		ADKSTAB LA102 Chimassorb 119

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22 Chaotic Advection and Its Application to Extruding Micro- and Nanostructured Plastic Materials

David A. Zumbrunnen
Laboratory for Advanced Plastic Materials & Technology, Department of Mechanical Engineering,
Clemson University, Clemson, SC 29634-0921, USA

22.1 Applicability and Fundamentals

Chaotic advection-based processing of plastics is a new plastics processing technology that offers opportunities to enhance physical properties, impart functionalities, or create decorative patterns in extrusions. It can be used with existing polymer resins and is well suited to melt processing of shear-sensitive materials. Droplet dispersions or solid particle mixtures can also be produced. Both miscible and immiscible polymer combinations can be used although structural outcomes differ. Structured plastics can be extruded that can contain, for example, thousands of layers, sponge-like assemblies, interconnected layers, percolating networks, ribbons, abundant submicron fibers, or oriented particles. Dispersions of droplets or solid particles can also be produced. Physical property enhancements that have been demonstrated include barrier (resistance to permeation) [1−3], toughness [4,5], and electrical conductivity [6,7]. Functionalities that have been demonstrated include controlled release of additives [8] and strain-sensitive electrical resistivity [7]. Plastics have also been produced with the appearance of realistic wood grains both inside and on surfaces of extrusions [9]. Both realistic (e.g., wood grains and stone appearances) and abstract patterns are obtainable. Because a large variety of microscale and nanoscale structures can be formed in extrusions even at fixed material compositions, opportunities are afforded for improving simultaneously several physical properties or performing optimization in tandem with minimization of material costs. Machinery and methods have special applicability to nanotechnology because nanostructured materials can be extruded in large quantities and in many forms such as film, sheet, tube, pipe, and fiber. In situ structure formation is controllable and repeatable so product optimization can be done efficiently. As with all blending processes, chemical reactions between material components, large viscosity differences, and polymer incompatibility can lead to processing difficulties.

Plastic materials that consist of two or more polymer types or that are composites of a polymer and a solid additive are typically manufactured by mixing or coextrusion through dies. These processing methods intrinsically restrict the variety of structural outcomes and compositions so that plastic materials may not have optimal physical properties or minimized cost. Functionalities may also be difficult to obtain. The goal of mixing is to break down domains of polymer components often to give a dispersion of droplets, whereas coextrusion arranges polymer components only into discrete layers. Often, a desired fine-scale internal structure in a plastic can be obtained only at particular compositions. Applied to polymer processing, *chaotic advection* provides a means to form a wider variety of microscale and nanoscale internal structures in plastics even at a fixed material composition [5]. Plastics are regarded as composite materials and not simply as mixtures or coextruded layers with the realization that structure of a composite can influence physical properties more than composition. Machinery and control systems have been developed that induce chaotic advection in polymer melts for extruding cast and blown film, sheet, rod, tubing, fibers, and other plastic products. Because the fine-scale structure in extrusions can be controlled during their manufacture and a greater variety of structure types are attainable than with mixing, machines have become known as *smart blenders*. Methods are applicable to polymers and other materials such as ceramic slurries that are processable in a liquid or liquid-like state and that are thermally compatible. Solids are incorporated by first mixing with a polymer to obtain a masterbatch which is supplied to the smart blender in lieu of a pure polymer component melt.

Chaotic advection is a subject of fluid mechanics that denotes the chaotic movements of passive particles in response to even simple flow fields [10,11]. Because of chaotic advection, it is now understood that complex particle motions in fluids do not require complex flow fields. Even where discrete particles do not exist in a polymer melt, this understanding is useful because small melt domains move, or *advect*, in a similar fashion. Simple flow fields allow controllable formation in melts of structures that can have both fine-scale features while also being physically expansive. For example, two polymer components can be arranged into thousands of thin alternating layers or into a blend consisting of long, submicron fibers. From a machinery perspective, device simplification and more controllable in situ structure development are made possible. A variety of

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blend morphologies are obtainable by *progressive structure development*, which is defined as the formation of structured materials via sequential in situ transitions from one structure type to another.

Progressive structure development is shown in Figure 22.1. By subjecting melts to chaotic advection, initially large melt domains (e.g., resin pellet size or larger) or melt streams are stretched and folded (steps 1—3) into alternating multilayers. Such stretching and folding is a characteristic of chaotic advection [12] and is a consequence of shear deformations and reorientations by the simple velocity fields. Simple velocity fields in smart blenders act on melt domains by shear deformation. Time-periodic changes or space-period changes in these velocity fields reorient the deformed domains to fold them. Shear deformation and folding cause domain sizes to reduce exponentially fast. Characteristic sizes of melt domains can reduce by several orders of magnitude as they move only distances of several centimeters in smart blending machines toward an extrusion point. Individual layer thicknesses can decrease rapidly to microscale or nanoscale. (1 micron = 10^{-6} m. Nanoscale is commonly regarded as <0.1 micron = 100 nm). Unlike multilayers obtained by conventional coextrusion, imbedded folds are present and stretching and processing can be continued to give a desired layer thickness in an extrusion.

While multilayer extrusions having very numerous thin layers have important applications such as permeation barriers, light interactive media, and impact resistant materials, they also serve as a template from which other structured plastics can be obtained [13,14]. Stretching and folding of polymer melt layers in a smart blender can be continued until individual layers rupture (Figure 22.1, steps 5 and 6). The ruptures grow due to interfacial tension forces. Because the number of layers is large and layers are geometrically similar, volumetric transformations in shape occur. In a blend of two immiscible polymers, simultaneous layer rupture in a multilayer melt gives an interpenetrating blend morphology [13]. Where one polymer component is present in an appreciably smaller amount, ruptures occur only in the minor component polymer. The ruptures coalesce preferentially in the direction of shear to give numerous long fibers of the minor component (Figure 22.1, steps 8—10). These structures can be broken into droplet dispersions such as those typically resulting from conventional mixing (Figure 22.1, step 7).

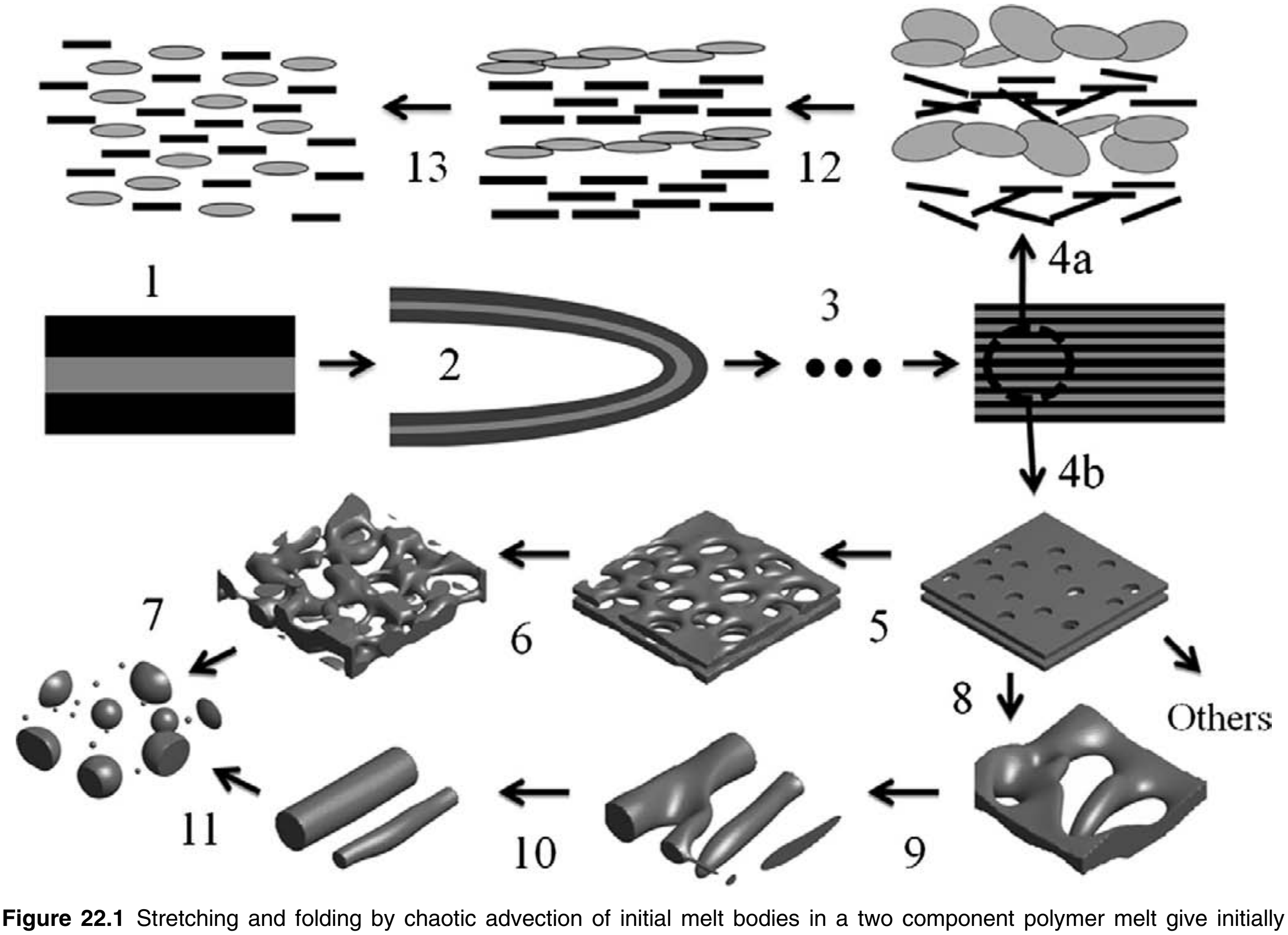


Figure 22.1 Stretching and folding by chaotic advection of initial melt bodies in a two component polymer melt give initially multilayer melts that transform by *progressive structure development* to a wide variety of polymer blend morphologies.

Characteristic dimensions (e.g., rupture size, fiber diameter, and droplet diameter) of these various blends are related to the parent layer thicknesses and thereby can be correspondingly small. Additionally, unlike mixing, numerous structure types are possible even at a fixed material composition. Any of these structure types can be captured in an extrusion. This attribute is important because physical properties can differ for each of the blend morphologies in Figure 22.1. For example, because melt flows through the ruptures in a multilayer melt, layers of the same polymer type become interconnected via coalescence and resulting extrusions are less prone to layer delamination.

Processing methods also offer new opportunities when applied to plastics containing small solids, such as carbon black and inorganic platelets or fibers and nanotubes. As shown in Figure 22.1 (steps 4a, 12), such solid particles can be localized in numerous thin layers that can have thicknesses less than 100 nm. Orientation results that can promote network formation more effectively impede diffusion or impart strength. Dispersions are also obtainable by continuing stretching and folding until layer thicknesses become smaller than the transverse dimensions of the solid particles (Figure 22.1, step 13). Such dispersions are theoretically optimal due to the underpinning chaotic motions that produce them.

22.2 Machinery and Process Control

Smart blenders have been developed for various purposes such as extruding cast film or sheet, filaments, or fibers or for manufacture of tubular extrusions such as blown film or pipe [16,17]. These machines can also be used for nanosolids dispersion and shear-sensitive material processing. They are often installable into manufacturing lines with little disturbance between existing screw extruders and downstream equipment such as chill rolls or bubble collapsing frames. They can discharge to combining blocks to produce extrusions that include melts supplied from separate screw extruders. In cast film or sheet and fiber applications, attached dies serve only to form an extrusion into a desired shape and dimension because melt structuring (Figure 22.1) occurs in the smart blender.

A basic smart blending system is given schematically in Figure 22.2. Polymer melts are supplied to a feed throat of the smart blender by screw extruders in prescribed proportions to give a desired composition in the extrusion. The melts enter a region in the blender where chaotic advection is induced by time-periodic changes in rotational speeds of stir rods controlled by a process control computer. The stir rods can be of simple geometry. Cylindrical stir rods are typically employed that are hydrodynamically tapered near a die attachment. As melt advances along the stir rods, melt domains are stretched and folded recursively by chaotic advection so that a layered arrangement first arises. Thick multilayers reduce in thickness as stretching and folding progress and the melt moves toward an extrusion point. Blend morphology changes can eventually occur in the melt due to layer breakup as discussed earlier (Figure 22.1). Morphology changes are depicted in Figure 22.2 by broken layers adjacent to the stir rods. Many derivative morphologies are attainable from multilayer breakup [5,14,15]. A particular morphology can be placed into an extrusion by operating the smart blender such that it occurs in the vicinity of the die entrance. At the extrusion point, the melt is formed by an attached die into a desired extrusion form such as a film, plate, or filament. By attaching a spinneret, multiple fibers can be produced. Unlike conventional processes, the die serves to impart only the final form. Consequently, die design is simplified and a single die can be used to produce plastic products having a wide variety of physical properties. Smart blenders for annular extrusions such as blown film differ in construction and are described later in this section.

The amount of melt structuring in the smart blender is specified through selection on a process control computer (Figure 22.2) of the number N of time-periodic speed changes of the stir rods. For example, small N yields a multilayer blend morphology whereas larger N and further stretching and folding by chaotic advection can lead to layer ruptures in immiscible polymer combinations and resulting morphology transformations. Particular blend morphologies are typically obtained with $N < 30$. By organizing polymer components into multilayers and refining the layers, one morphology type can lead in sequence to many derivative morphologies. Such progressive structure development can also be performed with melts containing solid additives such as carbon black, nanotubes, silica, or graphene platelets [6,7,18]. The smart blender system in Figure 22.2 can make use of structure–property–composition results, rheological measurements, and process parameters of prior studies. Such information can be compiled in a data base. As more information is collected, the smart blender can be used with increasing efficiency to obtain extrusions having internal structures associated with desired physical properties. In practice of course, such databases can become proprietary.

Chaotic advection is induced in a manner analogous to a twin vortex model used to describe concepts of chaotic advection [10,19]. In the twin vortex model, fluid motion and chaotic advection occur when adjacent idealized point vortices are repetitively activated. In an analogous fashion, chaotic advection is induced in the smart blender in response to periodic rotations of stir rods. The manner in which stir rods are rotated periodically is referred to as the *rod rotational protocol*. Requisite conditions for inducing chaotic advection in driven flows have been widely studied [20–23] and similar methods have been used in the design of smart blending machines [4,5,24–26]. Due to a pressure-driven axial flow and rod-driven circumferential flow, the flow field in a smart blender is three dimensional. However, the simple geometry of the stir rods instills chaotic advection principally within planes parallel to the cross-section of the smart blender barrel. The extent of melt structuring along the barrel by progressive structure development is selectable via specification of a number N denoting pairs of rod rotational speed changes while melt is resident in the smart blender. To clearly define N [4], let one rod in Figure 22.2 be designated as R_1, the other rod be designated as R_2, and Ω denote the number of rotations for a designated rod. For added generality, counter-clockwise rotations are given by $\Omega < 0$ and clockwise rotations are given by $\Omega > 0$ and let η_i equal the rotational displacement of rod i. In terms of these parameters, designation of R_1 rotating $\eta_1 = 3$ complete rotations and R_2 rotating simultaneously $\eta_2 = 1$ complete rotation is denoted by $[R_1(\Omega = 3) + R_2(\Omega = 1)]$. As an example, a specific rod rotational protocol for the smart blender consists of a periodic sequence of rod motions of N repetitions given by $[R_1(\Omega = 3)+R_2(\Omega = 1); R_1(\Omega = 1)+R_2(\Omega = 3)]$. For $N = 3$, rod rotations occur according to $[R_1(\Omega = 3)+R_2(\Omega = 1); R_1(\Omega = 1)+R_2(\Omega = 3)]$; $[R_1(\Omega = 3)+R_2(\Omega = 1); R_1(\Omega = 1)+$

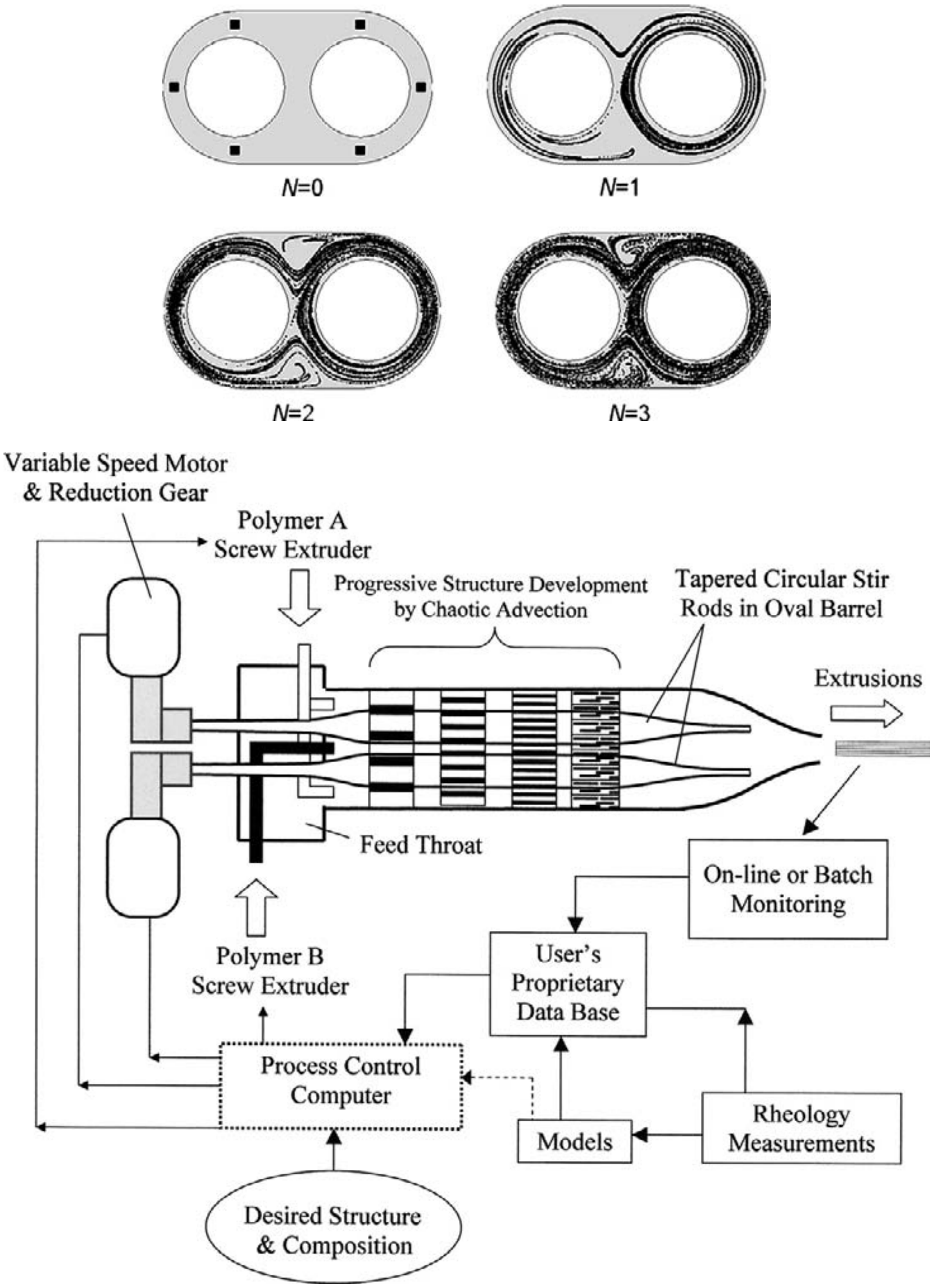


Figure 22.2 Schematic representation and process control features of a smart blending system.

$R_2(\Omega = 3)]$; $R_1(\Omega = 3)+R_2(\Omega = 1)$; $R_1(\Omega = 1)+R_2(\Omega = 3)]$. For a selected extrusion rate, rod speed is selected such that the desired value of N can be obtained while melt is resident in the blending section of the smart blender.

Chaotic advection in the smart blender is shown in the inset of Figure 22.2. Results were obtained through finite element modeling with a procedure analogous to those employed in chaotic mixing studies [27] where numerous particles are located initially within clusters. The shaded area represents injected major component polymer A. Six clusters are also shown. These represent injection of minor component polymer B melt from the feed throat of the smart blender. Because polymer A and polymer B are not yet subjected to chaotic advection, $N = 0$ for the initial injected melts. At $N = 1$, polymer A and B melts have moved a short distance along the stir rods and partial blending has occurred. Compositional uniformity is poor. Continued stretching and folding (Figure 22.1) lead to larger number of layers and improved compositional uniformity at smaller length scales. In effect, both polymer A and B are folded about each other [13] although layering may be most visually apparent in the minor component. The evident particulate structure for $N = 3$ actually corresponds to a highly layered blend morphology. Discrete layers are no longer evident because layer thicknesses have reduced to below the printed particle size in the illustration. It can be discerned though that smart blenders can be effective mixing machines where a mixed condition is achieved by structuring melts to reach fine scales. Layers can be produced of smaller thicknesses than the smallest material particles [28,29]. When extensive chaotic advection is specified, structured plastic materials result with internal characteristic dimensions at the microscale and nanoscale.

Examples of industrial smart blenders are shown in Figures 22.3 and 22.4 [17,30]. Both units are scalable to a desired melt flow rate. The smart blender in Figure 22.3 is similar to the configuration given in Figure 22.2. Polymer melts from two or more screw extruders are supplied to a feed throat that discharges to a blending zone. Chaotic advection is induced by time-periodic rotations of stir rods rotated by variable speed motors. Minor and major component melts move toward an extrusion point where various types of dies can be fitted at a die attachment flange to form extrusions of desired forms. This smart blender has primary application for extruding cast films, sheet, fibers, and filaments and can be used to supply melt to a combining block. The smart blender in Figure 22.4 is used to produce tubular extrusions such as blown film, piping, and tubing. Because these units can replace conventional dies and internal moving surfaces can be controlled to give a variety of structured plastics (Figure 22.1), they are also known as *smart dies*. As with conventional dies, the smart die is supported by a cart that can be mounted on tracks. The cart houses variable speed motors such as in Figures 22.2 and 22.3. The motors rotate six cylindrical stir rods that are mounted within an annular blending volume formed between a mandrel and the barrel. Air is supplied to the interior of the tubular extrusion as with conventional annular dies to equalize the pressure internal to the annular extrusion with ambient pressure. Polymer melts from screw extruders are introduced into the blending zone with spiral melt distribution blocks such as used in conventional multilayer blown film dies. Spiral melt distribution gives a uniform melt injection into the annular blending chamber without melt weld lines so favored features of conventional dies are incorporated. Injected melts move upward along the stir rods. Current units allow attachment of two or three screw extruders. Because layers are folded about one another by chaotic advection and blended melts can be produced, tie layers can be omitted so fewer screw extruders are needed in comparison to conventional annular dies. After forming the desired structure in the melt such as the examples in Figure 22.1, the melt exits the blending zone and is extruded via an annular die lip.

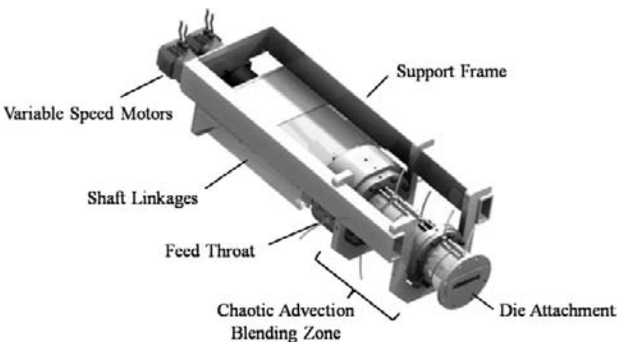


Figure 22.3 Industrial smart blending machine with two stir rods such as shown in Figure 22.2. Various types of extrusion dies can be attached to give extrusions such as film, sheet, rod, or filaments.

Data bases in Figure 22.2 can be organized in the form of a morphology map where key processing variables are related to a particular polymer blend morphology. A significant attribute of smart blending is that an approximate morphology map for process control purposes can be conveniently developed from trial runs. A smart blending system can be operated in a *transient operating mode* to rapidly identify all possible morphologies formable at specific compositions. To understand the control features and map construction, consider the simple morphology map in Figure 22.5 for polypropylene (PP) and low density polyethylene (LDPE) blend morphologies [4]. The amount of melt structuring in this map is designated by the number N defined previously that is related to the stir rod motion. Various morphologies are depicted symbolically for LDPE volume fractions (φ) of 10, 20, and 30%. In the transient operating mode, the stir rods are kept initially stationary until the minor and major component melts flow steadily through the smart blender barrel (Figure 22.2) and emerge in the extrusion as coarse, continuous streaks. This condition is

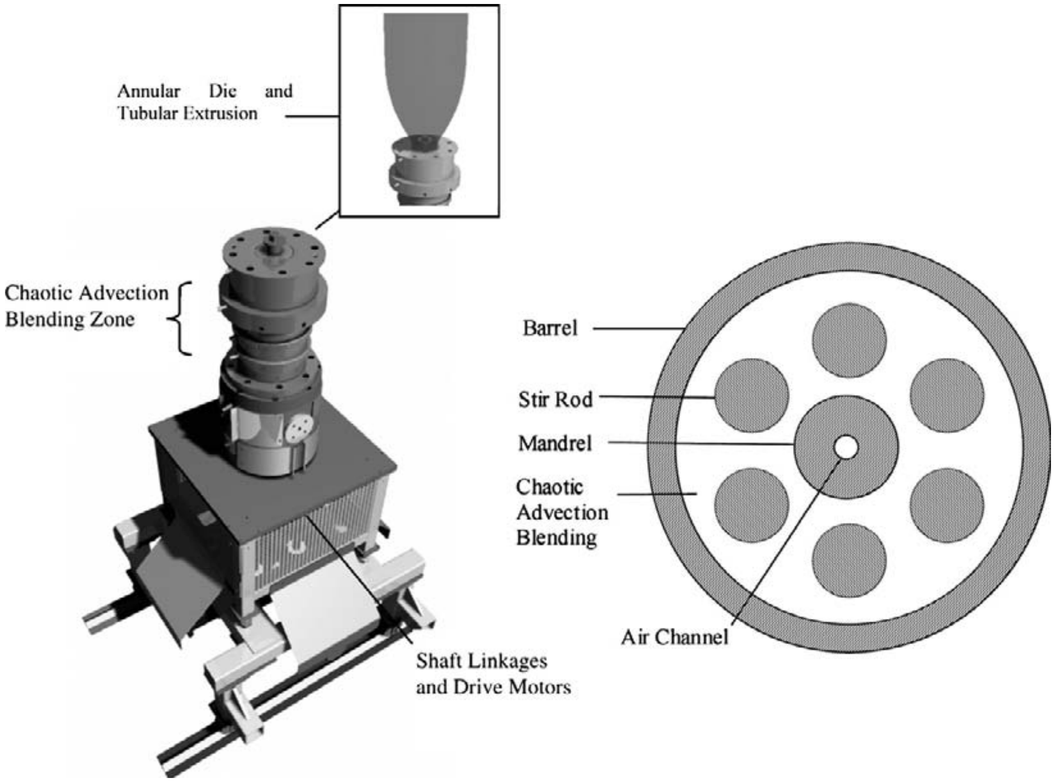


Figure 22.4 Industrial smart blender for manufacture of blown film and other tubular extrusions. Because the smart blender substitutes for conventional dies and allows online control of structure in an extrusion, it is also referred to as a "smart die".

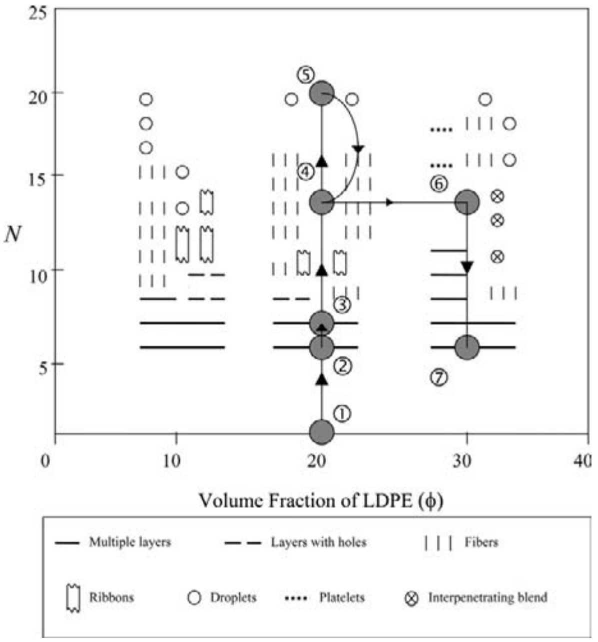


Figure 22.5 Example of a blend morphology map that can be compiled to guide machine operation. Databases can be developed in terms of pertinent melt properties to reduce trial-and-error used typically in polymer processing. Chaotic advection blending machines are thereby referred to also as *smart blenders* or *smart dies*.

designated *state 1* in Figure 22.5. Afterward, rod motion is started. In the subsequent extrusion, the extent of structuring from this point forward is related to the initial location of the melt within the smart blender barrel when rod rotation was begun. For example, melt near the exit of the blender is subjected to little structuring whereas melt located closer to the feed throat will become more structured as it travels within the barrel. Structure development occurs progressively. The polymer A and polymer B melts are stretched and folded by chaotic advection (Figure 22.1) to give the multilayer morphology at *state 2*. Few layers lead to larger number of layers (*state 3*) and subsequent morphologies are obtained via sequential morphology transitions made possible by progressive structure development. Fiber morphologies eventually emerge from their parent layers (*state 4*), followed by droplet morphologies (*state 5*).

To illustrate the dynamic operation of a smart blender and use of the morphology map, the designated value of N on the process control computer can be changed to restore *state 4* from *state 5* in Figure 22.5 if desired. Additionally, screw extruder flow rates can be changed to increase ϕ to 30% and reach *state 6*. Multilayers at *state 7* can be attained by reducing N, as shown. Such dynamic operation facilitates cost and property optimization of extruded plastics and can lead to more efficient research and development for new products.

22.3 Micro- and Nanolayered Plastics

Examples of multilayer blend morphologies with layers having thicknesses of less than a few microns are shown in Figure 22.6. All were extruded as cast films using a smart blender similar to the one shown schematically in Figure 22.2. Such morphologies can be useful in barrier, light interactive, or toughened plastics. In Figure 22.6a, a multilayer blend structure is shown in a blend consisting of 30% by volume ethylene vinyl alcohol copolymer (EVOH) and LDPE where the EVOH is used to suppress oxygen permeation [2]. Due to component immiscibility and the absence of a tie layer, EVOH and LLDPE layers detached upon fracture of the imaged sample that had been immersed in liquid nitrogen to improve component contrast in the scanning electron microscope image. However, to reduce delamination, the multilayer morphology of Figure 22.6a can be transformed to ruptured layers and ribbons that can impart good oxygen barrier properties. Notably, droplet morphologies typically result from mixing of these polymers and are associated with poor barrier properties in contrast.

In Figure 22.6b, an example is shown of very thin and numerous layers in an extruded 500 micron-thick film composed of 20% by volume ethylene propylene diene terpolymer (EPDM) and PP [29]. Individual layer thicknesses were about 100−200 nm and several thousand layers were present. The viscosity ratio (EPDM/PP) at the processing temperature of 235 °C ranged from 4 to 8 for shear rates during processing from 0.2 to 2 per second. Because of the propylene monomer unit in EPDM, interfacial tension with PP was small (1.07 dyne/cm). This multilayer morphology had very large interfacial area on the order of 10^6−10^7 cm^2/ml. Instabilities that seek to reduce interfacial area can give rise to a variety of derivative morphologies (Figure 22.1). These can initially retain the very small dimensions of parent layer thicknesses [14].

Whereas examples in Figure 22.6a and b pertain to immiscible polymer melts, Figure 22.6c pertains to a miscible polymer pair [31]. Submicron layers were formed in a blend of 30%

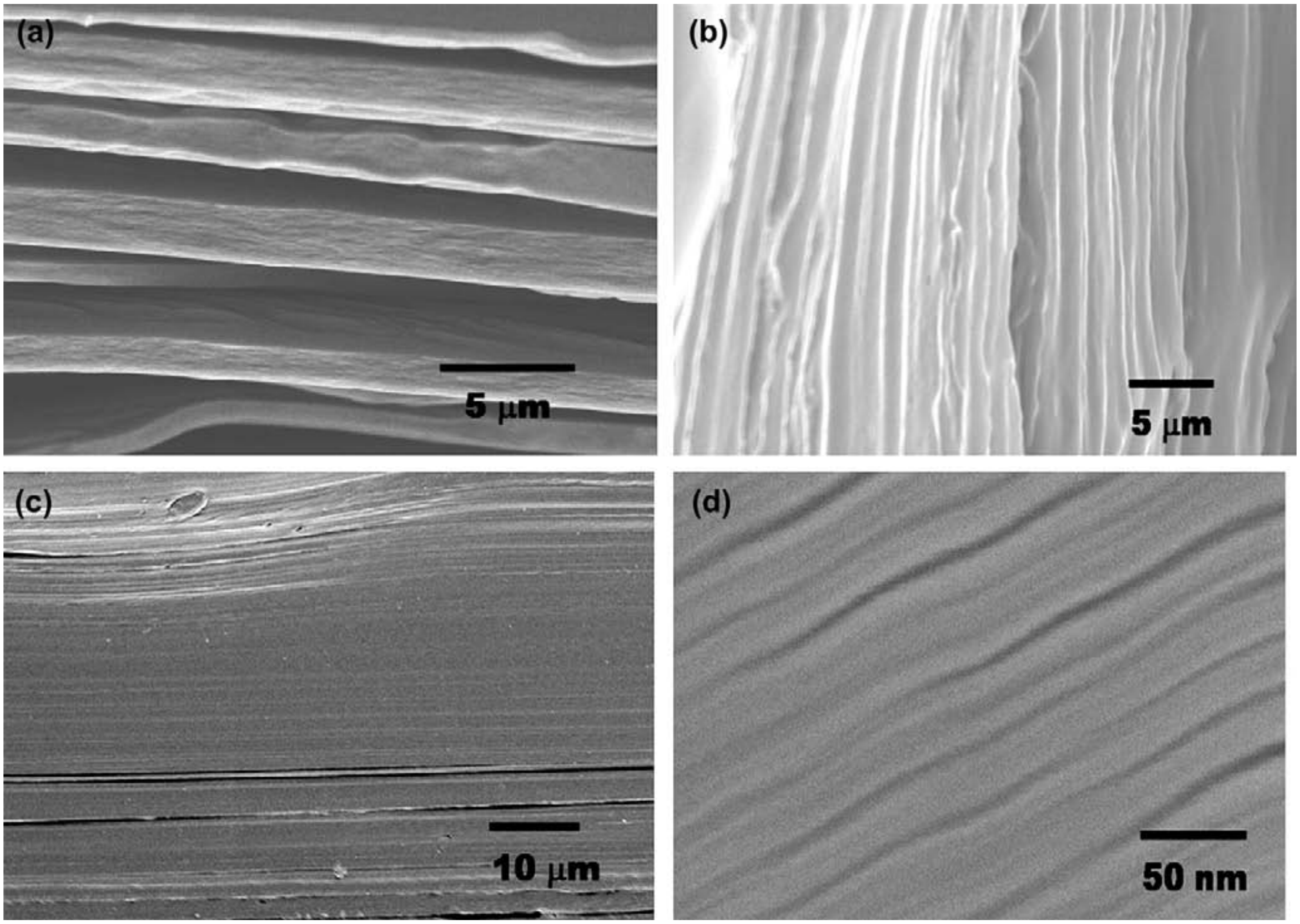


Figure 22.6 Scanning electron microscope images of microlayered and nanolayered plastics: (a) LLDPE and 30% by volume EVOH after cryogenic fracture, (b) 20% by volume EPDM and PP after cryogenic fracture, (c) 30% EVOH by volume and PA with EVOH removed by dissolution, and (d) 15% by volume LDPE and HDPE.

by volume EVOH and polyamide (PA). To improve phase contrast in the scanning electron image, samples were etched in a solvent so that some or portions of EVOH layers were removed. Thicknesses of layers were determined by separate transmission electron examinations to be less than 0.5 micron. The potential amount of layer refinement obtained with a smart blender is demonstrated for a blend consisting of 15% by volume LDPE and high density polyethylene (HDPE) [5]. Because interfacial tension was very low due to molecular similarity between these polymer types, very thin layers readily formed. Samples were fractured after immersion in liquid nitrogen for at least 5 minutes to reveal internal structure. Individual layers of less than 12 nm thickness in an extruded film of 500 micron thickness are shown in Figure 22.6d. The extruded film contains more than 25,000 layers. A progression from thicker and fewer layers to thinner and more numerous layers was documented and correlated to increasing *N*.

22.4 Polymer Blends

Instead of small flow clearances associated with screw extruders, comparatively large spaces can exist in a smart blending device so that physically expansive melt structures with small-scale features evolve. For example, the polymer component melt streams in Figure 22.2 are converted initially to melt layers that are expansive in the spanwise layer direction but are also very thin such as in Figure 22.6. The melt layers, while of practical importance such as when extruded to yield multilayer films, are parent structures to other morphologies via sequential morphology transitions (i.e., progressive structure development). By creating physically expansive and numerous multiple layers, a morphology transition that occurs at one location also generally occurs at other locations having the same degree of layer refinement. Specific locations within a multilayer melt having many layers lack uniqueness so morphology transitions can occur approximately volumetrically.

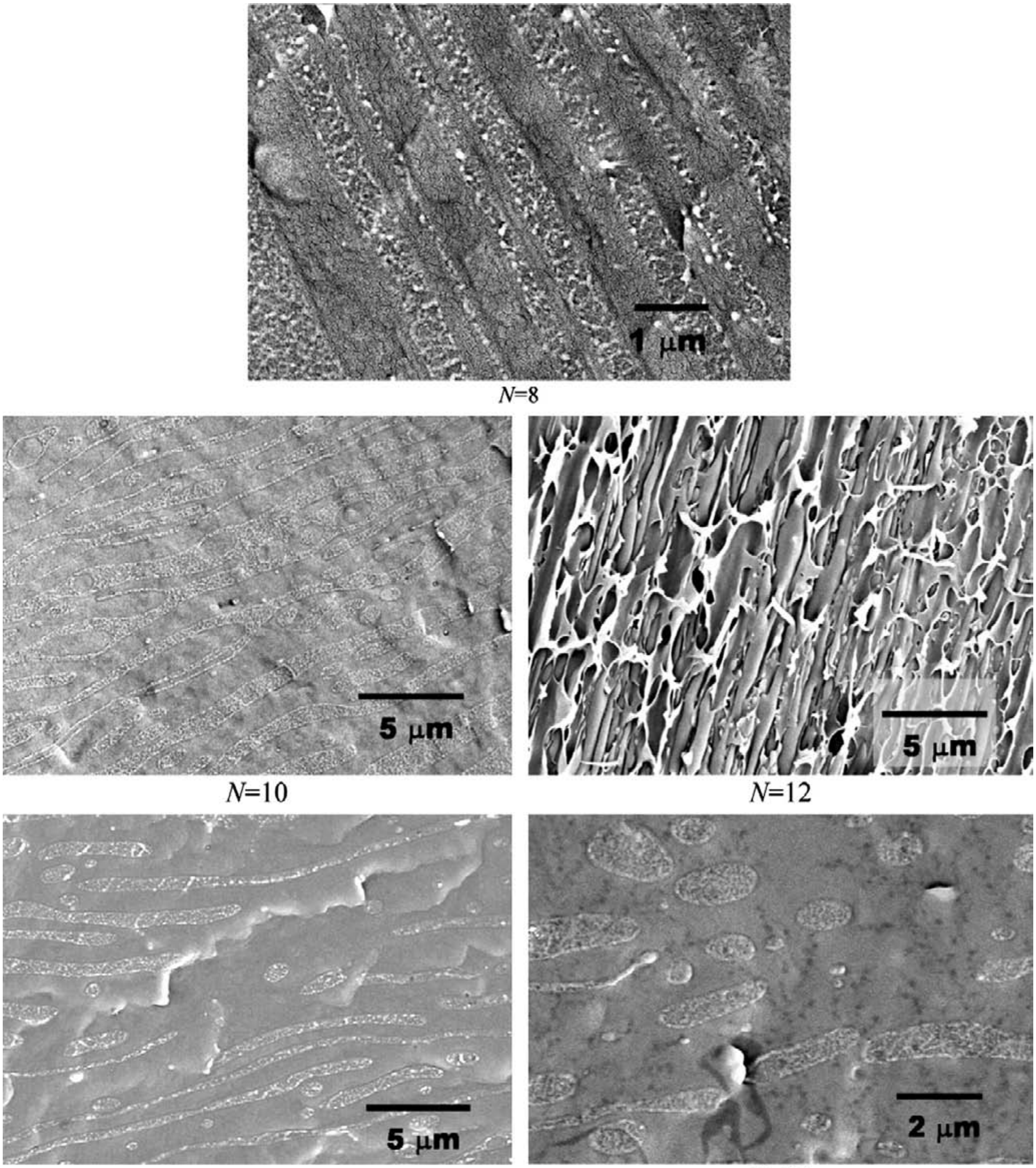
Where interfacial tension exists between melt components, the multilayers give rise to derivative blend morphologies such as depicted in Figure 22.1. Morphology results for PP–LDPE blends are given in Figure 22.7 at a LDPE volume composition of 30% [4]. These results and others at 10% and 20% LDPE are the basis for the morphology map in Figure 22.5. All such blends were extruded as films of 500 microns thickness with a smart blender similar to the one represented by Figure 22.2. By inspecting micrographs available for each *N* or fractional increment of *N* if necessary for clarity, the relation of parent morphologies to derivative morphologies was determined. Morphology development for $N < 10$ is similar to morphology development at the lower compositions of 10–20%. Initial PP and LDPE melt streams were converted to alternating layers such as shown for $N = 8$ in Figure 22.7. Rupture formation in a layer of one polymer component is accompanied by coalescence of adjacent layers of the other polymer component. Layer coalescence is evident for $N = 10$ where oval domains are remnants of LDPE layers in which adjacent ruptures form and enlarge. Hole growth in layers of one polymer component is accompanied by melt drainage from adjacent layers of the other polymer component. Melt drainage leads to layer thinning and promotes rupture formation in the adjacent layers [15]. The multilayer melt with $N = 8$ is eventually converted volumetrically to an interpenetrating blend for $N = 12$ in agreement with computational simulations [14]. The interpenetrating blend is a parent morphology to LDPE platelets and ribbons at $N = 18$ and to droplets at $N = 20$. In contrast, only a droplet morphology is obtainable by conventional processing methods such as screw extrusion.

A fibrous blend is shown in Figure 22.8 that consisted of 55% by volume polystyrene (PS) and PP [25]. This blend was extruded as a 2.5 mm filament. Numerous and long internal fibers are present with diameters less than 5 microns. Close inspection indicates that smaller diameter fibers are encapsulated by larger diameter fibers so that the extruded filament has a hierarchical fibrous structure [32]. Fibrous blend morphologies have been produced in other polymer combinations as well. For blends of Figure 22.7 but with lower LDPE concentrations of 10% and 20%, ruptures also occur among layers but separation distances between LDPE layers is greater so the interpenetrating blend morphology at $N = 12$ does not form. Instead, LDPE layers convert to long fibers which yield 1 micron droplets with increasing *N*. A comparative morphology development has been reported [4].

Fibrous blends can serve as internal reinforcements or perhaps electrical conductors, depending on the polymer characteristics comprising them. Where very thin fibers can be formed (<1 μm) for example, opportunities exist for enhancing crystallinity and tensile properties of the resulting blends especially when extrusions containing them, which themselves can be fibers, are drawn to promote polymer chain orientation [33].

22.5 Polymer–Solid Composites and Nanocomposites

Inorganic solids such as carbon black, nanoclays, graphene, nanotubes, and nanofibers are added to plastics to allow them to be used in applications traditionally reserved for metals and ceramics or to improve the performance of plastics to meet more demanding requirements. Solids addition can also allow expanded use of commodity polymer resins to give new plastic products at reduced cost. Examples of physical properties that can be improved include electrical conductivity, permeability, resistance to crack propagation, flammability, thermal stability, and flexural rigidity, and light interactive characteristics such as refraction index and polarity. When conventional processing methods are used with solid additives, the focus is typically on the degree of



N=8

N=10 *N*=12

N=18 *N*=20

Figure 22.7 Example of progressive structure development resulting from an initial multilayer blend morphology and the primary derivative morphologies producible in a PP/LDPE blend at a constant 70/30% volume composition.

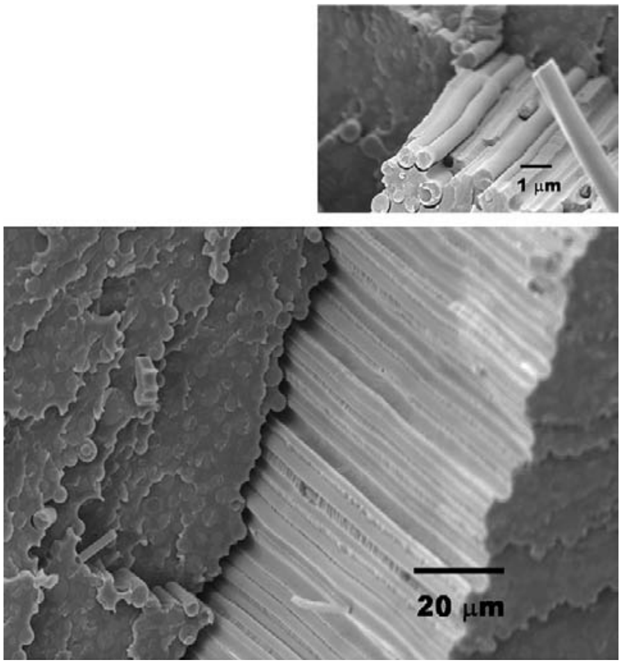


Figure 22.8 Low and high magnification views of a fibrous blend formed in an extruded monofilament consisting of PP and PS. Internal fibers contain smaller diameter fibers so the filament has a novel hierarchical structure that may be associated with physical property enhancements.

mixing so that structural outcomes and opportunities for property enhancements can be limited. In contrast, solid additives are arranged into specific structural types within a plastic by chaotic advection that are associated with physical property enhancements in recognition of the fact that structure can be more influential in determining physical properties of a composite than its composition.

Optical micrographs of composites consisting of linear low density polyethylene (LLDPE) and 3% carbon black by weight are given in Figure 22.9 where internal structures are revealed in thin translucent sections by cryogenic microtomy [7]. Such composites can be produced by supplying a smart blender with LLDPE as polymer A and a masterbatch composed of carbon black and LLDPE as polymer B in Figure 22.2. The masterbatch and LLDPE are stretched and folded by chaotic advection into multiple layers (Figure 22.1) until layer thicknesses become comparable to the sizes of carbon black particles such that extended particle networks form. The structured composite melt can be extruded from the smart blender in a desired form. The examples in Figure 22.2 were extruded as cast film. Electrical current flow is provided along the many thin striations. By changing the amount of chaotic advection in terms of the parameter N (Section 22.2), interconnectivity among striations is adjustable to alter directional conductivity properties and conductivity levels. In effect, percolating networks can thereby be constructed in situ in lieu of being simply stochastic outcomes dependent on particle concentration. The striated structure in Figure 22.9a is convertible, for example, to a structure such as in Figure 22.9b having less property anisotropy.

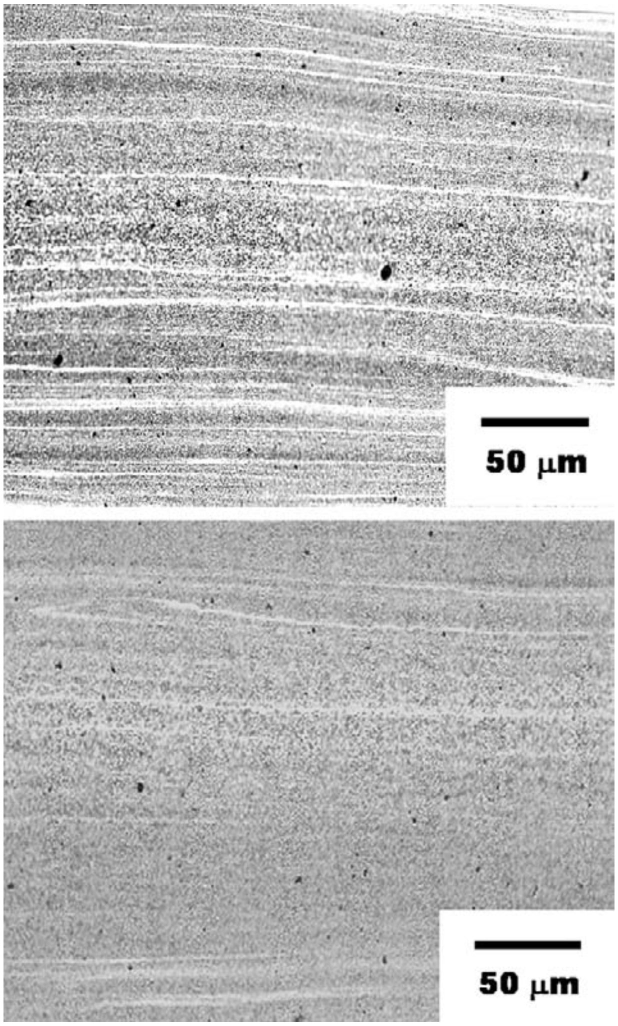


Figure 22.9 Optical micrographs of translucent 100 nm thick sections taken from extruded films with addition of 3% by weight carbon black. Interconnectivity of carbon black is controllable to impart distinct electrical properties.

An example of a novel clay nanocomposite is shown in Figure 22.10 that may be especially well suited to high barrier packaging, low permeation storage vessels and piping, impact resistant materials [5,18], and light interactive media. It makes optimal use of inorganic material in terms of physical property enhancement by localizing and orienting it within numerous layers. Clay particles when broken down through a process referred to as exfoliation consist of very thin (~1 nm) silica platelets having high frontal area (0.01 μm^2) and very low mass diffusivity [34]. When present in sufficient number in a plastic and especially when oriented, the platelets can effectively impede molecular diffusion, for example [35]. To produce the nanocomposite in Figure 22.10, a twin screw extruder is used to prepare a masterbatch of PA and nanoclay. Nanoclays and guidelines

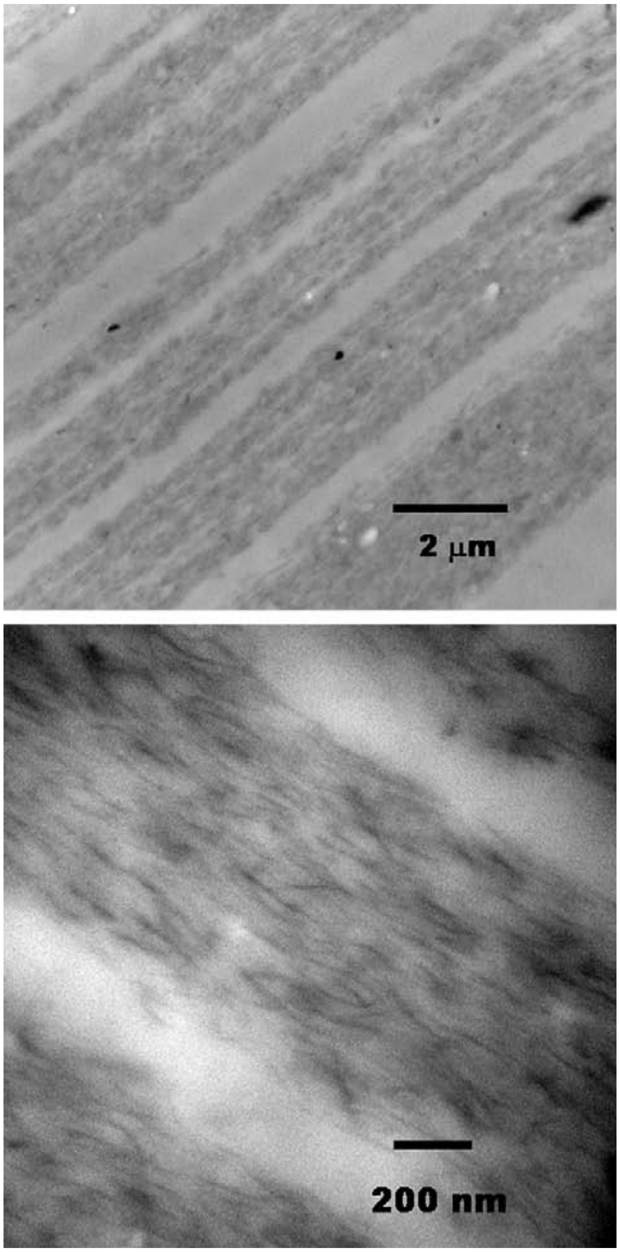


Figure 22.10 Novel nanocomposites extruded in film form with silica platelets both oriented and localized in numerous internal layers to give plastics with low permeability and other property enhancements. (Layers of matrix polymer separate both the platelets and platelet-rich layers. Internal layers and platelets are optimally oriented parallel to the film surface).

for their use are available from several manufacturers. The masterbatch and PA are supplied to the smart blender as polymers A and B (Figure 22.1) and can be extruded in a desired form such as film, sheet, or tubing using smart blenders such as shown in Figures 22.3 and 22.4.

The particular example in Figure 22.10, which was extruded as cast film, was produced with a masterbatch of 4% nanoclay by weight to give an overall 2% nanoclay loading in the resulting nanocomposites. A multilayer structure of platelet-rich layers and PA layers results such as in Figure 22.10a for $N = 10$. Platelets are oriented throughout the film such that their frontal areas are parallel to the extruded film surface and net permeation direction. Due to orientation and localization within numerous multiple layers, the clay additive is most influential in affecting physical properties for a given overall clay loading. The optimal structure allows reductions in nanoclay concentrations for a particular level of physical property enhancement. The average thicknesses of PA and platelet-rich layers are selectable via specification of N to the process control computer in Figure 22.2. The PA layers in the upper micrograph of Figure 22.10 are reduced from about 1 micron thickness to less than about 125 nm thickness in the lower micrograph by specifying a larger N. In tandem, the mean lateral separation distance between platelets within a platelet-rich layer is increased. The physical properties of resulting nanocomposites are thereby adjustable during smart blender operation so that product optimization can be performed efficiently.

Orientation of thin or oblong particles results from the alternating shear flows in smart blenders described in relation to Figure 22.1. Orientation can occur nearly volumetrically because chaotic advection effectively shuffles melt to different locations during blending and flow fields are simpler than those arising in mixing machines and screw extruders. Equivalently, particle orientation can be considered an outcome of decreasing layer thicknesses as chaotic advection proceeds. In effect, platelets, nanotubes, or oblong particle clusters orient in response to stretching and folding to reside with the layers containing them. As with carbon black and clay additives, processing methods can also be applied to nanotubes and nanofibers. Smart blending also offers a means to place nanotubes or nanofibers within minor or major components of polymer blends such as those shown in Figures 22.6—22.8 to impart additional structural effects to polymer blends. With smart blenders, physical properties of nanocomposites are not solely an outcome of the nanoscale dimensions of solid additives such as provided when conventional mixing is used but instead are also derived from structure at the nanoscale. The nanocomposites in Figures 22.9 and 22.10 are such examples.

22.6 Mixtures and Nanodispersions

Chaotic advection can be effective in dispersing a minor polymer component or solid additive in a major polymer component. Results of numerous chaotic mixing investigations have been reported that consider chaotic motions in passive tracer particles in a liquid [20—23,27,34]. For polymer blends, dispersions of small droplets in the minor component are often the goal of conventional processing methods such as mixing with twin screw extruders. Colorants and functional solids such as carbon black, nanoclay, graphene, and nanofibers are similarly mixed with host polymers to produce masterbatches or specialty plastic resins. (As mentioned in Section 22.1, however, structured plastics can have superior properties for an equivalent net composition because properties of a composite can depend more on structure than on composition.) A smaller droplet size in a blend is often pursued by operating mixing equipment at higher shear rates, promoting extensional flows via machine design and prolonging melt residence time. Unfortunately, the reduction in droplet size can be less than sought because droplet deformation and resulting breakup become more difficult to induce as the viscosity of the major component decreases as a consequence of shear thinning behavior. Molecular breakdown (i.e., chain scission) from viscous heating can also prove problematic especially in shear-sensitive fluids.

Droplet dispersions in a polymer blend are obtained differently in smart blenders than in conventional mixing machines. The general sequence to obtain droplets is depicted in Figure 22.1 based on experiments and computational models. Chaotic advection causes minor and major component polymer melts to become arranged into numerous and expansive multilayers. As the layers decrease in thickness and increase in number by continuing chaotic advection, breakup eventually occurs in the thinner minor component layers. Minor component droplets result that have diameters related to the thickness of their parent minor component layer. An example droplet dispersion in a blend of 20% by volume LDPE in PP is shown in Figure 25.11a where average droplet diameter is about 1 micron [4]. At 30% composition, somewhat larger droplets result (Figure 22.7, $N = 20$). Processing was performed for both examples with shear rates less than 1.5 per second so viscous heating was negligible. Droplet dispersions can also be formed at higher shear rates by chaotic advection as demonstrated in blends of PP and PA [37].

To obtain dispersions of solid particles, one or both polymer melts that are supplied to the smart blender in Figure 22.2 can contain an initial mixture of solid particles. The initial mixture can be a masterbatch produced with a twin screw extruder. Both polymer melts are stretched and folded to give structural arrangements such as shown in Figure 22.9a with carbon black and Figure 22.10 with nanoclay [38]. By continuing chaotic advection further and focusing on Figure 22.10, the PA layer can be reduced to a vanishingly small thickness so that the multilayer structure is no longer evident and an excellent dispersion of platelets results such as in Figure 22.11b. The dispersion consists of volumetrically oriented platelets due to stretching and folding of chaotic advection (Section 22.5). It can be shown mathematically that such nanodispersions are theoretically optimal dispersions due to the chaotic motions that underpin their formation.

Dispersions are obtained by specifying to the smart blender large values of the parameter N (Section 22.2). Even so, a variety of structural types are formed in the smart blender prior to the extrusion point due to progressive structure development. An extrusion with droplets such as in Figure 22.11a can be transformed to one having other blend morphologies such as depicted in the morphology map of Figure 22.5. Similarly, extrusions with the platelet dispersion of Figure 22.11b can be changed to extrusions that have platelets localized within many layers such as the example in Figure 22.10.

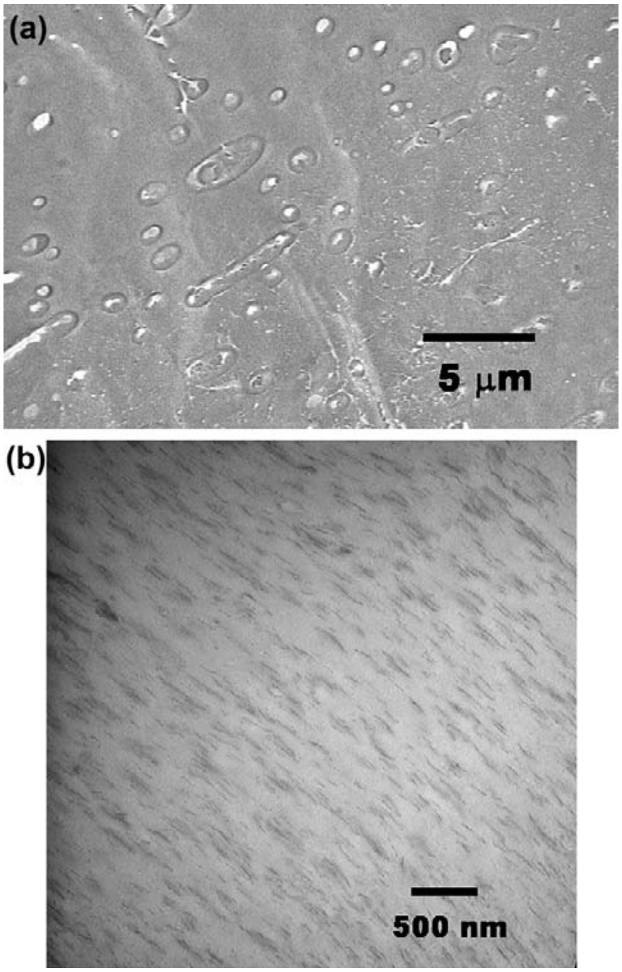


Figure 22.11 Examples of dispersions: (a) LDPE droplets in a blend of 20% LDPE and PP and (b) nanodispersion of silica platelets in an extruded film where platelets are volumetrically oriented.

22.7 Decoration

The natural world has an infinite variety of patterns in woods, rocks, and other materials. Similarly, due to progressive structure development of smart blending (Sections 22.1 and 22.2) and chaotic advection, extrusions can be produced with literally an infinite variety of appearances using machines such as those in Figures 22.2–22.4. Examples of simulated wood grains extruded as cast film are given in Figure 22.12 [9]. This example was produced in conjunction with an investigation of electrically conducting plastics to show early structure formation in an extrusion [7] with carbon black as an additive.

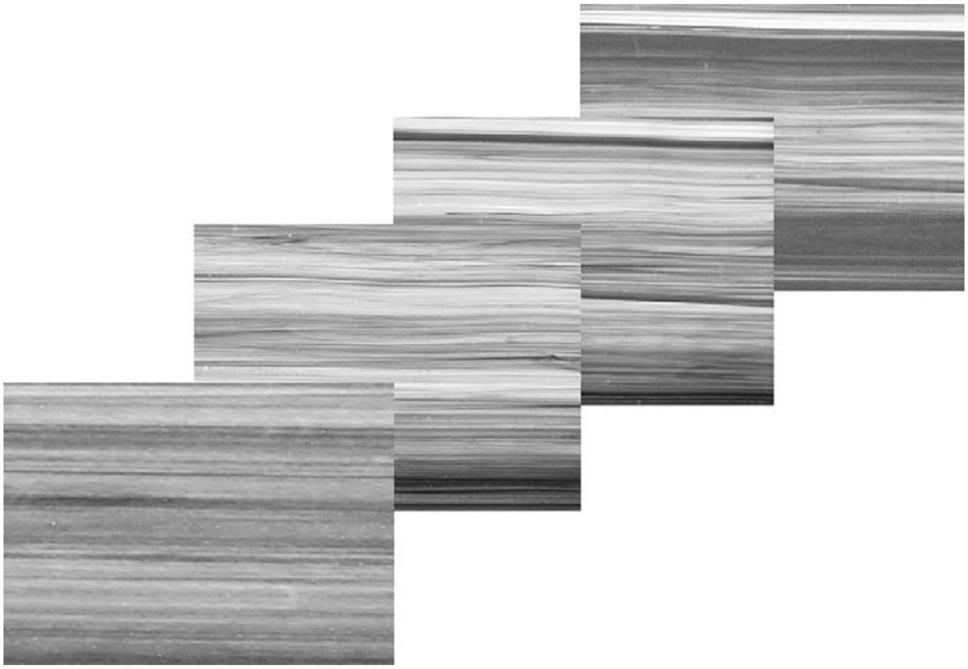


Figure 22.12 Realistic simulated wood grain patterns formed controllably in extruded film. Because chaotic motion underpins the process used to form them, each extrusion can have a unique pattern if desired. Stone-like and abstract patterning can also be imparted.

To produce these decorative plastics, the smart blender is operated to give ribbons that wrap in a helical format around stir rods (Figure 22.2). Such helical ribbons can be obtained by using a smaller rotational displacement η_i than specified (Section 22.2) for expansive layers such as shown in Figure 22.6. Desired colors are obtained by using pigmented polymer resins such as those from colorant manufacturers intended specifically to impart wood appearance. By extruding this structured melt through a die, the various wood grain patterns in Figure 22.12 form. Additionally, as with trees that have a layered structure in the form of tree rings disturbed by branches, chaotic advection introduces subtle and attractive intricacies into the simulated grain. Like cut wood, the simulated grain appears both on the surface and interior of extrusions. By dynamically changing the manner in which stir rods are rotated, simulated wood grain patterns can be repeated at intervals along an extrusion while the pattern within the interval remains unique everywhere. Alternately, the smart blender can be operated such that the wood grain changes continuously along an extrusion length. Repetition at specified length intervals can be useful where it is desired to match grain patterns at exposed joints of thick extrusions such as sheet or in ends of laminates. Nonrepeating wood grains can be desirable where large surfaces or lengths are involved such as in wall or floor coverings.

The ability to produce an infinite variety of simulated wood patterns is done via online control with no physical changes to the smart blender. Similar opportunities are available to form simulated rocks and abstract patterns in plastics or in ceramic materials processable as slurries. Due to pattern uniqueness and their chaotic advection basis, counterfeit proofing of products may also be achievable using these approaches. Many patterns that appear in extrusions have fingerprints of the chaotic motions used to create them.

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Part IV: Additives, Colorants and Fillers

23 Plastics Additives

Ernest A. Coleman
Honored Fellow of the Society of Plastics Engineers, Plastics Engineer & Chemist, C P Technology,
PA 17584, USA

23.1 Introduction

Plastics make useful complex shapes as well as inexpensive high-volume items. In order to meet these diverse demands, commercial polymers are modified with additives to make plastics.

Compounding of polymers with additives and modifiers to make commercially useful plastics is a business that is constantly changing due to new materials, price changes, improved processing machinery, changing customer needs, environmental laws and concerns, etc. Some needs are persistent such as the requirement to fabricate parts, ways to upgrade properties, how to correct for problems introduced by the use of additives to accomplish the first two items, and controlling costs. The following remarks deal with additives from these points of view. No perfect solutions exist, so polymer additives and modifiers is a truly dynamic field of study.

23.2 Overview

Polymers as made are usually not suitable for industrial use as plastics, so industry uses additives and modifiers to adjust the properties of the as made polymers to make most of the plastics used today. The first polymers that became available are natural products like cellulose, natural rubber, or simple chemicals like phenol and formaldehyde that make “bakelite.” In order to shape cellulose—the most abundant polymer on earth—into useful products, two things must happen.

First cellulose is modified by chemicals like acetic or nitric acid to make it easy to process. Then these chemically modified cellulose materials are cast into thin sheets or films, but thick shapes will crack, and even the thin forms have stiffness problems. Plasticizers like camphor and fillers like sand or sawdust corrected these problems.

Many thermoset materials like the phenolics (bakelite) have large shrinkage that will cause cracking. Fillers reduce this shrinkage and solid crack-free parts can be fabricated.

Based on these examples and many similar ones, polymer additives or modifiers are necessary to perform three essential functions. First, additives are required in order to process or fabricate many polymers. Several as made polymers have thermal stability limitations that force the producers to find and utilize stabilizers that allow melt processing.

Once this obstacle is addressed, room temperature storage can be a concern. Many polymers must be stabilized from the effects of oxygen, ozone, and other gases in the air. Exhaust gas from forklift trucks has been associated with odor problems in polypropylene food contact items.

Another example involves some polymers (and monomers) that will not wet reinforcing glass fibers; so wetting agents are used, in order to process the mixture into a useful plastic. These additives are usually put onto the glass by the glass manufacturer. Sometimes, the plastic compounder adds his own wetting agent to gain a competitive advantage, but in all cases, these additives are necessary to make the plastic function properly.

The second type of additive is for property enhancement. In the above example, a wetting agent may be necessary to process the polymer, but a coupling agent can be added as an enhancement to provide long-term durability. Fillers improve the flexural modulus and DTUL (deflection temperature under load). Color, odor, surface gloss, and other properties are improved by additives of this second category. Rubber improves impact resistance. Fibers improve both impact and modulus in many cases. Flame retardants enhance properties of a plastic and make it more valuable. Additives of this second type pay for themselves by giving much more performance value than the added cost of the additive.

The third type or class of additive corrects the flaws of the first two classes. Plasticizers are required to fabricate flexible PVC. Some of these plasticizers provide food for organisms like mildew and fungus. An additive is needed to correct this.

Additives are the essential ingredients that convert raw polymers into commercially useful plastics. Plastics that are fabricated into complex and useful shapes that meet so many needs of the modern world would not be possible without additives.

23.3 Thermal Stabilizers

23.3.1 Overview

Some synthetic polymers have chemical bonds that are less thermally stable than the chemically pure backbone of the perfect structure. These “weak links” often fail during

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melt processing and lead to reduced performance of the resultant plastic part. Some commercial polymers contain chemical impurities like catalyst residues and thermal decomposition products that further reduce thermal stability of the backbone chain of atoms that create the polymer.

Thermal stabilizers minimize molecular weight (MW) change during melt processing by blocking the adverse effects of polymer flaws and impurities. The most thermally sensitive polymers are PVC, PP, and POM (polyoxymethylene), but even HDPE can change MW during melt processing.

23.3.2 PVC

Several different chemical classes of additives are used for thermal stabilization of PVC. These include divalent lead compounds, tin and antimony based chemicals, and mixed compounds of cadmium/barium, calcium/zinc, and many others. In general, the lead based thermal stabilizers are used in electrical applications, the tin based ones are used for external uses in siding and other extruded shapes, and mixed compounds are used in plastisols and injection molded parts.

Thermal stabilization of PVC is complex because:

- different base polymers are used commercially
- use of various plasticizers alters the amount and type of stabilizer
- processing conditions change thermal stabilizer needs (twin screw vs. single screw for example)
- toxicity of the additive package
- cost, etc.

All of these topics are considered in detail in *Handbook of Vinyl Formulating*, second edition, Wiley-Interscience, edited by Richard F. Grossman.

23.3.3 Polyolefins

Polypropylene (PP) and high-density polyethylene (HDPE) represent two extreme cases of a wide variety of commercially important polymers. PP and HDPE behave differently when thermally stressed during the melting process. PP decomposes to low MW products and HDPE crosslinks; increasing MW. Both polymers have carbon chain backbones and hydrogen is the only other atomic species: the difference is in chemical structure.

HDPE is a linear chain of carbon and hydrogen in the form of methylene (-CH_2-) groups. There is a methyl group (CH_3) on the chain ends. PP is like HDPE, but every other hydrogen in the chain is replaced by a methyl group.

This change makes a big difference in thermal stability and many other properties as well. Considering only thermal stability, PP will undergo carbon-to-carbon chain breaks that accelerate with temperature. At the melting point, chains break so rapidly that the process results in a solid polymer becoming a wax, liquid, or even a gas. All this is related to the structural differences between HDPE and PP. In short, PP cannot survive melt processing without thermal stabilization.

HDPE does not decompose like PP. HDPE carbon chains are not destabilized by methyl groups; so the HDPE resists decomposition by heat better than PP. On the other hand, because the carbon chain is so stable, it will undergo crosslinking. Hydrogen atoms will be replaced by carbon chains, both short and long. This results in an increase in MW. To minimize this, HDPE must be stabilized against this type of change. In short, HDPE needs some thermal stabilization.

If the same thermal stabilizers are used for both polymers, the amounts required to survive one melting cycle without excessive change of MW are quite different; PP takes three to ten times the stabilizer, as does HDPE. Polymers that are between PP and HDPE in the number of side groups (methyl or alkyl groups that behave like methyl) require amounts of thermal stabilizers between the extremes noted.

The companies that manufacture these hydrocarbon based polymers are well aware of these thermal stability concerns and more. The additional concerns involve color, odor, surface, etc., problems related to the specific polymer and materials used in the synthesis. Catalyst residues can have major effects on these other properties and they must be handled accordingly. There are two methods: elimination and/or quenching with additives.

Hindered phenolic antioxidants are useful in addressing some of these concerns. Each manufacturer has different standards and needs related to the exact polymer and its synthesis conditions. This is why there are many different thermal stabilizer systems in use for this large class of hydrocarbon based polymers. The best sources of current information are patents along with analytical results. Even this is not perfect because some additives might undergo chemical changes during thermal processing of the material that they are protecting.

23.3.4 Polyoxymethylenes (POM polyacetals)

The chemistry of the POM family of polymers and copolymer makes them extremely sensitive to acids, excessive heat, and many different types of impurities including many additives (colorants, fillers, etc.). Some grades are also sensitive to bases. Manufacturers of these useful engineering polymers warn processors and end users about these concerns. So long as processors and end users observe the guidelines for each specific grade, there will be no need for additional additives in most cases.

23.4 Nucleating Agents

Nucleating agents are used with polymers that can crystallize in order to speed cycle times. After melting, it is solidification rate of the plastic into a useful shape that controls processing and cycle time. Both amorphous and crystalline polymers are subject to molded-in stresses that are a result of the tool geometry. These are the concerns of injection molding and extrusion experts since they are controlled largely by tool geometry and processing conditions.

Crystalline polymers have an additional concern. When they cool, they also crystallize. The amount of crystallization and the type of crystals formed are controlled by thermal history, cooling rate, and additives. There are specific additives that will speed or slow crystal formation and they will also affect the exact crystal that forms.

Fast crystallization allows faster molding cycles or clearer extruded thin film. Nucleation speeds this crystallization process. Crystallization is a complex subject because there can be a downside as well as immediate economic advantage. Many different types of chemicals can nucleate crystallization. The effect is specific for the polymer and the chemical. Glass fibers, pigments, talc, etc. can nucleate crystallization for some polymers.

If crystallization is too fast, crystal size will be small. This is desirable for clear film but for some polymers in time, there will be a growth of crystallite size along with a change of properties.

There is another meaning for nucleating agent that must not be confused with crystal nucleation described above. In the foaming process, dissolved fluids in the polymer must come out of solution, form a gas bubble and create a foam cell. In this application, the number of nucleating agents can control cell size. Shock nucleation is a mechanical process that is generally independent of material nucleating agent. All of this applies to the foaming process and not crystallization.

Some polymers crystallize in more than one crystal type. This leads to different properties from the same polymer. For example, PP has three well known crystal forms; The alpha (α) is the usual form with a melting point of 164 °C. Special nucleating agents will produce the beta (β) form with a MP of 150 °C. This crystal form is more ductile and impact resistant than the alpha but it is thermodynamically less stable, so it reverts to alpha. The third form is gamma (γ) and it is formed by crystallization after high sheer in a thin section. It is the "living hinge" that is so important in PP items with moving parts. Flexing immediately after molding is a factor in some products. Other crystalline polymers have different types of crystals that might be commercially useful.

23.5 Antioxidants

23.5.1 Primary Antioxidants

Antioxidants (AO) function in the environment and protect polymers for long times at ambient conditions. Several different chemical types of antioxidants serve different polymers and different functions. Some that are in commercial use are discussed below.

Phenolic type AOs are very effective as thermal stabilizers as well as providing long term environmental protection. The chemistry of this class of AOs is based on the well known food additive butylated hydroxy toluene (BHT). BHT is an effective AO for many polymers but its low MW and poor solubility in many polymers limits use. These limitations are overcome by the wide range of chemical structures all based on BHT that are commercially available. Cost of this class of AOs is falling as the various types come off patent and production in Asia steps up to meet demand.

23.5.2 Secondary Antioxidants

Secondary AOs extend the life of the more expensive phenolic type primary AOs. They also delay onset of color from used up phenolic type AOs. As phenolic primary AOs react with oxygen, they form different chemical structures that are yellow to tan in color. These quinone type structures are not AOs and they are expensive, having formed from expensive primary AOs. Chemists have dealt with this problem by developing secondary antioxidants that keep quinones from forming until all the secondary AOs are consumed.

There are two different chemical types of secondary AOs. Both have the common properties of low cost relative to primary and the ability to be oxidized to colorless materials before the quinones can form from primary AOs. Organic phosphite and organic sulfur compounds modified to fit the needs of specific polymers are the chemicals that are used.

Sulfur based secondary AOs sometimes have odor problem but they are very effective in rubber based plastics. They will react with phosphites, so mixed secondary AOs are never used.

Phosphite type secondary AOs sometimes have water sensitivity, so there are many different materials offered for each specific polymer and end use. Some of the newer secondary AOs of this class approach or exceed primary AOs in cost, but this is justified by reduction of color and falling cost of some primary AOs.

Interaction of the sulfur and phosphorus types of chemicals can be a problem in recycling. If it is suspected that these two different types of chemicals are present in a mixed recycling blend, additional secondary AO of one type should be added in excess to provide long environmental life without color formation. The same is true when using these systems as thermal stabilizers.

23.5.3 Hindered Amine Light Stabilizers (HALS)

Hindered amine light stabilizers (HALS) were developed as photostabilizers and/or metal deactivators. It was soon determined that the oxime structure functioned as an AO as well. In fact, these AOs are almost self-regenerating so they last for long times. They also serve their original functions, thus they often do double and even triple duty. These additives are responsible for high performance PP used in artificial turf that is expected to perform for up to a decade and more.

HALS are used whenever high performance is desired and the chemistry of the plastic allows. HALS cannot be used with halogen containing compounds such as PVC or halogenated flame retardants. Based on the success of HALS, other oxime based AOs are under development. They may be less expensive than HALS in some cases.

23.5.4 Lactones

Lactones are similar to HALS in some of their chemistry but their nitrogen free chemistry allows use in the presence of halogens. Some natural products have lactone structures and they function as food antioxidants. Lactones are becoming the AOs of choice in some plastics as their popularity grows.

23.5.5 Vitamin E

Also known as, *dℓ*-α-tocopherol, vitamin E is an antioxidant that is used commercially in polymers. The synthetic form of vitamin E will function as well as the natural product in polymers; most of these uses involve food contact or biodegradable polymers.

23.5.6 Carbon Black

Carbon blacks come in many different varieties. Some grades have AO properties especially in high concentrations. Many grades of plastics that are stored or used out of doors contain high levels of these blacks and lesser amounts of conventional more costly AOs perform satisfactorily. In some cases, the AO can be eliminated altogether.

23.5.7 Thin Films

When thin films are extruded, special care must be taken to avoid loss of additives by sublimation. The high surface area and high temperatures of extrusion make this a critical issue for all high surface parts exposed to high temperatures. This is the reason that some AO molecules have very high molecular weights to keep them from volatilizing. Other parts of the AO molecule improve compatibility with the polymer that they are designed to protect. This is why some AO molecular structures look so big and complex; they have to be that way to function.

23.6 Flame Retardants

23.6.1 Halogen Free

Halogen free flame retardant systems are highly desirable because they have fewer toxicity and regulatory issues than the sometimes more effective halogen systems. This is an active area for research, and new additives and tests are appearing with increased frequency. Some halogen free systems use phosphorus or nitrogen chemistry and others are based on inorganic minerals.

23.6.2 Inorganic Flame Retardants

The least expensive, most used, and possibly least toxic flame retardant (FR) is aluminum trihydrate (ATH) and similar inorganic hydrates. These materials must be used at very high loadings (sometimes exceeding 60% by weight) so they function as fillers as well as FR materials. They function by decomposing to liberate water at temperatures exceeding the melt processing temperatures of many polymers, so they are not used in many of the high temperature thermoplastics such as PA, PBT, PC, etc. Even PP is beyond the limits of ATH. When ATH decomposes, steam results. If this happens during melt processing, the polymer is foamed. ATH is used in polyethylene wire and cable (W&C) formulations as well as thermoset polymers like epoxy and thermoset polyesters. So long as the temperature does not exceed 200 °C, ATH is safe to use (but check first before doing large scale processing).

Magnesium hydroxide is an inorganic hydrate that is more thermally stable than ATH. It can be used in PP and similar high melting thermoplastics. Like ATH, $Mg(OH)_2$ must also be used at high concentrations to achieve good FR performance.

These high concentrations of FR minerals tend to increase part density and brittleness. Some polymers can react with them as well. Thermoplastic polyester like PBT cannot be used with them for this reason. The big advantage of these inorganic materials is low cost as well as their white or light color and the non-toxic benefits. Sometimes they are used at low concentrations with other FR materials as cost savings additives. Sometimes they provide other benefits in certain electrical applications like ion sequestration.

23.6.3 Other Halogen Free Systems

Additives based on melamine, phosphorus, and other char making materials are finding use in specific FR systems. The phosphorus based systems appear to function best with oxygen containing polymers. The char is believed to be a complex phosphorus oxide based coating that blocks oxygen from coming into contact with monomer or other flammable materials. The melamine based systems form chars that are based on nitrogen as well as phosphorus in the case of melamine phosphate systems.

Nano particles dispersed in polymers are presumed to block or slow down the contacts between oxygen and fuel. This reduces burning rate and allows other flame retardants to extinguish the fire. This binary system approach can be cost effective by reducing the amounts of FR materials required. This also allows maintenance of many physical properties that otherwise would be altered by larger amounts of additives as often happens with the other FR systems.

Some polymers have some unique chemistry that allows the use of relatively low amounts of additives that catalyze a molecular rearrangement that provide some flame resistance. Polycarbonate (PC) is an example. It is a polymer based on para orientation of chemical bonds. These para bonds can be changed to meta bonds by traces of sulfonic acids. Meta linkages are less flammable than the original para ones. Of course, some other properties are changed as well. Other aromatic based polymers take advantage of this chemistry. "Nomex" is a meta bonded form of the better known "Kevlar." Kevlar with para bonds has better properties but Nomex is more flame resistant and is used by firefighters worldwide.

23.6.4 Halogen Systems

Traditional antimony/halogen systems are still in wide use because they are proven by years of successful applications in the electronic and electrical markets. There are many applications where thin sections (<1 mm) must be flame retarded to meet UL V-0 or V-5 standards where only halogen systems are effective.

One of the more popular systems is decabromodiphenyl ether (DECA) and antimony trioxide. DECA has been under attack but so far, it seems to be less toxic than several closely related bromated aromatic compounds that have been banned in Europe and elsewhere. Some of the concern about DECA occurred when decabromodiphenyl accidentally got into the human food chain. The similarity between the two different chemical names (decabromodiphenyl and decabromodiphenyl ether) is not easily detected by those who have not studied chemistry, and this may have contributed to some of the concern. On the other hand, there are real toxicity concerns about many brominated organic chemicals.

High melt processing temperatures require more thermal stability in the FR systems and this usually means the more expensive bromine compounds. Remember, the FR system must be stable at processing conditions and decompose to extinguish the fire at temperatures slightly above the highest processing temperature. When the thermal properties of the polymer allows, chlorine based compounds are used with antimony oxide, because they usually decompose at lower temperatures and they are usually less expensive than their bromine counter parts.

Halogen based flame retardants are special chemicals. They are required to be relatively non-corrosive, low toxicity, and yet, liberate corrosive halogen compounds that react with antimony oxide at fire temperatures. Some of these chemicals have chemistry similar to PVC and, thus, sometimes they require thermal stabilizers to withstand thermal processing.

PVC and other highly halogenated polymers are useful in construction applications (sometimes, after they are upgraded with antimony oxide) such as siding, windows, and electrical systems including commercial W&C uses. Some of these PVC type polymers are used in blends with more flammable polymers to make flame resistant business machine housings with stringent FR specifications. These are excellent materials that make use of several properties of PVC as a blending additive. ABS, SBR, and similar polymers are blended with PVC for these applications.

23.7 Color and Colorants

Pigments are solid materials that scatter as well as absorb light. Dyes are soluble materials that absorb light but do not scatter it. Thus, the color from dyes is often brighter, sharper, transparent, or cleaner than that from pigments.

Most plastics use pigments for color in spite of the above because pigments, in general, are more thermally stable, more stable to exposure to light, and not prone to "bleeding" or exuding out of the plastic to discolor objects in close contact. Pigments produce opaque colors in thick sections and translucent ones in thinner sections. Most colors in a common series look better if they all have similar degrees of translucency at the same thickness. Therefore, depth of color or opacity as well as color must be matched when working with pigments in plastics.

When it was determined that some colorants might hurt the environment, they were no longer available or they were manufactured at off shore locations. Some colorants are safe under all end use conditions but can be a problem when discarded at the end of their useful life. Other colorants might be a problem in fires or when incinerated.

Because of this concern, today some dyes are used as pigments by converting the soluble dyes to insoluble pigments. There can be processing problems with these materials because sometimes they can dissolve or melt in the polymer carrier at high temperature. When these pigment dyes come out of solution upon cooling, they crystallize in different sizes and/or shapes than intended, thus altering color. This alters color and transparency leading to customer problems.

Color is a most interesting field of study. An introductory course of several days' length is offered by SPE and it is useful even for plastics professionals not directly involved with color.

Some of the reasons that certain colorants are more expensive than others are worth a little investigation. Copperphalocyanine (CPC) blues and greens are relatively non-toxic colorants, but they are manufactured overseas for the most part because the process has many byproducts that are hard on the environment. Cadmium colors (reds, oranges and yellows) are manufactured from cadmium compounds that are highly toxic. The colorants (cadmium sulfoselinides) are non-toxic but their products of incineration are toxic. All of these concerns and others apply to several classes of polymer additives and modifiers that themselves are only mildly toxic.

23.8 Fillers

Calcium carbonate comes from natural sources such as bone, limestone, shells, or it can be made synthetically. It can be pure enough to take as medicine (anti-acid), or it can be ground up rock with many impurities (also used as anti-acid). It may be the most widely used filler. (A similar claim can be made for carbon black or carbon in all its many forms.) Calcium carbonate is widely used in PVC as an acid acceptor, in polypropylene as a filler, and in many thermosets and thermoplastics as an inexpensive filler.

Precipitated grades as well as the pulverized ones can be surface modified. The precipitated calcium carbonate that is used in polypropylene (and other similar thermoplastic resins) is usually surface modified with stearic or isostearic acid.

$CaCO_3$ is an extremely important commercial material for a few large volume polymers; both thermoplastic and thermoset. If one grade does not work in your application, ask your vendor as well as other vendors for alternatives. There will be two or three grades for most applications, but only one or two will generally give superior performance. As in all additive situations, keep looking and asking until you get the results you want!

Carbon black provides a black color that protects many thermoplastic polymers from the damaging effects of sunlight (UV) by absorbing the damaging energy. Certain carbon blacks will function as antioxidant materials and others are used as jet black pigments. Still other grades function as conductive fillers for EMI shielding.

Carbon blacks are made from many different raw materials including natural gas, petroleum, coconut shells, and other varied organic materials both natural and synthetic. Fibers like polyacrylonitrile, bamboo, cotton, etc. are the sources of other interesting forms of carbon fibers and filaments. Other carbon forms are becoming available from special gas phase chemistry yielding fullerenes and tube forms. These are small scale at the present time, but the future might be very bright for these dark materials. Reinforcing carbon blacks are essential ingredients in many elastomers used in car and truck tires.

The structure of carbon black involves size, shape, and connection of fundamental particles into high levels of structure that gives the reinforcement. Carbon blacks have surface areas measured in tens to many hundreds of square meters per gram. For this reason, intensive mixing is often required for ultimate dispersion. Degree of mixing can be judged by viewing a thin film against a strong light. Dispersion measurement requires a microscopic inspection of thin film or a pressure drop test with an extruder, screen pack, and differential pressure gauge.

Research on carbon based materials like the fullerenes (buckey balls), single wall nano tubes (SWNT), and graphene (single layer of graphite) is leading to many new and improved products for electromagnetic shielding (cell phones) and advanced computer flexible folding flat screens.

Silica occurs in different crystal forms and impurity levels. Its low cost and widespread availability are offset by its density (2.65 g/cc), hardness (7 on mho scale), and concern about toxicity of some but not all grades. Its wide geographic distribution makes it available in all parts of the world. So it is widely used. The crystalline form of silica causes silicosis or white lung when inhaled in excess as occurs in some mining operations and machining crystalline silica filled plastics.

Clay is another common material of wide ranging properties. Like all fillers, just because one grade or type does not perform satisfactorily does not mean that all grades will fail. Some time with your vendor's technical department can pay off here in finding inexpensive filler with unique value to your application. Clay is becoming important in some nano composites because it can be exfoliated into nano thin platelets.

Talc is white and soft, so it is a valuable filler. The flat shape of talc particles adds reinforcing value in addition to simply acting as a filler. Asbestos does occur in some talc deposits, so the location of the talc mine from where your talc supply comes could be important in some demanding applications.

Mica can vary in color, but this is offset by better physical properties than talc in some filler applications. There are many forms of this widely distributed mineral. The naturally thin sheets of mica can be exploited by exfoliation to the nano thickness range.

Wood and nut shell flours are natural products that serve as both fillers and reinforcements due to their fiber structure. Moisture levels are a problem in many applications. These materials may become much more important in the future as recycled wood products become abundant. Public concern as well as technology may get involved in some of the applications, and it is becoming politically correct to use some renewable resource in your compounding.

Fly ash is another product that comes from an increasing awareness of our environment. Some applications have been found in polymers for fly ash and in time there will be more. Modern technology is involving public relations and environmental issues more and more. Whenever these issues can be turned into commercial benefit for your company or organization that should be the direction of research when the cost can be justified. Quality products must never be sacrificed, however. *Slag* is also being processed into filler form for plastics. Inexpensive fillers like slag, fly ash, etc. must be carefully evaluated for toxicity.

Wollastonite is a mineral that has enjoyed some success as an asbestos replacement as well as finding niche markets on its own. The shape is elongated so there is reinforcement as well as filler applications. A large use is in asbestos replacement applications.

Glass spheres are a product of ground up glass from bottles and jars, as well as special grades that are made for specific applications. The major use of this product is in reflective paints (those reflective white stripes on black top roads are due to this material). In polymer applications, glass beads impart geometrically flat surfaces in injection molded parts along with good color. Glass beads are used with glass fibers and thus balance reinforcement and warping.

Hollow glass and mineral spheres have all the advantages of solid glass spheres, plus lower density. The increased cost may be completely offset by the reduced density (when volume or area pricing is used). Replacing expensive resin with hollow spheres of lower density is often a very good trade off. Most applications are in thermosets, where the spheres do not have to withstand high compressive forces. Furniture manufacturers make extensive use of hollow low-density fillers in syntactic foam for legs, arms, and even tops. These materials have found wide use in aerospace applications as well.

Injection molding pressures range between about 10,000 and 30,000 psi, and this will crush most hollow spheres. In general, the lower the density, the lower the compressive strength of the hollow spheres; so only low pressure fabrication can be used.

Recycled materials of many types are coming onto the market. Some companies may even choose to make polymers specifically as compatibilizing additives for selected types of recycled materials. The construction, pipe, and transportation industries are candidates for many of these applications. Ground thermosets with high filler loadings will be an important source of new fillers and manufacturers may be required to use these products in some applications. Recycled textile fibers can serve as reinforcements, which add value to composites if they can be collected in usable forms.

Portland cement is inexpensive, widely available, and water curable. It has been tested in several polymers as an additive that causes the composite to harden with time of exposure to moisture, turning a thermoplastic into a more durable thermoset.

23.9 Reinforcements

23.9.1 Overview

Reinforcing fibers for plastics are used in several ways. They can be wrapped around polymer tubes, laminated between polymer surfaces, laminated to the surface, woven into complex shapes containing polymer as an adhesive matrix, extruded as long or short fibers into polymer composites, and blended with polymers to make carpets with fiber reinforced backings. This discussion is limited to mostly short fibers (under about 2 cm) that are used in thermoplastics that are intended for melt processing applications.

Reinforcing fibers are used for improving the strength of composites. The vector direction(s) of the strength improvements, the value of those improvements, application and manufacturing techniques, and special needs must be considered when selecting the fiber for the application. If very smooth surfaces must result, random short fiber injection molding material may not be adequate. Rocket casings must be lightweight and reliable, so special fabrication techniques and fibers are used. Electrical and thermal conductivity can be the reason for choosing a certain construction over a less expensive one.

Glass fibers have proved themselves in many difficult applications. This was not always the case, but surface modification of various grades of glass fibers over the past 50 years has led to a wide variety of fibers for many different applications.

E glass is most common in thermoplastic composites. The E stands for glass that has superior electrical properties, C is for glass with the best chemical resistance, and S is for highest strength glass formulation.

S glass is the strongest and it tends to be used in thermoset plastics where filament winding or pultrusion is used; these maximize the strength, nickel coated glass is conductive, and hollow fibers with improved strength to weight ratios are still being tested for cost/benefit in many composites.

There are still concerns about the use of glass fiber for some applications, like high temperature fluoropolymers that might liberate hydrogen fluoride (HF) during processing, acetal resins that are sensitive to trace amounts of impurities, polymers that are processed at temperatures too high for many usual surface modifiers for glass, and some durability issues concerning thermosets (crazing, weathering, etc.).

Even with all these concerns, glass fibers are the standard against which other fibers are compared. Glass fibers and indeed all rigid fibers have a tendency to introduce some warping in thermoplastic composites. This warping is related to the fiber, which is stiff and non-shrinking, and the plastic melt which is initially soft but later hardens. When this occurs with some degree of bonding between the fiber and the resin, there will be molded in forces that can result in warpage in the part. Some work with glass fibers that have three lobes has led to a reduction in this type of warpage. Another approach to the problem is to mix fibers and fillers (glass spheres) to reduce the warpage.

An experimental low melting glass fiber will soften at the processing temperature of the engineering plastic like polyether ether ketone (PEEK). Then, as the resin cools, the glass will move a bit to accommodate the shrinkage of the matrix resin. In theory, this will provide strength enhancement without molded-in stresses normally found with conventional fiber glass reinforcements.

The latest new development in glass fiber innovation is a commingled glass and polymer fiber. This morphology allowing close contact of the two materials is offered in hopes of improving the wetting of the glass more completely.

Graphite or carbon fibers are very high modulus materials that are conductive (electrical and thermal) and withstand flexing within their elastic limits very well. The surface is inert so it is difficult to modify. As a result, the full value of these materials is seldom realized in many applications unless the fibers are placed individually to maximize their value. An immense amount of work has been done on this surface modification problem by some excellent scientists, but progress has been slow. Current interest in fullerenes and micro tubes (SWNT) may help in this area.

The very high flexural modulus and the light weight make carbon fibers the material of choice for many aerospace parts and high tech sports equipment. With just a slight improvement in surface adhesion, the use could skyrocket. So far this problem has not been solved, but many small improvements are upgrading the value of carbon fibers constantly.

Kevlar® is a high temperature polymeric fiber that is tough. Surface bonding is a concern but less than in the case of carbon fibers because Kevlar is more flexible. Price will drop as supply is increased and more manufacturers come into the business. Many of the applications that might have gone to carbon will go to Kevlar because it can be modified to meet end use requirements easier than carbon fibers.

Polyethylene can be spun in the gel form (5% UHMWPE in decahydronapthalene) to a very high strength fiber on the basis of the free-breaking length. (Free-breaking length is the height to which a fiber can be lifted before breaking under its own mass.) The best UHMWPE fibers have a free-breaking length value of 336 km compared with Kevlar of 193 km, carbon of 171 km, and steel with a value of 37 km. This measure of strength to weight is truly impressive for polyethylene. The low melting point (145 °C) and the difficulty of modifying the surface to make it reactive with coupling agents are serious limitations that are yielding slowly to research efforts. Special applications in body armor justify the current price of $45−85/kg.

Stainless steel is an excellent conductor of electricity. Very fine diameter SS fibers can be added to many polymer composites without loss of mechanical strength or toughness. This has led to their use in injection moldable electrically conductive RFI/EMI shielding applications.

Cotton and cellulose fibers like s*isal* have good high temperature properties (equal to or even above nylon). Some cotton fibers are as long as 4 in. Water removal is a problem in the use of natural fibers, but benefits including renewable resource may offset the difficulties. Polymer coated cotton fabric is widely used in many different applications. Some excellent work on recycled wood and natural fiber composites for use in construction is being done at the USDA Forest Products Laboratory in Madison, WI.

Wood flour (sawdust) is used in PE or PVC to make the popular grades of plastic lumber that competes with pressure treated wood. Plastic lumber is maintenance free and colorable, giving it a big advantage over lumber in several specific applications like outdoor decking.

Woven and non-woven synthetics are finding use in many niche markets; some of which are quite large. Kevlar is growing so fast that it is mentioned by itself, but there are many other materials just looking for problems that they alone can solve. PTFE fibers have been used in low friction acetal resin for example and PTFE covered glass is used in domed stadiums.

Mineral fibers are coming onto the market place every so often. They tend to be brittle but inexpensive. Some must be checked for toxicity (asbestos type). As new applications arise, the user of these (and other) fibers must remain alert to new developments in toxicity concerns.

23.10 Impact Modifiers and Impact Modification

One theory holds that failure begins at a flaw. If flaws are kept below a certain critical flaw size, failure will be prevented. This is seldom possible, so rubber particles are used to dissipate the point of the crack so that the crack can no longer propagate through the brittle matrix resin. According to this view of why plastics fail in impact or stress situations, rubber particles must be placed in the path of the crack to prevent failure. The questions to be answered concern the amount of rubber and the size of the particles. Apparently, there are some flaws that require many small rubber particles and there are some flaws that require fewer but larger rubber particles. For each polymer matrix there is an optimum size or sizes of particles. These rubber particles do not have to be spherical, but they frequently are. The rubber phase is not compatible with the plastic phase and this can lead to uneven distribution of the elastomer in the resin matrix. There are several ways to overcome this fundamental problem.

The rubber phase can be in a copolymer that has blocks of elastomer and blocks of matrix polymer. This will make the elastomer compatible with the continuous polymer phase. Many polymers of the A-B, A-B-A, A-B-C, etc. exist.

The rubber phase can be grafted to the polymer phase. The rubber toughened nylons are a spectacular example of this technology. A variation consists of polymers grafted to elastomers to provide a three dimensional interface. The rubber phase can be encapsulated inside of a particle rich in the matrix resin.

Sometimes, the rubber particles are mixed with the plastic without special compatibilizers due to an unusual affinity between the two phases; one of which is crosslinked and the other is not. Some thermoset systems are formulated in this fashion.

The above discussion assumed that a propagating flaw was the cause of failure. It would be better if the flaw never existed. Many modern impact modifiers are designed to prevent the formation of the flaw. The approach here is to prevent the polymer phase from yielding by extending the elastic range of the polymer by control of monomers.

The above discussion points the need for different types of impact modifiers. Some are used to prevent flaws, and some minimize the effects of these flaws even though they do not prevent flaws. Some impact modifiers modify the effects of flaws that are caused by other additives. There are many materials to serve these many different functions.

- Thermoplastic elastomers
- Random copolymers
- Vulcanized or thermoset elastomers
- Polymers grafted to elastomers
- Elastomers grafted to polymers
- Block polymers
- Plasticizers

In addition to serving as impact modifiers, many of the above materials can also function as compatibilizers. This is because all of them have two different phases with the exception of the vulcanized or thermoset elastomers. At least one of the phases must be compatible with a known polymer in order for these materials to be commercially useful. If the other phase is compatible with a different commercial polymer, then you have a compatabilizer that is also an impact modifier. Because of the similarity of technology and growing interest in both impact modification and compatabilization, there will be more materials appearing every year for the next decade or longer.

23.11 Miscellaneous

23.11.1 Coupling Agents

Coupling agents chemically bond dissimilar materials together even in challenging environments. When plastic composites are made with inorganic reinforcements, wood fibers, or other fillers, these materials tend to separate from the plastic and make the composite weak if they are not compatible with the plastic. *Coupling agents increase the time that it takes for dissimilar materials to fail in service.* The improvements are measured in orders of magnitude. Many of our modern high performance plastics would not exist without coupling agents. There are some special cases where polymeric coupling agents can react with metal oxides, amines, or with themselves to form crosslinked composite structures that have commercial value as well as great scientific interest. The best coupling agents for many polymers are based on silane chemistry. Some other materials are claimed to act as coupling agents. These products must be carefully checked for durability (especially in wet or humid environments) because they do give some short term property and even processing improvements, but they may not last as well as true durable coupling agents.

23.11.2 Surface Modifiers

Surface modifiers change the physical chemistry of mineral and fiber surfaces. Hydrophilic surfaces, as commonly found with many mineral fillers, can be made hydrophobic by surface modification. Mineral and glass fibers can be treated so that the polymers they reinforce will wet their surfaces. Surface modifiers are chemically bound to one surface and physically attracted to another surface or material. They unite dissimilar materials with physical and chemical bonds, where the physical bond is not permanent and the chemical bond is. Again, silanes are very effective in these applications, but so are some titanates, and chemicals like stearic acid.

23.11.3 Wetting Agents

Wetting agents have a physical attraction for both surfaces involved. Wetting agents have no permanent chemical bond to the surfaces that they wet. Therefore, wetting agents are easily extracted from composites by means of solvents and, consequently, they are not permanent. They cannot survive in water or high humidity because they are extracted or the water comes between the wetting agent and the hydrophilic surface, thus destroying the temporary bond. Many titanates and organic surfactants (both ionic and non-ionic) are examples of additives that function in this application.

23.11.4 Biocides

Most synthetic polymers are of little or no food value to bacteria, mold, mildew, etc. The exceptions appear to be polymers that contain nitrogen like nylon or polymers that contain plasticizers that are appetizing to the microbes involved.

Additives used for biological defense cover the spectrum from ones with odors that offend rodents to toxic materials that kill mold and mildew. There is a wide range available but there are still reports of squirrels electrocuted while biting through power lines.

Plasticizers for PVC are a special problem that must be carefully considered when making formulations for shower curtains and other applications that involve good growth conditions for mildew and fungus. There are many additives to consider for each application and the user has a wide field from which to select. Quaternary ammonium salts prevent bacterial attack. A very old and well known biological control agent is coming back into popularity.

Silver salts are well known to inhibit many kinds of biological species. This technology is currently the material of choice for many plastics.

23.11.5 Plastizers

Plasticizers are a high volume class of additive mainly used in just one polymer, PVC. There may be as many as three hundred or more simple chemicals and polymers that have been used commercially over the past decades.

Acrylic polymers are used in outdoor applications of rigid PVC formulations. Other ABS and SBR polymers are used in less demanding applications.

The workhorse for flexible PVC is DOP (Dioctyl phthalate, bis-2-ethylhexyl phthalate, and several other names). Questions about toxicity have been raised and addressed, but some concerns still exist. This has led to DNP (Dinonyl phthalate), citric acid esters, and many other substitutes. Many of these are more expensive and less effective than DOP, but safety concerns keeps them on the market, especially in toy applications.

Some FR grades of flexible PVC use phosphorus based plasticizers. There are special plastizers for non-skid vinyl floor tile. These applications illustrate many of the specialized needs of PVC that require specialty plasticizers.

23.11.6 Mold Release Agents

Some mold release agents are sprayed directly onto the tool steel of the mold. These include among others some silicone and some fluorocarbon based materials. Other mold release agents are coated or sprayed onto the surface of the molding powder. This is done in batch blenders just before pack out to avoid passage through an extruder. Most release agents that are melt blended with polymer can be applied in this alternative fashion.

Mold release agents function by coming to the surface between plastic and tool. Some like certain fluoropolymers do not mix or dissolve well in the polymer but they do have a good affinity for the die or mold surface. Other mold release agents dissolve in hot polymer but come out of solution during the extrusion or molding process.

Mold release agents may have more than one function. Some stay on the plastic surface and lubricate the plastic. Others bring other additives with them as they go the shape or part surface. This is useful for surface active additives like biocides and some UV stabilizers.

Sometimes mold release agents function too well and interfere with printing, gluing, and painting. Changing from a calcium salt of a fatty acid to barium or zinc salt can make all the difference. A good metal deactivator such as calcium stearate is a mold release agent, but it might hurt printability of the part surface in some systems.

When mold release agents dissolve in the melt, they can reduce melt viscosity and function as a processing aid. Many processing aids also function as mold release agents.

Since the class of chemicals that function as mold release agents is broad (salts, amides, polymers, etc.), many individual members can have more than one function. Function varies with polymer type as well as chemistry of the mold release agent.

23.11.7 Others

There are dozens of other additives that are used occasionally. Along with these additives comes special processing techniques like grafting an additive to a polymer to keep it immobile. Small amounts of polymers like polymethylmethacrylate (PMMA) will often improve surface appearance. Traces of PA 6 will make PA 6, 6 a bit easier to process and a bit of recycled PET will reduce the cost of some polyesters like PBT. Many of the major additives discussed in this article are important enough to have books written about their use. Some of the books that this author uses are noted below.

Polymer Modifiers and Additives, by John R. Lutz and Richard F. Grossman. Marcel Dekker, Inc. 2000 ISBN 0824799496.

Coloring of Plastics Fundamentals second edition by Robert A. Charvat. Wiley-Interscience 2003 ISBN 0471139068.

Plastics Additives third edition by R. Gächter and H. Muller. Hanser Publishers 1990 ISBN 3466156801.

24a Coating Plastics

Jamil Baghdachi
Eastern Michigan University, 430 Forest Avenue, Ypsilanti, MI 48197, USA

24a.1 Introduction

Almost all surfaces are coated to enhance substrate properties. Coatings are also used to protect, decorate, and functionalize surfaces. Coatings are everywhere. There are coatings on buildings, furniture, appliances, cabinets, consumer IT devices, on airplanes, trucks, trains, and cars; both outside and on the components. Whether you drink beer or soft drinks, there are coatings on the inside and outside of the bottles. Coatings come in many chemistries and there are many application methods. The coating on the inside of the potato chip bag is applied in much different way than the outside coating.

Plastics are the materials of choice for a wide variety of structural applications from buildings to automobiles, airplanes, electronics, and medical devices. The consumption of plastics in a variety of industries, ranging from electronics to transportation, will continue to rise through the end of the decade and beyond. Plastics in electronic applications are expected to experience the largest annual growth rate (4.5%) while the transportation and construction industries, which are largely dependent upon economic climates, are expected to experience a minimal or even decline in growth. Although the state of the economy is believed to have a strong influence on the growth rate of certain industries, and thus consumption of plastic within them, some industries, such as appliances and toys which are usually tied quite closely to economic liquidity of assets, are displaying moderate increases in expected growth rates.

The major advantages of choosing plastics as alternatives to metals are numerous including (1) ease of manufacturing, (2) lower material cost over metal alternatives, (3) corrosion resistance properties and (4) ease of casting, tooling, and styling latitude.

Such advantages have led to the increased use of plastics, particularly in the transportation industry, for both interior and exterior applications. There are a variety of plastics utilized in the transportation industry which range from thermoplastics to thermosettings (these terms will be discussed later). In the United States, approximately 20% of the automotive market segment still uses poly (urethane), but with the advent of a greater desire to recycle, poly(olefin), poly(vinyl chloride) (PVC), and ABS plastics, are becoming more popular.

24a.2 Plastics as Substrates

Polymers that produce plastics are usually classified into two main categories: thermoplastics and thermosets; hence, resulting in either thermoplastic or thermoset plastics. Thermoplastics are moldable, fusible, and recyclable. Thermosets, on the other hand, are insoluble, infusible, and can only be utilized as regrind material.

24a.2.1 Thermoplastic

Within the class of plastics, each type of thermoplastic material can be further subdivided to commodity, intermediate, engineering, and advanced. In the *commodity* classification lie such plastics as low density poly(ethylene) (LDPE), poly(propylene) homopolymer (PP), crystal poly (styrene) (PS), and rigid PVC, pipe grade.

Intermediate—Poly(methyl methacrylate) (PMMA), acrylonitrile-butadiene-styrene terpolymer(ABS), high-heat, cellulose acetate butyrate(CAB), and thermoplastic olefin elastomer(TPO) are all classified as “intermediate” thermoplastics. *Engineering* thermoplastics include such plastics as acetal poly(oxymethyiene), nylon-6/6, 30% glass fiber, poly (carbonate) (PC), and poly(phenylene sulfide)(PPS)(1). Among thermoplastics there are also “specialty” plastics that are frequently utilized, the specialty plastics include the following:

ABS—acrylonitrile-butadiene-styrene

SAN—styrene acrylonitrile
PA—poly(amides) (nylon)
PC—poly(carbonate)
POM—poly(acetals)
PPO/E—poly(phenylene oxide/ether)
PET—poly(ethylene terephthalate)
PET—poly(butylene terephthalate)
PPS—poly(phenylene sulfide)
PSU—poly(sulfone)
PAR—poly(arylate)
PES—poly(ester sulfone)
PI/PAI—poly(imide)/poly(amide imide)
PEI—poly(ester imide)

24a.2.2 Thermoset

Thermosets are usually grouped only by their general chemistry. Most often used thermosetting plastics include alkyd poly(ester), general purpose epoxy, general purpose phenolic, and black urea-formaldehyde [1].

24a.2.3 Coating Plastics

Plastics are coated with thin layers of paint for several reasons: (1) Enhanced aesthetics; (2) greater barrier to moisture and chemicals; (3) improved resistance to UV light, weathering, and mechanical damage; (4) Electrostatic dissipation; and (5) improvement of surface quality, i.e., to fill pits, voids, porosity, etc. The color, gloss, and distinctness of image (DOI) reproduction is important when coating plastics, just as it is when coating metal, wood, or any other substrate, because of the need to match lot-to-lot as well as the need to match adjacent coated substrates, if applicable. For instance, in the coating of automobiles, it is common practice to place a bumper fascia adjacent to the steel hood and fenders. This mandates an exact color match on both plastic and metals.

A major challenge in coating plastics is the adhesion of various types of coatings. This challenge is brought about because some plastics are affected by the elements of the environment both before and after the coating.

Except for temporary and protective coatings, all other types of surface coatings must adhere tenaciously to the substrates and preferably last as long as the object itself. Since coatings must function by surface attachment only, the nature and condition of the surface is critical to the success of any durable coating venture. In evaluating a coating, what is being evaluated is much more than a thin film of the coating or the interface between that one coating and one substrate. When we bend, twist, solvent wipe, expose to environmental conditions, and scratch, we are testing the adhesion, the mechanical properties and strength of perhaps several interfaces.

In most cases, it is desirable to have a coating that is difficult to remove from the substrate to which it has been applied. An important factor controlling this property is the adhesion between the substrate and the coating. In formulating a coating, it is critical to remember that difficulty in removing a coating can also be strongly affected by how difficult it is to penetrate through the coating and how much force is required to push the coating out of the way as the coating is being removed from the substrate as well as the actual force holding the coating onto the substrate. Furthermore, the difficulty of removing the coating can be strongly affected by the roughness of the substrate. If the substrate has undercut areas that are filled with cured coating, a mechanical component makes removal of the coating even more difficult, analogous to holding two dovetailed pieces of wood together (Figure 24a.1). Surface roughness affects the interfacial area between the coating and the substrate. Because the force required to remove coating is related to the geometric surface area, whereas, the forces holding the coating onto the substrate are related to the actual interfacial contact area, the difficulty of removing a coating can be increased by increasing the surface roughness [2]. However, greater surface roughness is only an advantage if the coating penetrates completely into all irregularities, cracks, and crevices of the surface. Failure to completely penetrate can lead to less coating to interface contact than the corresponding geometric area and will leave voids between the coating and the substrate, which can cause problems. The physical chemistry of adhesion has been reviewed [2].

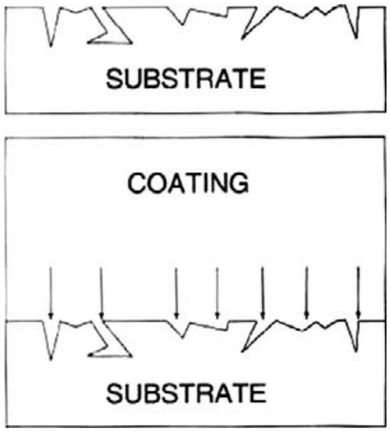

Figure 24a.1 Schematic representation of a hypothetical surface profile and a mechanical adhesion.

Coating systems that crosslink slowly minimize the increase of viscosity of the continuous phase [3,4]. Because viscosity of the vehicle drops with increasing temperature, baking coatings can be expected to provide better adhesion than a similar composition coating applied and cured at room temperature. This confirms that the observation that superior performance is obtained with high temperature baked, slow--cure primers when excellent adhesion is a critical requirement.

In contrast to most clean metal surfaces, there can be a serious problem of wetting in order to achieve adhesion of coatings to plastics because some plastic substrates will have such low surface tensions that it may be difficult or impossible to formulate coatings with sufficiently low surface tension to wet the substrate. Polyolefin plastics, in particular, are difficult to wet. Frequently the surface of the polyolefin plastic must be oxidized to increase the surface tension and provide groups for interaction with polar groups on the coating resin. The surface can be treated by soaking the plastic in an oxidizing solution, by flame treatment, or by exposure to a corona discharge. The treated surface should be coated soon after treatment because it is not stable and unoxidized molecules with low surface tension can migrate to the surface of the uncoated treated plastic. Difficulties in wetting plastics can also result from residual mold release agents on the surface of the plastic. Mold releases must be removed completely before coating.

Adhesion to plastics can be enhanced if the resin molecules from coating can penetrate into the surface layers of the plastic. Penetration would take place through free of volume holes; hence, raising the glass transition temperature (T_g) above the plastic substrate generally promotes adhesion. The T_g of the plastic can be lowered by penetration of solvent from the coating into the surface of the plastic. This, in turn, may permit penetration of the resin molecules from the coating into the surface of the plastic. Hence, the solvent selection in formulating the coating can be critical in achieving adhesion to plastics. In selecting solvents for articles fabricated from high T_g thermoplastics, such as PS and PMMA, care must be taken not to use a solvent system with too high a rate of evaporation in order to avoid crazing (qv), i.e., cracking at the surface.

The highest quality coating will show excellent results only if the surface pretreatment (cleaning and priming) is performed correctly and the overall system is maintained up to its potential.

Since coatings must function only by surface attachment, the nature and condition of the adherent surfaces is critical to the success of any coating venture. By “surface” we usually mean that portion of the substrate with which the coating interacts. For a porous surface such as most of the plastics, a low viscosity coating might reach a depth of several hundred nanometers or more. A rough surface provides more surface area than a smooth one of the same gross dimensions. In addition, the surface will usually have a chemical composition different from that of the bulk and in some cases the surface composition has little in common with the bulk composition either through adsorption of contaminants from the environment or from segregation of bulk constituents at the surface. The outer layers can be loosely bound or tightly adhered and might have high or low cohesive strength in themselves. Contaminant and segregated bulk components are not always homogeneously distributed in the surface region and inhomnogeneities can lead to potential corrosion sites, weak bond areas, and bond discontinuities that can concentrate stress. A single molecular layer of contaminant can prevent proper wetting by the coating or a weak substrate boundary layer can provide the “weak link” for reduced coating adhesion and premature failure.

Engineering plastics might be anisotropic as the result of the manufacturing or forming process where some flow or machine direction is introduced. This is usually the case with fiber-reinforced sheets such as the fiber-reinforced plastics used in the automotive industry. Careful control of fiber orientation is sometimes used to enhance mechanical strength in a particular direction. Components of the plastic can migrate to the surface and it is common to find low molecular weight polymers or oligomers, plasticizers, pigments, mold release agents, and shrink control agents, and other processing aids as well as adsorbed contaminants in the surface region.

Plastic films will have a machine direction or some anisotropic polymer orientation if they are blown or otherwise stretched in the manufacturing process. These also can have low molecular weight fragments, oxidized polymer, plasticizer, processing aids, and lubricants and slip aids, adsorbed water and organic contaminants, and other surprises in the surface region.

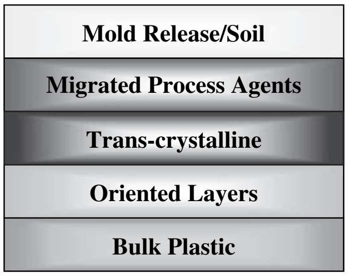

Figure 24a.2 Representative surface multiplicity of a thermoplastic plastic (PP).

More so than with metals, the surface regions of plastics are dynamic regions, Figure 24a.2, continuously establishing new equilibrium internally and with their surroundings [2]. In flexible, amorphous plastics, above the glass transition temperature, low molecular weight components are able to diffuse out of the bulk and into the surface region while elements of the surroundings can diffuse into the plastic. A well-known example of the latter is the migration of plasticizer from vinyl film, causing the film to shrink. If the film is part of a coated construction, the plasticizer can migrate into the organic layer and change its mechanical properties. If the coating is an effective barrier to plasticizer migration, the plasticizers can build up in the interfacial region causing delamination.

The nature of a plastic surface can change rapidly in response to its surroundings. Even when the bulk of a material is in the glassy state, the surface region can be quite mobile, owing to the presence of low molecular weight polymer and contaminants. Polymers having polar and non-polar regions in the chains can present different segments at the surface depending on whether the surroundings are polar or not. Wiping a surface with an ionic solution will cause the polar groups to orient toward the surface, while the same treatment with a non-polar solvent such as hexane can bring the non-polar aspect to the surface.

Choosing surface treatments and primers is as important to success as choice of coating. All must be considered at once since success depends on their proper interaction. Surface treatments are operations that change the morphology or composition of the substrate surface and may involve adding as well as removing or rearranging material. Primers are usually thin organic coatings applied to the surface (which might also have been treated) to give a more reproducible and durable surface for the coating. In all cases, the major reason for treating or priming is not necessarily to improve the adhesion but rather to produce a controlled, reproducible and durable surface in order to obtain a more predictable coating.

The cheapest and least controlled is to simply accept whatever surface is present and make no attempt to change it. This can be entirely adequate in many constructions. Solvent wiping can remove many organic containments but requires ventilation and that the solvent be changed as needed to avoid re-depositing contaminants (the "steady state" situation). Abrasion usually leaves abrasive residue embedded in the surface and the fresh surface of many materials can be quite reactive so that it changes rapidly on exposure to air or to cleaning solvents. Electrical discharge and plasma, or corona treatment, are often used to enhance the polarity of low surface energy plastics. Chemical stripping or acid etching removes the outer layers and replaces them with a more controlled layer, but as with solvent cleaning, there is the danger of re-deposition or poor stripping if the enchants are not kept clean and at the proper concentrations. Etching followed by deliberate deposition of a controlled surface can provide the most reproducible surface but at the greatest expense.

Conductivity in a primer is achieved through the incorporation of conductive pigments into the primer. The reason for making a primer conductive is to provide a path to ground for subsequent electrostatically applied topcoats. The "grounded" part allows one to achieve higher transfer efficiency of "charged" topcoat particles in the electrostatic spraying process because the electrostatically charged topcoat particles are attracted to the part. Typical conductivities required in the primer to achieve sufficient grounding of the part when applying 60—80 KV of electrical energy to the topcoat particles lie in the range of 120—160 Ransburg units (<1000 Ω/sq.) [1]. Ransburg units are measured on a Ransburg gauge (a modified Wheatstone bridge that is placed on the conductive surface and the capacitance is measured using a 9 V battery across a 1 cm distance).

Primers are not always necessary when applying a coating to plastics. Class "A" surfaces, those free from defects (pits, porosity, etc.), do not require a prime coat unless the part is to be coated electrostatically. Primers are most often used to fill voids, provide a path to ground for subsequent electrostatic coating operations, or to provide additional protection for substrates poor in durability or chemical resistance.

Primers are also utilized to fill voids, pits, and porosities often associated with molded plastics. The surface defects in plastics can arise as a result of stress from cutting, drilling, sanding, or can be inherent in the molding process or in the plastic composition itself. Considerable research has been conducted in an attempt to develop a coating type which would eliminate the painting problems associated with sheet molding compound (SMC), a plastic known to exhibit many surface defects. Problems associated with SMC include loss of primer adhesion (chipping), solvent attack and its resultant effect on mechanical properties, porosity of the substrate (including voids, cracks, and mold lines) and general wetting of the substrate. All of these factors will affect the reproduction of gloss, DOI, and color of the topcoated substrate. Other properties affected include weatherability, chemical resistance, and physical and mechanical properties of the painted plastic composite.

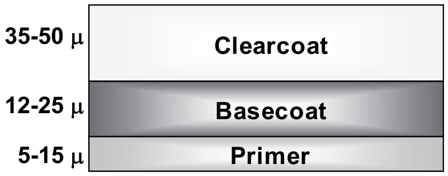

Figure 24a.3 Representative plastic coating composite.

A coating for plastic does not differ much from that typically utilized on steel or other substrates in that a primer is applied, followed by a basecoat and a clearcoat (Figure 24a.3). The film thicknesses of the associated coatings are 5—15 microns of primer, 12—25 microns of basecoat (dependent upon the hiding power of the pigments utilized in the basecoat or clearcoat), and 35—50 microns of clearcoat. The coatings can be applied wet-on-wet, dependent upon the chemistry of each respective coat. Most often the primer is applied baked, and then the subsequent basecoat/clearcoat is applied wet-on-wet. The term "wet-on-wet" refers to the ability to flash the first coat at ambient conditions for a few minutes (without the need to heat cure the coating to it's fully crosslinked state) after which the next coat is applied, flashed, and the two films baked to promote crosslinking. In the case of waterborne coatings, however, it is necessary to remove at least 90% of the solvent (water and a small amount of coalescing agents) from the coating before applying a subsequent coating. The removal of 90% of the solvent is most often accomplished by an infrared flash off for 1—5 minutes or through a combination of infrared heat and convection heat.

24a.2.4 Coating Materials and Trends

In general, metals and plastics share the same chemical class of coatings. For plastics though, the coatings are more elastomeric in nature and obviously there are no concerns for corrosion protection properties. Most important issues and quality concerns for plastic coatings are adhesion, chip, scratch and environmental chip resistance, and gloss maintenance. Most high-end plastic coatings consist of several layers of coatings. The basecoat is the pigmented coat that is responsible for providing color. It is covered, in a wet-on-wet spray process, with a clearcoat that provides durability, chemical resistance, chip resistance, and DOI (often referred to as the "wet" look).

24a.2.4.1 One- and two-component systems

A solvent-borne coating generally consists of several major ingredients: resin, crosslinker, rheology control agent, catalyst, pigment(s), flow and leveling additive, and solvent.

The resin (often referred to as the binder, vehicle, polymer) is responsible for the main attributes of the coating when cured with the crosslinker (or crosslinking agent). The curing, or network formation, is often accelerated through the use of a catalyst. Rheology control agents, often referred to as sag control agents, are added to impart shear thinning behavior when under high shear (i.e., spray application) and rheology or anti-sagging behavior when under low shear [1]. Pigments are introduced to impart color, gloss control, and/or ultraviolet protection.

The amount of pigment utilized depends upon the color and the hiding power required of the coating. The flow and leveling additive is often introduced to relieve surface tension variations between the coating and the substrate [1] to eliminate craters or pinhole formation. Solvents are added as necessary to achieve flow under application conditions. When coating plastics, it is of particular importance to choose solvents that will not degrade or attack solvent sensitive materials (i.e., PC). Stress crazing due to solvent attack can dramatically lower the physical properties of the coated part [1].

24a.2.4.2 Primers

In difficult-to-paint substrates, such as the TPO, an adhesion promoting/conducting primer is necessary. Excluding difficult-to-paint plastics, one has the option to next apply a primer surfacer. The primer surfacer, composed most often of a poly(ester) crosslinked with a blocked isocyanate or melamine, is applied at a dry film thickness of approximately 25 microns by conventional spray application equipment. The primer is often made conductive to increase the transfer efficiency of the electrostatic topcoating procedure. The function of the primer surfacer is to provide filling and leveling properties as well as some chip resistance to the substrate. Cure conditions range from 80 to 150 °C for 20 minutes.

24a.2.4.3 Basecoats

Two types of basecoats can be used. A one-part solvent or waterborne lacquer-type coating that provide aesthetic feature but it would not be useful for exterior exposure. For more demanding service environments such as automotive parts, solvent-borne basecoat, consisting of poly(ester) or acrylic binder to be crosslinked with melamine or isocyanate, is applied at a dry film thickness of between 12 and 25 microns, depending upon the color. Poorer hiding colors, such as red, yellow, and white colors, require the higher film builds, whereas metallics and the darker shade colors are applied at the lower film builds, The solvent-borne basecoat is allowed to flash off (evaporate) solvent for three to five minutes at ambient conditions prior to applying the solvent-borne clearcoat. This process of applying one coating over another, where the first coating is not in a crosslinked or cured state, is referred to as the "wet-on-wet" process.

The waterborne basecoat consists of a urethane or an acrylic dispersion. The basecoat may be crosslinked with a blocked isocyanate or melamine curing agent. The basecoat is prebaked (with infrared or thermal convection ovens) to release a majority of the water (>90%) prior to clearcoat application.

24a.2.4.4 Clearcoats

As with basecoats, there are thermoplastic and thermoset coatings. A lacquer-type either solvent-based or waterborne can be applied and processed; however, such clearcoat will not be durable if used under harsh and outdoor environments. For more challenging application, a solvent-borne clearcoat is usually spray applied over the basecoat at a dry film thickness of 35−50 microns. The thermosetting clearcoat, responsible for UV protection, chemical resistance, chip resistance, and so on, is most often composed of a hydroxy functional acrylic binder together with a melamine or isocyanate crosslinker. UV light absorbers and hindered amine light stabilizers (HALS), are added to achieve better free-radical oxidative degradation resistance which results from exposure to sunlight.

The clearcoat is referred to as a two-component (2 K, 2-part, 2-component) clearcoat when an isocyanate crosslinking agent is utilized as the crosslinker. The isocyanate must be added to the hydroxy functional acrylic just prior to spray application to prevent premature gelation (crosslinking). Cure conditions for isocyanate crosslinked systems range from ambient to 120 °C for 30 minutes.

Thermosetting one-component, or 1 K, clearcoats are equivalent to 2 K clearcoats with the exception that they are crosslinked with melamines. Cure conditions can be lowered to as much as 110 °C through the addition of acid catalysts but generally lie in the range of 120 °C for 30 minutes. Blocked isocyanate crosslinked versions of 1 K clearcoats are also available, but cure requirements necessitate 140 °C or higher to deblock the isocyanate and allow it to react. Typically, blocking agents on the isocyanate include methyl ethyl ketoxime and malonate esters.

24a.2.4.5 Environmentally friendly coatings

24a.3 Powder Coatings

There are several types of powder coatings available, classified by resin type. These include, polyester, polyurethane, acrylic epoxy and the hybrid systems. The major impetus for growth can be attributed to the virtual "pollution free" finishing system as well as the dramatic leap forward in materials and equipment technology that makes them essentially 100% transfer efficient (with recycling spent powder). Major powder coating Research and Development (R&D) goals for the year 2010 and beyond include (1) reducing baking temperature, (2) improving thin-film capability, and (3) providing low gloss exterior durable systems.

Thermosetting powder coatings tend to begin crosslinking at or near their melt temperature. This can severely limit the smoothness capability of a deposited coating. Cure temperatures of these thermosets generally lie in the range of 140−175 °C. As such, these coatings can only be applied and cured over thermoset plastics, such as SMC, that have a higher heat distortion temperature than that required for the powder to crosslink. Applications for these high curing temperature powders have included chip resistant primers as well as in-mold primers.

Several vinyl ether functional poly(urethane) powder coatings have been formulated that show a sharp melt temperature at 40 or 60 °C and no crosslinking until 120 °C. This wide gap between the melt and crosslinking temperature allows better flow and leveling prior to full cure. The crosslinking temperature is effectively lowered through the use of a latent cationic initiator that decomposes just prior to crosslinking. The lowered cure requirements of these powders allow one to use them on a wider variety of plastic components.

24a.4 Electron Beam and Ultraviolet Curing Coatings

The major advantages of radiation cure technology are speed of cure, reduced emissions, 100% solids systems, and elimination of ovens or other sources of thermal energy (less energy consumption). The UV coating is usually comprised of unsaturated monomers that polymerize with UV light (in the presence of a photoinitiator, which absorbs radiation and begins polymerization) in a matter of seconds.

Durability of the coatings on plastic is influenced by the chemistry of the topcoat. Two-component coatings, particularly those crosslinked with isocyanates, have better weathering characteristics than one-component coatings, typically crosslinked melamine-formaldehyde. The durability of the coating, as described previously for plastics, can be enhanced through the proper selection of stabilizers, such as UV absorbers and HALS.

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24b Colorants for Thermoplastic Polymers

Bruce Muller
Plastics Consulting Inc, 682 S.W. Falcon St, Palm City, FL 34990

Colorants are formulations of pigments or dyes and additives used to internally color plastics.

Three categories of colors are used to manufacture thermoplastic colorants. The color categories include pigments, dyes, and special effect colors. All three color categories are manufactured and sold in powder form as shown in Figure 24b.1. It is a common misconception that dyes are liquids, but in fact dyes are powders that are similar in appearance to organic pigments.

The five colorant categories include dry color, liquid color, paste dispersion, masterbatch (or concentrate), and compounded color (or precolor). These colorants almost always contain dispersants and other additives. Masterbatches also contain resins or polymers. Liquid colors and paste dispersions contain liquid carriers in addition to the powdered colors and additives.

Dispersants and other additives that are commonly used in colorants will be discussed later.

24b.1 Some Useful Color Terminology

Color matching is the process in which pigments, dyes, and special effect colors are combined to achieve a specified color in a specific polymer. A color match often contains additives in addition the colors, such as dispersants and stabilizers. Most additives have very little effect on the color match, as they are colorless. Exceptions are additives like inorganic flame retardants, glass fibers, and high loadings of fillers, which do drastically affect the final color match.

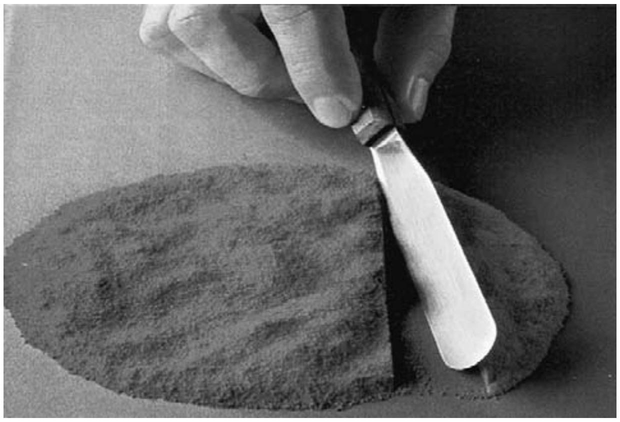

Figure 24b.1 A typical pigment or dye powder used in all forms of colorants.

Hue is a traditional color name, such as red, blue, or green. Color wheels in Figures 24b.2 and 24b.3 show the hues in the spectrum which are typically listed as red, orange, yellow, green, blue, indigo and violet (ROY G BIV). Each hue represents a specific wavelength of visible light. Often the terms color and hue are used interchangeably, even though they do not mean exactly the same thing. Many remember the hues of the color wheel and the color order with the mnemonic ROY G BIV.

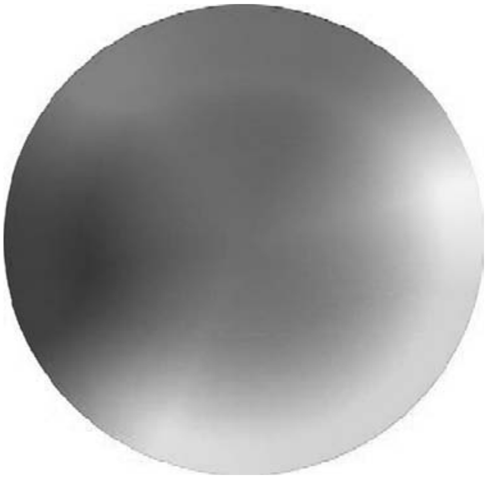

Figure 24b.2 A standard color wheel.

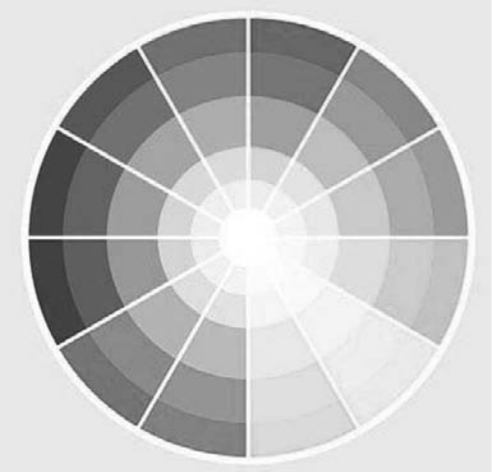

Figure 24b.3 Tint colors added to the color wheel.

*Chroma i*s the intensity, saturation, or purity of a color. The highest chroma of a hue is the color as it appears on the outer edge of the color wheel in Figure 24b.2. An example of a hue (color) toned down or reduced in intensity is powder blue or sky blue as compared to royal blue as seen in the tint color wheel in Figure 24b.3. Moving toward the center of Figure 24b.3 depicts toned down colors which are usually accomplished by adding white pigment to the primary hue.

Value is the relative degree of lightness or darkness of a color. An example of value is light blue to dark blue.

Tint is the term used to describe a hue (color) that has been lightened. An example is red mixed with white to create pink as shown on the inner circle of the color wheel in Figure 24b.3. In this example pink is a tint of red.

Shade is the term used to describe a hue (color) that has been darkened. An example is red mixed with black to create maroon. In this example maroon is a shade of red.

Dispersion is the degree with which pigment and additive agglomerates are broken apart and remain that way during the molding or extrusion process. Poor pigment dispersion may appear as specs in plastic parts causing poor appearance and may potentially cause a loss of physical properties.

Distribution is the degree with which colorants and additives are mixed uniformly through the polymer. Poor color distribution may appear as streaks, swirling, or blotches in a plastic part.

Spectrophotometer is an instrument used to numerically quantify colors under all light sources. It provides a wavelength by wavelength spectral analysis of reflecting or transmitting properties of colored objects. Combined with a computer, it will display a curve representing light energy absorbed over the visual spectrum. A spectrophotometer can determine color metamerism. Figure 24b.4 is a bench top spectrophotometer and Figure 24b.5 is a portable hand held spectrophotometer. Both of these spectrophotometers will interface with a computer and printer to display the reflectance curves and color differences when used to compare two colors.

Figure 24b.4 Bench Top Spectrophotometer.

Figure 24b.5 Hand held spectrophotometer.

Colorimeter is an instrument used to numerically quantify colors by illuminating the sample with light through three primary color filters. It does not have the ability to determine metamerism.

Metamerism or *metameric* is a phenomenon of two colors matching under one light source like daylight (white light), but not matching under another light source, such as light from an incandescent light bulb (yellowish light).

Thermochromism is the ability of a material (color) to change color as the temperature changes.

Black light is a type of ultraviolet light that is below the normal visual range. It is often used to identify fluorescent pigments, dyes, or optical brighteners.

24b.2 Pigments

Pigments are classified as inorganic and organic. Both pigment classes are insoluble in resins and therefore require high shear to become properly dispersed in a resin. Quality dispersion of pigments requires wetting the pigment surface, dispersing (breaking up the agglomerates with shear) and distributing them uniformly through the resin. Many colorants contain both inorganic and organic pigments and dyes, as well as non-colorant additives and resin. Wetting the pigments is enhanced by adding surfactants (wetting agents) to the formula. Proper wetting of the pigments is crucial to properly develop the full strength of the colors.

Inorganic pigments are generally characterized by large particle size with small surface areas. Inorganic pigments are often lower in cost, easier to disperse and provide better opacity than organic pigments. They generally have good chemical resistance, do not cause warpage and do not bleed or migrate from most polymers. They range from having very poor heat and light stability to excellent heat and light stability. Most inorganic pigments are dense mined products.

Some examples of inorganic pigments are: iron oxides, titanium dioxide, cadmiums, lead chromates, chromium oxide, and mixed metal oxides. Some pigments including those containing cadmium, lead, and mercury are considered heavy metals and are often regulated. Most special effect pigments are inorganic, larger particle size and often do not require as much shear or wetting as conventional pigments to properly disperse them.

Organic pigments are synthetic pigments that do not occur naturally in nature. Organic pigments are characterized by small particle size with high surface areas and are generally translucent and more difficult to disperse than inorganic pigments. Organic pigments range from poor to very good heat stability and light stability and are usually considered less toxic than heavy metal pigments. Some examples of organic pigments are phthalocyanine, azo condensation, perylenes, quinacridones, and carbon black. Organic pigments are often bright in hue, translucent, and must be checked for permanence. A well known exception to the aforementioned issues is carbon black. Carbon black has the highest opacity of all pigments and is light stable and permanent. Organic pigments that are permanent in injection molded or extruded polyethylene (PE) parts may easily bleed from a similar PE used in a low shear process like rotational molding. Phthalocyanine blues and phthalocyanine greens and a few other organic pigments often cause part warpage. Organic pigments are generally higher in cost per pound than similar to hue inorganic pigments, but usually require lower loadings to achieve bright colors.

24b.3 Dyes

Dyes are synthetic colors that are soluble in plastic resins. Due to their solubility, dyes are very easy to disperse. Most dyes used in thermoplastics have excellent heat and light stability. Dyes are strong, bright, transparent, or translucent at higher loadings. These are excellent attributes. Some examples of dyes are anthraquinone, pyrazolones, quinophthalones, and quinolines. Dyes are used in many engineering polymers including but not limited to acrylic, PC, nylon, ABS, and styrene. Dyes bleed from most polyolefins and many other resins. Dyes cover a broad color spectrum from non-coloring optical brighteners to fluorescents, to non-fluorescent conventional hues and black. Dyes are commonly used in tail light lenses, reflectors, and signage. The optical brightener dyes are also used as whiteners in laundry detergents. These same optical brightener dyes may be used in plastics, but they are expensive and they have very poor light fastness. Optical brighteners are often combined with pigments and dispersed into polymers in the manufacture of fluorescent pigments. The polymers are then ground to pigment particle sizes and used as pigments in other polymers dissimilar to the fluorescent pigment resin matrix. This technique produces pigments that have reduced bleeding tendencies in polyolefins.

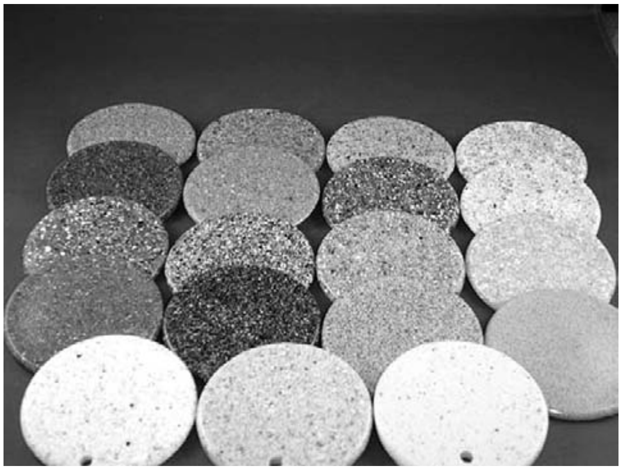

Figure 24b.6 Rotationally molded granite colors.

24b.4 Special Effect Colorants

Special effect colorant examples are pearlescents, phosphorescents, metallics, and a variety of colorants like Saran and a few ground thermosets. The ground thermosets and Saran are used to make granite effects colorants for high shear processes like injection molding. Granite effect colorants, for the low shear rotational mold process, may also be produced with conventional pigments compounded into PE. The colored compounded pellets are then coarsely ground or pulverized to colored specs ranging from 35 mesh (500 μm) to as large as 16 mesh (1.18 mm) powder. Figure 24b.6 shows a broad range of colors produced with this technique. The range of colors that can be produced for the rotomolding process is almost unlimited.

The color matched compounded large specs allow for unlimited granite color combinations and effects for rotomolded parts as seen in Figure 24b.6. This method is not well suited to high shear processes, like injection molding and extrusion, as the shear created in the process will disperse the compounded colors into the base resin. Granite or speckled colors are normally made using thermosets in injection molding to eliminate melting the specks into the base resin.

Pearlescent pigments and metallic pigments are available in a wide range of colors and particle sizes. Larger pearlescent and metallic particles tend to produce brighter less opaque colors, while smaller particles produce better opacity with lower luster. Some metallic pigments are coated to reduce their oxidation rates and improve their heat stability.

Additives are typically non-color ingredients that are added to colorant formulas for a specific purpose. The most common additives used are surfactants, to improve the resins ability to wet out the pigments, to achieve good dispersion. Zinc stearate is commonly used as a surfactant like other metallic stearates and waxes. Antioxidants and UV stabilizers (UVA) are commonly added to improve heat and light stability. Some antioxidants protect the resin during processing and some work synergistically with the UVA to improve the outdoor weathering. Antistats, blowing agents, impact modifiers, glass fibers, internal mold releases, antiblock, slip, flame retardants, smoke suppressants, laser markers, fillers, and nano tubes are a few of the other common additives used with colors to formulate colorants.

24b.5 Colorant Forms

There are five forms of colorants available to plastics processors. The five forms of colorants are dry color, masterbatch or concentrate, liquid color, paste dispersions, and compounded color or precolor. All five forms are generally color matched, contain other additives and are dispersed aggressively. All five coloring methods have advantages and disadvantages. Some coloring methods are more suitable than others for certain processes and resins. Compounded color will work efficiently in all processes, but is usually the most expensive method used to color thermoplastics. Compounded colors are available for solid or liquid polymers.

Dry color is a finely divided powder, but sometimes it is provided in a granular form. Dry color is commonly available as a powder, but some dry color manufacturers also produce a more dust free granular form typically referred to as dustless dry color. Dry color is produced by dispersing the formulated ingredients in a high intensity mixer or by preblending the ingredients in the formula and then micropulverizing them. Today, manufacturing dry color in a high intensity mixer is the most common method used. The greatest advantages of dry color are low cost, they can be preweighed or unitized by the manufacturer, low inventory space required, low use levels and fast delivery. The beneficial fact that the colors and additives have not been subjected to a heat history prior to the processing operation is often overlooked. The lack of processing heat history may be very important when using marginally heat stable pigments and additives. The same dry color may often be used successfully to color more than one similar resin like PE and PP to yield a similar color. The disadvantages of dry color are at the processor they require high intensity mixing, can be dusty, difficult to clean equipment, difficult to change colors and difficult to transfer and automate. Dry colors may reagglomerate and absorb moisture during shipping and storage. The dustless dry colors flow and automate better and may clean up easier than the more sticky non-dustless dry colors. Both dustless and non-dustless dry colors require mixing in high shear mixing equipment to achieve the best dispersion. Dry color is typically used at levels of 0.1−0.5% in the final product. Dry color is suitable for most processes except liquid systems like plastisol, cast and blown film, and high speed automated processes like blow molding.

Masterbatch or *concentrate* is sold in a pelletized or granulated form. Historically, in the United States the product was referred to as concentrate, because, originally masterbatch referred to single pigment dispersions made for rubber. We suggest the term originated from mastering a batch of pigment before adding it to the main rubber batch. At present there is a trend in the United States to refer to concentrates as masterbatch. The Canadians and Europeans have historically referred to this pelletized form of colorant as masterbatch. Masterbatches are manufactured using extruders, batch mixers like the Banbury, two roll mills, and specialty mixers that combine the continuous and batch mixing processes like the FCM. Granulated and diced masterbatches are usually produced on a Banbury or a two roll mill. The majority of masterbatches are manufactured using single and twin screw extruders that produce pellets. The pellets may be strand cut (Figure 24b.7) or underwater cut (Figure 24b.8).

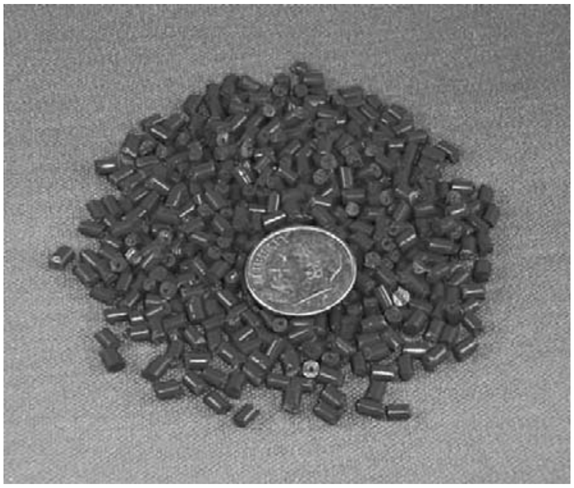

Figure 24b.7 Strand Cut Mini Masterbatch Pellets.

Strand cut pellets are normally cylindrical and the underwater cut pellets are more spherical or even flat pan cake shaped. Diced pellets are generally square cubes or pentagonal. Natural resin pellets are also produced by both pelletizing methods. The underwater cut masterbatch pellets

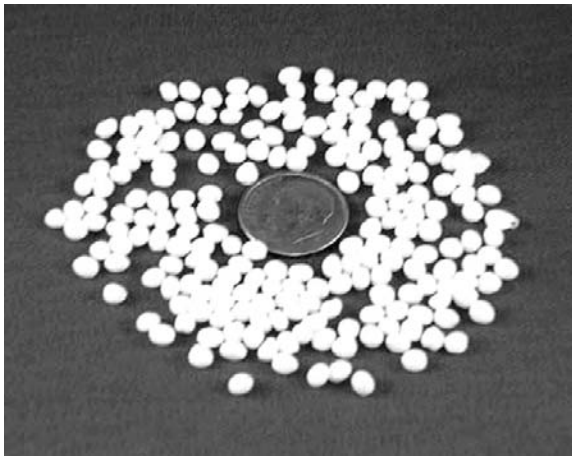

Figure 24b.8 Underwater Cut Mini Masterbatch Pellets.

Figure 24b.9 Three colors of micro pellets.

vary from 0.014−0.024 in. micro pellets (Figure 24b.9) to 0.025−0.078 in. mini pellets and strand cut pellets from 0.080 in. to as large as 0.250 in. (1/4 × 1/4 in.) diced cubes.

Historically, masterbatch pellets were sized to match the size of the virgin natural pellets (about 1/8 × 1/8 in. or larger). Over time both natural and masterbatch pellets have gotten smaller, primarily due to the predominance of underwater pelletizing. Pigment and additive concentrations vary from 15 to 80% in very highly loaded masterbatches. The typical pigment and additive loading range is from 40 to 65%. The balance of the masterbatch formula is resin or a blend of resins. An advantage of a masterbatch is the dispersion of the pigments and additives is superior to their dispersion in dry color. Other advantages are the pellets are dust free to handle and easy to transfer, feed, and automate. Some disadvantages of masterbatch pellets are they require more inventory space than dry color and liquid color and generally require longer lead times for orders than dry color. The colors, additives, and resin have one or more additional heat histories before the final process. Often, masterbatches are manufactured using resins that are dissimilar to the resin used in the final product. The dissimilar resin may change the processing characteristics or physical properties of the primary resin. The dissimilar resin is almost always used without the knowledge of the end user. For example LDPE and EVA are often used for the concentrate carrier for LMDPE, HDPE, XLHDPE, PP, and Nylon. General purpose styrene has been used for the concentrate carrier for ABS, SAN and even PC masterbatches. If physical properties are important to the processor, the masterbatch carrier must be specified and a certification of the resin used should be required. Masterbatches are normally used from 1 to 5%. Industry terminology for masterbatch let down ratios are 100−1 (1%), 50−1 (2%), 33−1 (3%), 25−1 (4%) and 20−1 (5%). Thin products like film often use much higher levels of masterbatch to increase opacity. Film masterbatches may also contain high quantities of additives like slip and antiblock which requires higher usage levels of the masterbatch. Often the slip and antiblock masterbatches do not contain color and are used in addition to the color masterbatches. Masterbatches are suitable for most processes except rotational molding and liquid resin systems like plastisol and silicone.

Liquid color or *liquid concentrates* are pigments and additives dispersed in a liquid vehicle used in thermoplastic and thermoset non-vinyl (PVC) polymers. Liquid colors are often universal allowing the same liquid color to be used in resins as dissimilar as PE and styrene. The pigment dispersion is usually superior to that of masterbatches and far superior to dry color. Liquid color is manufactured in sand mills, ball mills, and high shear mixers like the Cowles. Pigment loadings range from 12 to 70%. The liquid color viscosity is closely controlled and maintained at a low enough viscosity to allow the liquid color to be pumped and metered, but at the same time high enough to prevent pigment settling. This viscosity compromise maintains high pigment loadings for economical usage with a pumpable viscosity for easy automation. The viscosity of water is 1 centipoise (cps) and the typical liquid color is 6000−8000 cps. This viscosity is similar to the viscosity of 40 weight motor oil. The advantages of liquid color are very low cost, superior pigment dispersion, no previous pigment, additive or resin processing heat history, compact storage, and it is extremely easy and inexpensive to automate. Disadvantages of liquid colors are the pigments may settle over time and require mixing of the liquid prior to use. Liquid colors must be stored in a non-freezing environment. Special liquid color metering and dispensing equipment is usually required for each processing machine. The most commonly used peristaltic metering pumps are low cost, do not require cleaning, and are portable from one processing machine to another. The pumps are easy to install, with a small modification to the molder or extruder feed throat. The liquid color is normally metered directly into the molding machines feed throat directly under the hopper. One disadvantage of liquid color is that there are very few manufacturers compared to dry color and masterbatch manufacturers, so there may not be a competent local liquid color supplier. Liquid color is used from 0.25 to 1.5%. It has been successfully used in all plastics processes, but has been slow to become readily accepted in all industries.

Paste dispersions are pigments and additives dispersed in liquid plasticizers used to color PVC or vinyl compounds. The plasticizers used are often similar to the plasticizers formulated in the vinyl. Paste dispersions are a very old method of coloring PVC, especially plastisol which is PVC in a liquid form. Paste dispersions are manufactured with methods and equipment similar to the ones used to manufacture liquid color. The viscosities are generally much higher due to the fact the pigment dispersions are generally stronger and more concentrated than liquid color. Higher loadings reduce the use cost and eliminate pigment settling. Paste dispersions are generally not pumped and metered into the processing machine allowing them to be manufactured with higher pigment loadings that create higher viscosities or a thicker paste.

Compounded color or *precolor* is a dispersion of pigments and additives compounded into the base resin. Compounded color, sometimes referred to as hot melt compound, is used by the processor as shipped, without mixing or blending. Most compounded resins are processed through an extruder. Compounded colors are sold in pellet form (Figure 24b.10).

Figure 24b.10 Strand cut compounded silver color.

The extruder may be a single screw or twin screw and it is usually less sophisticated than a masterbatch extruder. Color pigment and additive loadings are much lower in compounded colors than masterbatches. Compounded resins usually contain from 0.25 to 2% pigment and additives.

Compounded colors are usually the most expensive method of coloring resins. The cost is high because all (100%) of the resin is shipped in to the compounder, extruded, repackaged, and then reshipped. Masterbatch on the other hand requires only 1−5% of the finished product to be extruded, packaged, and reshipped. The advantages of pelletized compounded resins are excellent dispersion of the colorants and additives. In plant mixing equipment is not required, which reduces the possibility of plant mixing and weighing errors. The compounded pellets are easy to convey to the processing equipment. The compounded color disadvantages are, it is expensive, and all the resin and pigments have at least one heat history prior to using it in the final process. Compounded color requires the most storage area and the shipping and packaging costs are high. The shipping costs are high because the resin is shipped to the compounder and then reshipped to the processor, which doubles the transportation costs and often doubles the packaging costs. When using a toll compounder, there are processing losses which must be taken into account when calculating the actual cost of using a toll compounder.

24b.6 Other Resources

The following are the other resources to learn more about color for plastics:

Coloring of Plastics Fundamentals, by Robert A. Charvat

Industrial Inorganic Pigments, edited by Gunter Buxbaum

Billmeyer and Saltzman's Principles of Color Technology, third edition by Roy S. Berns

25 Dispersants and Coupling Agents

***Chris DeArmitt*[1] *and Roger Rothon*[2]**
[1] Applied Minerals, Inc. 110 Greene St., New York, NY 10012, USA
[2] Manchester Metropolitan University, 3 Orchard Croft, Guilden Sutton, Chester, CH3 7SL, UK

25.1 Introduction

Additives are crucial to the successful application and proliferation of plastics. Small amounts of the appropriate additive can make the difference between a useless material and one with excellent mechanical properties and durability. Antioxidants and other stabilizers are used in parts per million concentrations, and yet without them some of today's most successful plastics such as polypropylene and PVC would not be commercially viable at all. Dispersants and coupling agents are also additives which, even when used in low concentrations, can have a profound effect on the performance and viability of plastic materials in diverse applications from packaging to consumer appliances, electronics, automotive, and aerospace.

Dispersants adhere to the particles but have no strong or specific interactions with the surrounding polymer. Coupling agents also adhere to the particulate matter but, in contrast to dispersants, they must also adhere to the polymer through chemical bonds or through chain entanglement (Figure 25.1). As we shall see, dispersants and coupling agents provide different advantages and are selected based upon the needs of the application in question. Contrary to popular belief, good coupling is not always the desired option.

25.2 Dispersants

25.2.1 Terminology

Dispersants are one of many types of surfactants and have the classic surfactant structure, being composed of two (or more) segments with distinctly different chemistries and, therefore, properties (Figure 25.2). The very name surfactant stems from the propensity of such molecules to accumulate at, and influence the properties of, surfaces. They are said to be surface active.

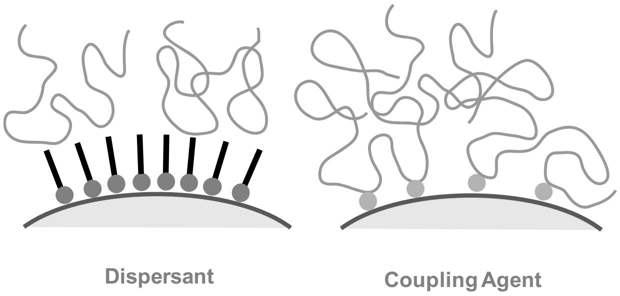

Figure 25.1 Schematic representation of dispersants and coupling agents.

The general structure of a dispersants is
A — **B**
or
Anchor — **B**uffer

Examples would be block copolymers of the structure A-A-A-A-B-B-B-B or low molecular weight molecules such as $CH_3{-}(CH_2)_n{-}CO_2H$

25.2.2 Basic Principles

Several modes of dispersant actions are known, but the main ones are steric stabilization, charge stabilization, and a combination of the two, aptly named electrosteric stabilization. The latter two rely upon charges and are only practicable in polar media such as water. In polymer systems, steric stabilizers are the preferred type. Steric stabilization is contingent upon three factors:

1. Strong anchoring of the dispersant "head" to the particle/inclusion
2. Solubility/compatibility of the dispersant "tail" with the surrounding polymer matrix
3. Sufficient "tail" length to prevent particles from approaching closely enough for van der Waals forces to dominate and force particle agglomeration

Crudely speaking, the dispersant can be conceptualized as a molecular spring on the surface of the inclusion. As particles approach, the springs are compressed, and if bonded well enough that they are not dislodged from the filler surface, then they bounce back to their preferred conformation, thus preventing particles from becoming close enough to fall into a deep potential energy minimum. Each of the three aspects listed above will be covered individually.

25.2.3 Coupling to the Filler/Inclusion

As mentioned, the dispersant must be well anchored. The strength of bond needed depends upon the circumstances. For

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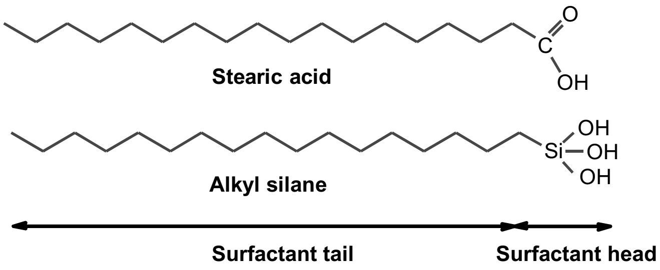


Figure 25.2 Surfactant structure showing the "tail" and "head" groups.

example at room temperature a weak, van der Waals interaction between dispersant and inclusion may be enough to prevent the dispersant from becoming displaced from the surface. In thermoplastics and thermosets, where high temperatures and/or high shear rates are the norm, there is a far greater tendency for the extreme conditions to challenge the dispersant—inclusion bond. The so-called weak bonds such as van der Waals forces are not enough to ensure adequate bonding, and the strong bond types such as ionic and covalent bonding are employed instead.

25.2.4 Bond Strengths

van der Waals <5 kJmol^{-1}
Ionic ~20 kJmol^{-1}
Covalent ~300 kJmol^{-1}

Whereas van der Waals interactions are non-specific and exist between all substances, both ionic and covalent bonding require specific chemistry to take place between the dispersant "head" and the inclusion surface. In consequence, such bonding can only occur if there are appropriate sites on the filler surface for such chemistry to take place. Thus, it is observed that the dispersant anchor group must be chosen such that it matches the available sites (if any) on the surface.

As an example, stearic acid forms stable, ionic bonds with the surface of calcium carbonate and is the preferred dispersant for that filler in most commercial applications due to a combination of good performance and low cost. However, that dispersant in not efficacious on silica because it cannot bind to the surface groups, which are predominantly silanols.

Trialkoxy alkyl silanes are effective dispersants for silica because they can bond to the surface silanols. However, that type of dispersant has inappropriate chemistry to bond to calcium carbonate and is therefore ineffective on that type of filler (Figure 25.3).

It has been said that fillers are either basic or acidic and furthermore that acidic dispersants should be used on basic fillers and that conversely, basic dispersants should be used on acidic fillers. However, this simplistic approach is fallacious. Firstly, a large study showed that all mineral fillers are in fact amphoteric (Table 25.1). That is, they possess surfaces that are both acidic and basic. Furthermore, even a cursory glance at known dispersant — filler pairs will refute the above simplification. As one example, trialkoxy silanes are known to be excellent dispersants for silica but both the dispersant and the filler are known to be acidic in character. A further consideration is the definition of acid and base to be employed in the case of fillers and dispersants. The most usual meaning of those terms is that of Brønsted-Lowry Acids and Bases but that terminology applies to ionic systems, for example aqueous solutions and thus is not applicable to filler-polymer systems which are of much lower polarity. For polymer-filler systems, the type of interaction to consider is that of Lewis Acids and Bases whereby Lewis Bases are able to donate a pair of electrons and Lewis Acids are able to accept a lone pair of electrons. Several studies have shown that Lewis Acid—Base interactions are responsible for adhesion and so it should come as no surprise that they are a factor in the adhesion of dispersant molecules to fillers.

A study was conducted to find the optimal dispersant chemistry for a wide range of fillers. The dispersant tail group was a twelve carbon linear hydrocarbon chain and was kept constant. The dispersant head group chemistry was changed in order to discover which chemistries were able to bond to each type of filler surface. Head groups that bonded were found to be effective dispersants whereas head groups that could not find sites to bond to remained in solution and could

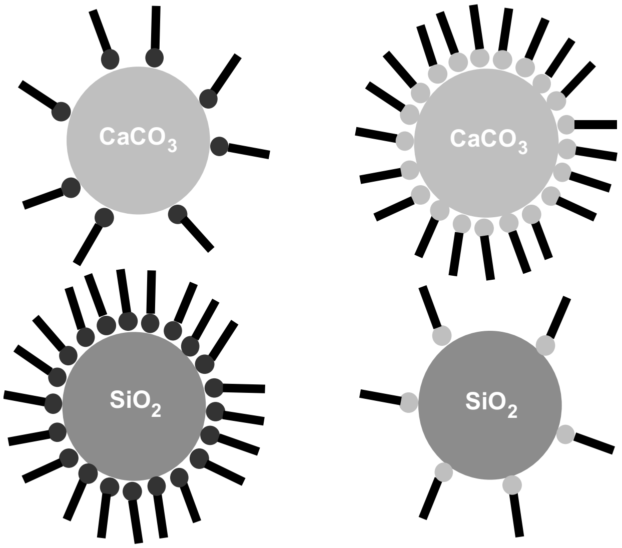


Figure 25.3 $CaCO_3$ and silica with stearic acid and silane dispersants.

Table 25.1 Most effective dispersant head groups for different fillers

Filler Type	Best Dispersant	Second Best	Third Best
Calcium carbonate	Succinic anhydride	Carboxylic acid	Primary amine
Dolomite	Sulfonic acid	Carboxylic acid	Succinic anhydride
Magnesium hydroxide	Succinic anhydride	Trichlorosilane	Carboxylic acid
Mica	Primary amine	Trichlorosilane	Sulfonic acid
Talc	Trichlorosilane	–	–
Silica	Trichlorosilane	Sulfonic acid	Succinic anhydride
Wollastonite	Primary amine	Succinic anhydride	Carboxylic acid
Titanium dioxide	Succinic anhydride	Carboxylic acid	Trichlorosilane

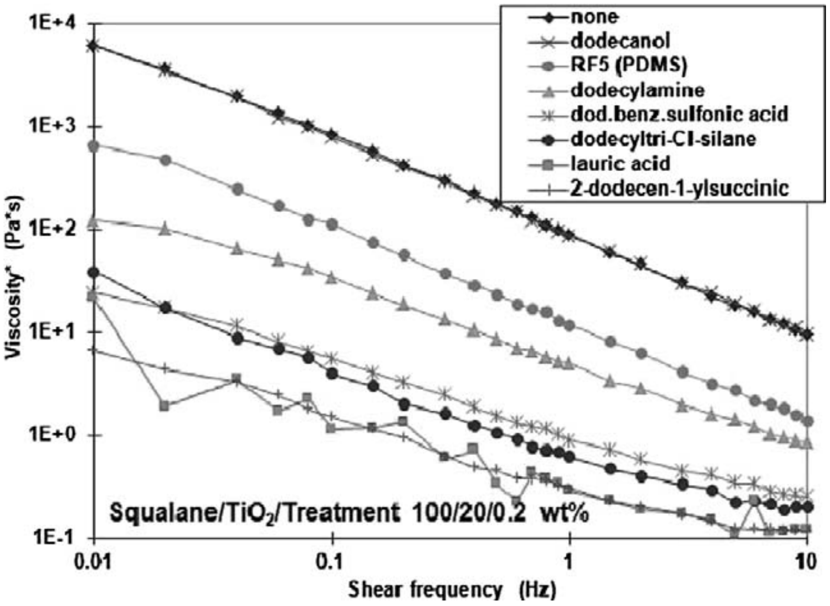
not perform their function as dispersants at the filler surface. The methodology was to disperse each filler type in a hydrocarbon oil (squalane) which served as a model for the polymer phase, for example polyethylene or polypropylene. These filler dispersions tended to exhibit high viscosity as no dispersant had yet been added. An excess (more than the amount needed to make a monolayer) of each potential dispersant was added and the viscosity was seen to drop dramatically if the dispersant head group was able to bond to the filler surface in high concentrations. On the other hand, test dispersants that failed to bond, because of incorrect head group chemistry, resulted in no change in dispersion viscosity. In this way, the drop in viscosity was used to rank the dispersant head groups in terms of their propensity to bond to each filler type. Oscillating viscosity measurements were chosen because they are known to be very sensitive to particle dispersion (Figure 25.4).

For the case of the particular grade of titanium dioxide tested, a hydroxyl head group did not bond at all to the filler surface as no change in viscosity was noted compared to the case with no dispersant present (denoted "none"). In contrast, carboxylic acid and succinic anhydride head groups were very effective at bonding surfactant to the particles and resulting in 1000-fold drop in viscosity. The best three dispersant head groups are listed for each filler (Table 25.1).

Some interesting observations can be made. Firstly, as stated earlier, basic fillers like calcium carbonate adsorb both acids and bases such as the primary amine. Likewise, acidic particulates like silica adsorb acids. Dolomite, which is usually considered to be essentially the same as calcium carbonate, actually displays substantially different surface chemistry.

The common anchoring groups for dispersants and coupling agents, such as carboxylic acids, anhydrides and organisilanes perform well as expected. However, sulfonic

Figure 25.4 Rheological evaluation 20 wt% dispersion of TiO_2 in squalane with 0.2 wt% added dispersant.



acids also perform well although they are not commonly used as dispersants or coupling agents commercially. Other head groups with potential include sarcosine, phosphonic acids, and the trisilanols of polyhedral oligomeric silsequioxanes.

The results show how sensitive the rheological test is for finding an optimal dispersant. However, the results shown may not be valid for every type of talc, silica, calcium carbonate, etc., because dispersant adsorption varies depending upon the surface chemistry of the fillers and that may change from deposit to deposit and may alter depending upon processing techniques and contamination picked up during handling. In particular, it should be noted that the results for titanium dioxide are in no way representative of titanium dioxide in general because TiO_2 is invariably coated with proprietary inorganics and organics, so its surface chemistry varies tremendously.

An effective surface treatment chemistry for talc has eluded scientists for decades because the talc platelet faces are inert and only the edges contain reactive sites. The rheological study confirmed that talc did not respond to any of the usual dispersant types, but, surprisingly, trichlorosilane was seen to be very efficacious. This could pave the way for effective dispersants and coupling agents for talc.

The dispersants found using the rheological test were used to surface treat fillers, and the properties of the resultant composites were measured. In many cases, the dispersants were found to be very effective. The limitation of the rheological dispersant optimization method is that it measures only the amount of additive adsorbed at room temperature and not the strength of the bond between dispersant and filler. Methods to measure the strength of adsorption are available and include inverse gas chromatography and flow microcalorimetry.

25.2.5 Compatibility with the Polymer

According to the criteria for steric stabilization, the dispersant "tail" must be soluble in, or at least compatible with, the polymer. Solubility is governed by the principle that like dissolves like. In more scientific terms, it means that the dispersant tail and the polymer must be of similar polarity, or more precisely of similar solubility parameter. Therefore a perfluoroalkyl tail would be well suited to PTFE, an alkyl dispersant tail would be ideal for polyethylene and polypropylene, and a high polarity polyethylene oxide type tail would work in polymers such as PVC, PET, and nylons.

The reason that solubility of the tail is important lies in the mechanism for steric stabilization whereby the tail acts as a molecular spring. Long-chain tails adopt a random coil configuration, where the size of that coil (radius of gyration) increases depending upon how well the chain and the surrounding polymer interact. Although the shape and size of the polymer coil are perturbed by the proximity of the filler surface, the same trend applies, namely that a good solvent for the polymer leads to a larger polymer coil. A large, well-solvated chain covers a greater volume and stabilizes the particle better against agglomeration. When particles approach and the coil is compressed compared to its ideal, equilibrium conformation, it acts to regain that preferred configuration by springing back and repelling the incoming particle. So, at least for long-chain steric stabilizers, the ability of the polymer to solvate the tail is essential.

25.2.6 Tail Length

In reality, other factors become as, or more important, than selecting the dispersant with the ideal polarity. One essential observation is that long-chain dispersants are not needed to achieve many of the desirable effects associated with good dispersion, namely decreased viscosity (better processability), good gloss, raised impact resistance, and for pigments, higher tinting strength. Stearic acid has only an 18-carbon chain length, and yet it is a highly effective dispersant used in many situations. It was shown in the rheological study mentioned previously that a chain length of just 3–4 carbons is enough to reduce viscosity to a minimum.

Such short-chain dispersants cannot adopt a random coil configuration; they will be more or less linear molecules no matter the ability of the polymer to solvate the chains. In fact, molecules like stearic acid on calcium carbonate pack together so tightly that there is no possibility for the polymer to penetrate between the chains and interact with them anyway. Thus it is found that in reality, short-chain dispersants are often rather efficacious and need not be tuned to exactly match the polymer they are used in. The length of the chain can be tuned but in reality, stearate groups are so inexpensive that other types cannot compete in any but the most specialized applications. Similarly, in theory, the best dispersant tail is one with a polarity matched closely to that of the matrix polymer. However, in practice, hydrocarbon tail types predominate as they are available and at low cost.

25.3 Practical Use Considerations

These aspects are similar for coupling agents and are covered in more detail in that section.

25.3.1 Pre-Coating

Dispersant may be added by the filler manufacturer. That entails additional cost but reduces water uptake during transportation and storage.

25.3.2 In Situ Treatment

In situ coating is less expensive as the dispersant is added during extrusion. The dispersant melts and dissolves in the polymer melt which acts as a solvent to facilitate the surface treatment.

25.3.3 Amounts to Use and Surface Coverage

Optimal dispersion is normally found at a monolayer of dispersant. This can be detected by measuring viscosity. The viscosity of the filler dispersion in solvent or polymer will decrease as dispersant is added and then level off at monolayer coverage. Adding too much dispersant may cause problems in the composite as free dispersant molecules can interfere with antioxidants. It can also lead to problems with adhesion and printability as the excess dispersant blooms to the polymer surface forming a weak boundary layer (i.e., a waxy layer with low cohesive strength).

25.4 Types of Dispersants

The types of dispersants are similar to the types of coupling agents because in both cases, the chemistry needed to bond the additive to the filler surface is the same.

If the type of coupling agent is not chosen properly, then it will usually act as a dispersant instead. For example, if an organosilane is used that bonds to the filler but the chemistry or reaction conditions do not allow it to bond to the polymer, then it will disperse but not couple. Thus, additives that are labeled as coupling agents do not necessarily couple.

25.4.1 Organosilanes

Silanes with an unfunctionalized hydrocarbon tail will disperse but not couple. Functionalized organosilanes cannot react with polyethylene or polypropylene because those polymers are inert, and thus coupling does not take place with those polymers.

25.4.2 Titanates

Titanates are usually referred to as coupling agents. However, when one looks at the property benefits claimed, such as improved dispersion, better flow, and higher gloss, it becomes clear that these additives are, in fact, dispersants and not coupling agents.

25.4.3 Unsaturated Acids

Unsaturated acids, such as those based on polybutadiene, can be used as effective dispersants in situations where the double bonds are not able to react chemically with the polymer matrix.

25.4.4 Acid-Functionalized Polymers

These additives are normally used as coupling agents whereby the acid groups (e.g., acrylic or maleic) adhere to the filler, and the polymer chains entangle with the matrix polymer chains. If the coupling agent has polymer chains that are too low in molecular weight then they cannot entangle, and it will act as a dispersant rather than as a coupling agent. Similarly, if the coupling agent polymer is not miscible with the matrix polymer then entanglement will not occur, but dispersion may be improved instead.

25.5 Property Effects

Many advantages result from the use of dispersants, and these will be covered separately.

25.5.1 Flow/Processability

The addition of any particulate matter to a fluid results in an increase in viscosity (although rare exceptions do exist). As progressively more filler is added, the viscosity rises until flow is so slow, and therefore extruder throughput is so poor as to be economically unviable as a commercial process. At still higher filler levels, viscosity approaches infinity, and the polymer melt cannot flow at all (Figure 25.5).

Using a dispersant allows reduced viscosity (improved productivity) at constant filler loading. A dispersant also enables the use of higher filler loading while maintaining constant viscosity.

25.5.2 Impact Resistance

Dispersants can raise impact resistance, especially unnotched impact resistance (see chapter on Functional Fillers for Plastics for a description of impact resistance measurement and trends). There are two effects responsible for it. Impact resistance is sensitive to any large particles as they concentrate stresses and thereby act as flaws (Figure 25.6). When impact takes place, cracks initiate from those larger filler particles or agglomerates of smaller particles. Addition of dispersant reduces or removes agglomerates that could otherwise have led to cracks.

The second mechanism by which dispersants improve impact resistance is by reducing bonding between filler and polymer. When impact occurs, the filler debonds from the polymer to create multiple microvoids as each filler particle debonds. These voids or crazes help to adsorb energy. It is well known that crazing is a mechanism to improve impact

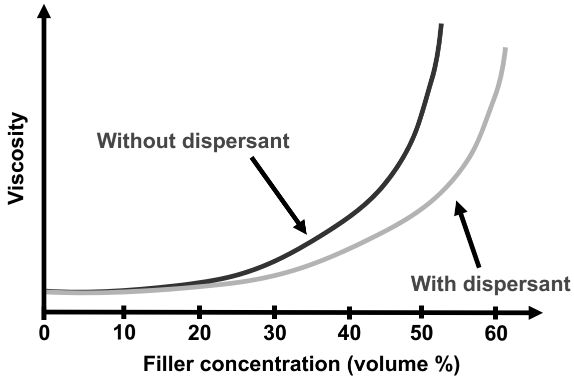


Figure 25.5 The effect of filler and dispersant on viscosity.

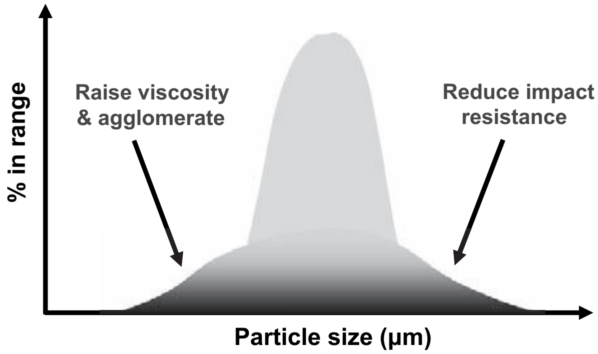


Figure 25.6 The effect of particle size and agglomerates on properties.

resistance. Elastomeric impact modifiers also work through crazing. Hard fillers are not nearly as effective as elastomers at raising impact resistance. However, fillers can raise modulus and impact resistance together, something not possible with elastomeric impact modifiers.

Of these two mechanisms, namely dispersion and debonding, by which dispersants improve impact resistance, the relative importance of each is not known because both effects occur simultaneously, and the effects cannot be separated.

Smaller particles agglomerate more readily and require more mixing energy to separate. Nanofillers are worst of all and can be impossible to disperse properly. Researchers tend to plot properties versus the filler particle size as reported on the suppliers' datasheet. This leads to problems in understanding and interpreting the experimental results. Firstly, the size distribution is important, not just the mean particle size (Figure 25.6). Secondly, it is the size of the filler particles in the final composite that counts, not the size printed in the datasheet. Experiments on stearic acid-coated calcium carbonate compounded into polymer using a twin screw extruder showed that larger particles (above about 1 micron) disperse perfectly, whereas particles smaller than that tended to agglomerate. Nano calcium carbonate with a datasheet particle size of 70 nm actually formed agglomerates larger than 100 microns in diameter (Figures 25.7—25.9). Not surprisingly, the impact resistance of that latter material was very low.

The ability to disperse the filler will depend upon its tendency to agglomerate, the screw design of the extruder, extrusion operating conditions, and whether dispersant or other additives that adsorb onto the filler are present (Figure 25.10).

25.5.3 Gloss

Gloss is higher for smaller, well-dispersed filler particles so dispersants are of value. Lower angles of gloss measurement are more sensitive to gloss reduction due to filler addition than are higher angles. Fillers can and are used to degloss surfaces, for example to prevent glare from reflected sunlight or to suit the preferences of a given market. Large filler particles are effective at reducing gloss levels.

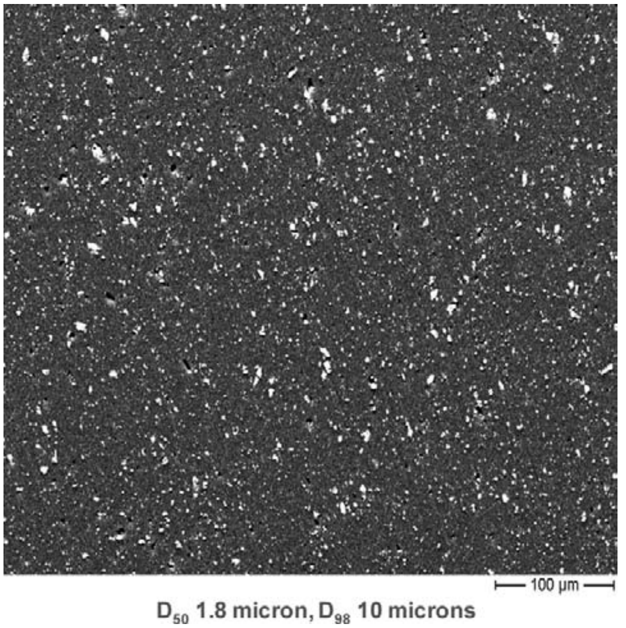


Figure 25.7 Stearic acid-coated calcium carbonate dispersed in thermoplastic via twin screw extrusion; no agglomeration.

25.6 Coupling Agents

25.6.1 Introduction

While very loosely used in the scientific and especially trade literature, the term coupling agent is interpreted here as meaning a class of adhesives used to firmly bond (couple) polymers to inclusions such as fibers and particulate fillers. This coupling has the effect of increasing the interfacial

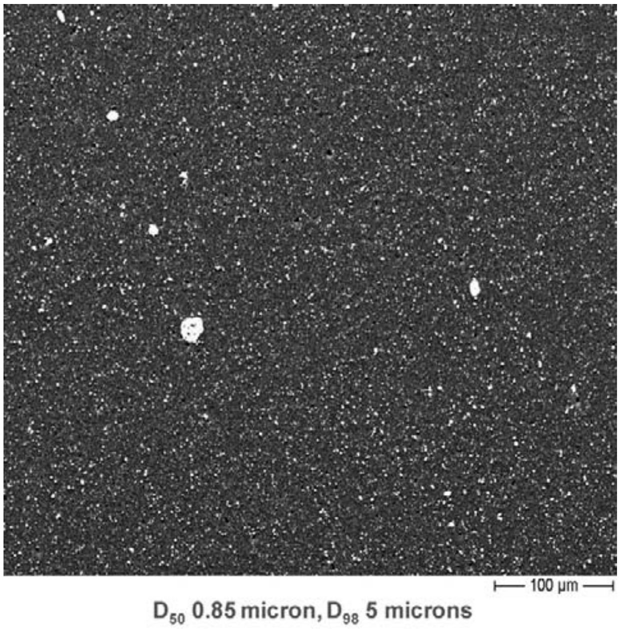


Figure 25.8 Stearic acid-coated calcium carbonate dispersed in thermoplastic via twin screw extrusion; mild agglomeration.

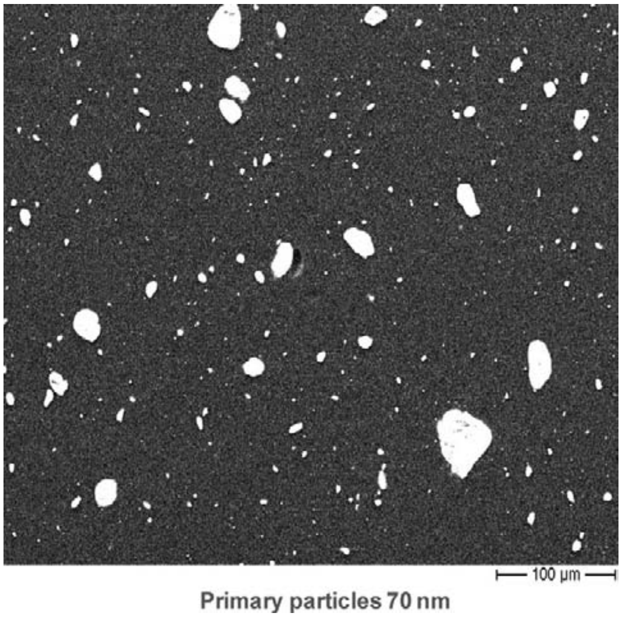


Figure 25.9 Stearic acid-coated calcium carbonate dispersed in thermoplastic via twin screw extrusion; severe agglomeration.

stress required to debond the filler—polymer interface, which, in turn, results in higher tensile and flexural strength, increased stiffness at high strains, and sometimes improved toughness. The coupled interface also reduces water absorption giving improved property retention and often better electrical stability under humid and wet conditions.

As described earlier, dispersants can also improve polymer processing and some composite properties, but they do not give the strong interface that coupling agents do. Much of the confusion in the literature arises from failure to discriminate between the beneficial effects due to dispersion and to coupling and from the tendency to describe any additive that produces an improvement as a coupling agent. To further complicate matters, the best coupling agents are often also good dispersants and so bring about improvements by both dispersion and coupling mechanisms.

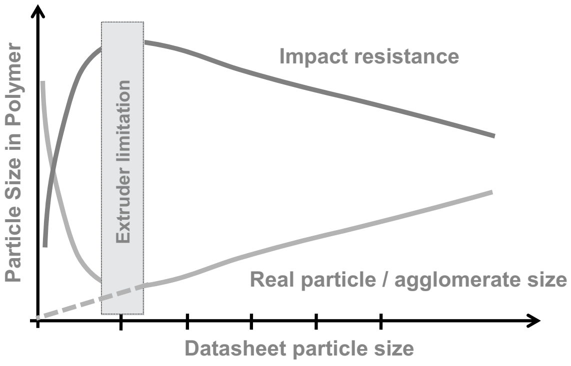


Figure 25.10 Agglomeration versus particle size.

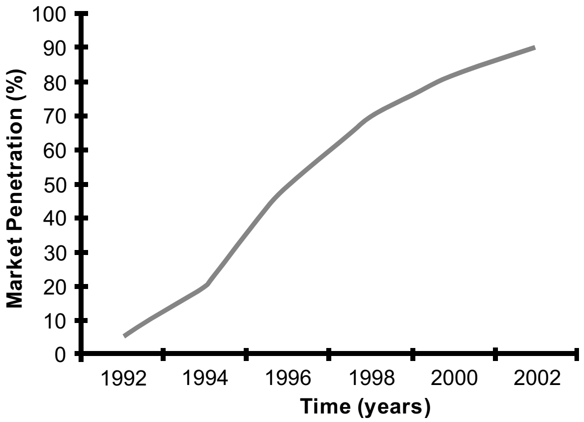


Figure 25.11 Growth of the European automotive energy tire market (presented as percentage penetration of the initial equipment market).

Coupling agents are a very important ingredient in many high performance polymer composites. A striking recent example of this is the green or energy tire technology in which carbon black had been replaced by precipitated silica. As shown in Figure 25.11, this technology, which is only made possible by the use of coupling agents now dominates the automotive tire market in Europe.

25.6.2 Terminology

The definition of the term coupling agent, as used in this article, has been described above. As the non-polymer component being coupled may be in fiber or particulate form and may or may not be a reinforcement in the traditional sense, the general term "inclusion" is used here for this component.

25.6.3 Differences Between Dispersion and Coupling

The differences in the effects due to dispersion and to coupling arise from the nature of the inclusion interphase that is present. In the case of dispersion, this interphase is relatively weak and easily destroyed by strain or by the ingress of water. In the case of coupling, the interphase is much more resistant.

These differences are well illustrated in Table 25.2, which compares the effect of a non-coupling and a coupling surface treatment on precipitated calcium carbonate in an EPDM elastomer. Both additives improve processing (minimum viscosity) by a similar amount. This is a dispersion effect and shows that the coupling agent used in this case also possesses this ability. The dispersant lowers tensile strength, high extension modulus, and tear strength while the coupling agent increases them compared to the untreated filler. This is due to the differences in interphase strength mentioned above. Detergent swell is a complex property; influenced by dispersion, coupling, and the hydration resistance of the interphase, and we see that both approaches bring about a significant improvement but that coupling is the better of the two.

Table 25.2 A comparison of dispersion and coupling agent effects in sulfur-cured EPDM filled with precipitated calcium carbonate

Property	No Treatment	Dispersion	Coupling
Minimum viscosity at 160 °C (Monsanto Rheometer)	18.6	10.0	10.0
Tensile strength (MPa)	10.0	4.5	13.3
Modulus 300% (MPa)	2.3	1.4	3.7
Tear strength (N/mm)	16	10	24
Detergent swell (%) (15 detergent 72 hours at 95 °C)	2.7	0.9	0.1

25.6.4 History

Before discussing the main types of coupling agents in any detail, it is useful to look at the history of coupling agent technology:

Industrial use of coupling agents can be traced back to the early days of glass reinforced unsaturated polyesters. Such resin-based composites were introduced in the 1940s and were of great interest, as they had excellent stiffness to weight ratios and were potentially able to substitute for metal in many applications. Their strength was found to rapidly drop off under humid or wet, conditions, however, with losses of about 60% being experienced. This loss in strength, which severely limited their commercial uptake, was found to be due to water degradation of the resin fiber interphase, and this led to a search for fiber treatments that could reduce or prevent such attack.

The first successful glass fiber treatment found was a chromium complex of methyl-methacrylate. The initial versions of this product were the first coupling agents and reduced the strength losses under humid conditions to about 40%. This chromium-based chemistry was improved and later commercialized by DuPont and is still in use with glass fiber to some extent today.

The US air force was very interested in using glass fiber reinforced unsaturated polyester resins, but required even better humidity resistance, and so they funded research into better coupling agents. This research was quickly successful and led to silicon-based products that reduced the losses to under 10% and resulted in the birth of the organosilane coupling agent family, which still dominates the market over 40 years from their first introduction.

While there have been many attempts to find alternatives to the organosilanes, these have had limited success. The main competitive products are based on organic derivatives of titanium, aluminum, or zirconium but have only achieved niche use.

One of the main limitations of the organosilanes is their lack of success on fillers with basic surfaces, notably calcium carbonate. This has driven the development of acid or acid precursor coupling agents such as carboxylic anhydride grafted polymers. After a long gestation period, these coupling agents are beginning to make a significant commercial impact. This has been accelerated by the growing use of wood reinforced polymer composites where they are more effective than the silanes.

As described above, coupling agents were initially developed for use on glass fibers, and this remained their main application area for several decades. As a consequence most of the developments were aimed at this market. Gradually applications were developed for particulate fillers, but this remained a relatively small market sector until the 1980s when “green” or energy tire technology started to emerge. This technology allows carbon black to be replaced by precipitated silica/organosilane combinations, with a significant reduction in fuel consumption. This application has mushroomed until it is now a major consumer of organosilane coupling agents and has led to a new focus in technical development and to new types of silane coupling agents.

The most recent significant development in the market place has been the very strong growth in the use of cellulose fiber reinforced composites, especially those based on wood fiber and powder. Coupling agents are often used in these formulations, especially to reduce water absorption and accompanying loss of properties. Maleic anhydride grafted polyolefins have been found to be very suitable additives for this purpose, and this has led to a marked increase in their use.

25.6.5 Basic Principles

Coupling agents are essentially bifunctional molecules, where one functionality is able to react with the inclusion surface and the other with the polymer, thus coupling the two together. All coupling agents can therefore be regarded as having the simple structure:

A — B — C

or

Anchor — **B**uffer / **B**ridge — **C**ouplant

The challenge for the chemist is to find the functionalities A and C and to find a linking structure B that produces a molecule that is stable, non-hazardous, and easy to use. This may seem a simple task, but the author can verify that many of the potential structures result in products that are insoluble, high melting, compounds which are often impossible to use in any commercially useful way.

25.6.6 Anchoring the Inclusion

In practice, very few groups are utilized for bonding to the surface of the inclusion, the principal ones being certain metal hydroxides or derivatives of carboxylic acids and their precursors. Although the commercially used anchor groups are limited, all those shown effective for bonding dispersants to fillers, for example in the previously mentioned rheological study, should also be suitable anchor groups for coupling agents.

The origins of coupling agent technology being in glass fiber based composites meant that the main emphasis, at least until recently, has been on groups that can form strong, stable, bonds to glass surfaces. The principal potential anchoring site on glass and many silicas and silicates are the surface hydroxyls (silanols). The chemistry is discussed in more detail later, but certain metal hydroxides, notably those of chromium, titanium, aluminum, zirconium, and silicon are able to condense with these surface groups and potentially provide the desired bonding. This is the basis of the main coupling agent technologies in commercial use today. The biggest problem is that the coupling agent metal hydroxyls are also able to condense with themselves and can quickly lead to intractable solids, before any significant reaction with the inclusion has taken place, unless they have been stabilized in some way prior to use. In the case of some of the metals, this stabilization is achieved by converting the OH groups to alkoxy ones; with others this does not work, and the more extreme method of using low pH is employed.

While the metal hydroxide technology described above is suitable for glass and many siliceous fillers, it is not effective on other classes of important fillers such as carbonates, sulfates, and carbon blacks.

Carboxylic acids or their precursors, such as anhydrides, are successfully used for anchoring to basic inclusions. They also function well on amphoteric ones, and so their application spectrum overlaps to some degree with the metal hydroxides.

There is a small group of inclusions left which are not reactive with either type of functionality. The principal ones are carbon blacks, sulfates such as barium sulfate, and pure talcs. Of these, carbon blacks already possess a reactive surface which gives rise to similar effects that would be found by coupling and so do not really need treatments. The other inclusions mentioned, especially talc, remain a challenge and have provoked much research effort. Interestingly, trichlorosilanes were shown to be effective on talc although that technology is not yet commercialized. Carbon fibers are another type of filler that have no intrinsic bonding sites on the surface, instead they are post treated, for example using oxidation, to introduce reactive sites and enable coupling.

25.6.7 Coupling to the Polymer

Finding suitable groups for this are easy for some polymer types and very difficult for others. More polar polymers, for example nylons 6 and 6, 6 are able to interact well with fillers even in the absence of coupling agents. Their low polarity prevents them from bonding well to filler surfaces.

Polymers that are crosslinked by peroxide or other means are among the easiest, with unsaturated groups such as vinyl or methacryl being adequate. There has been a lot of interest in unsaturated organic acids especially oleic and similar types, but, with the exception of acrylic and methacrylic acids, these have generally been found to be ineffective. While acrylic and methacrylic acids can achieve coupling, they are not easy to use.

Sulfur-cured elastomers are also relatively easy, using groups such as mercapto or polysulfide.

Condensation polymers such as polyamides and polyesters like PET are a little more difficult but are quite reactive at processing temperatures and can be reacted using groups such as amines and epoxides.

The most difficult polymers are thermoplastic polyolefins such as polypropylene and polyethylene. These have no obvious chemical handle. Some of the early work utilized the azide functionality, but this is a very hazardous group and no longer of commercial interest. More recent work uses unsaturation in combination with peroxide or possibly mechanochemical grafting with the ultimate expression of this being to pre-graft the inclusion reactive functional group onto the polymer or to copolymerize with it.

Table 25.3 lists the principal polymer functionalities now used and the corresponding polymers.

25.6.8 Bridging the Two Together

This is the tricky bit and this is what really determines which structures are practical.

With carboxylic acid anchoring groups, it is not too difficult and they can be connected to a variety of functionalities through simple hydrocarbon chains. The principal limitation is with groups that would themselves react with the acid. The amino-functionality is a prime example of this.

With metal hydroxylic anchoring groups it is different. The polymer reactive groups are nearly always organic in nature, but with the exception of silicon, none of the metals that has suitable hydroxyls form stable metal carbon bonds. It is primarily this ability that makes silicon-based compounds the

Table 25.3 The main polymer reactive functionalities used in coupling agents

Functionality	Main Polymers Used In
Unsaturation (e.g., vinyl or methacrylic)	Unsaturated polyesters, acrylics, peroxide cross-linked elastomers
Sulfidic (e.g., mercapto or polysulfide)	Sulfur-cured elastomers
Amino (e.g., primary, secondary, or a combination)	Polyamides, epoxies
Epoxy	Epoxies, polyesters (PET, PBT)

most widely used coupling agent type. With the other candidate metals, the polymer reactive group is attached through a relatively stable ester link (metal—oxygen—carbon) often with an adjacent carboxyl functionality to increase stability further.

25.6.9 Practical Use Considerations

The practical process of using coupling agents plays a big part in determining commercial acceptability. There are two main ways of utilizing them—pre-coated onto the inclusion or added during the composite preparation stage (in situ method). Both have advantages and limitations, and both are widely used. The pre-coating method can be broken down further into wet and dry coating.

25.6.10 Pre-Coating

This is generally significantly more costly than the in situ method, except where the inclusion is produced under conditions (such as a slurry) that allow the coating to be incorporated without extra processing. Glass fibers are a classic example, as they have to be coated with sizes, etc., immediately on production, in order to preserve their strength. Many coupling agents can then be incorporated into this coating process. The advantages of pre-coating include better control of the process, especially freedom from interference from other components in the composite formulation, and the ability to safely treat any evolved gases (significant quantities of alcohol can be released from the reaction of organosilanes with inclusion surfaces). On the down side, any fresh surface generated during composite production will remain untreated.

25.6.11 In Situ Treatment

The in situ method is usually significantly cheaper and can deal with the fresh surface question. It is less controlled than the pre-coating method, however, and prone to interference from other surface active species that may be in the formulation. Evolved gases from the coupling reaction can also be a significant problem.

The physical form of the coupling agent plays a very important role in determining its suitability for either method. Low volatility and high flash point are fairly obvious advantages.

With the in situ method it is essential that the coupling agent dissolves in the polymer (or in some cases monomer). In connection with this, the additive needs to be fluid at the processing temperature.

For pre-coating, the additive needs to be a liquid at the coating temperature, or to be readily soluble in a solvent that is of low hazard in the process (water being the most suitable).

For the best results a combination of pre-coating and in situ is sometimes employed.

25.6.12 Amounts to Use and Surface Coverage

One of the most common questions is how much coupling agent to use. There is no quick answer to this, but there are some simple guiding principles.

The most straightforward approach is to find the amount of additive that can just cover the surface of the inclusion, if it is spread one molecule thick. This gives rise to the monolayer concept.

While simple in principle, there are several factors that increase its complexity. At the simplest level, one just needs to know the specific surface area of the inclusion and the orientation of the coupling agent molecule at the surface (giving rise to a footprint area). The specific surface area is accessible by a number of methods, of which the BET nitrogen adsorption method is the most commonly used. The footprint area has been calculated by molecular modeling for a number of coupling agents and for different orientations (where this is relevant). From these two parameters, one can calculate the number of molecules required to give a monomolecular coverage of unit weight of the inclusion and using Avogadro's number and molecular weight, this can be converted into a weight percent figure. A typical example follows for coverage of a particulate filler with a specific surface area of 10 m^2/g by two different organosilanes of known coverage (Table 25.4).

Complexities arise from a number of sources. The nitrogen used to obtain the specific surface area is a very small molecule and may access surface that is not available to the coupling agent. Where this is a concern, one may use dye absorption to get a more meaningful specific surface area or even carry out an absorption isotherm using the coupling agent itself. In the rubber industry it is common to use cetyltrimethyl ammoniumbromide (CTAB) as a suitable large molecule for measuring the appropriate surface area of fillers such as carbon black and precipitated silicas. Methylene blue dye is also used.

The spacing of reactive groups in the inclusion surface is also an issue. The coupling agent molecules may be able to form a monolayer, but not all of them may be able to find surface groups to react with. This may not be a problem when, as is often the case, the coupling agent molecules can also react with each other, but can be an issue when they cannot.

While the monolayer concept is easily understood, its relevance to final properties is less clear. With some coupling agents, property changes can start with the first fraction of

Table 25.4 Calculated monolayer coverage levels for two different organosilanes on filler with a specific surface area of 10 m^2/g

Organosilane	Coverage (m^2/g)	Monolayer (Weight %)
Gamma-aminopropyl trimethoxy silane	360	10/360 = 2.8%
Vinyl trimethoxy silane	525	10/525 = 1.9%

a monolayer and increase up to and past the monolayer level. With others there is a sharp optimum at or near the monolayer level and excess additive is very undesirable. Durability, especially under humid conditions, can follow a different pattern and generally requires at least monolayer coverage.

It has also been found that coupling agents often deposit non-uniformly with islands several molecules thick being present, together with uncoated surface. In this case, higher addition levels are required.

25.6.13 Types of Coupling Agents

The main types of coupling agents in commercial use are described below. Most, if not all of them, have other applications, mainly in the wider adhesive and dispersant markets. The discussions here are limited to their use as coupling agents. It is worth noting that there is little difference in the polymer reactive groupings; the main differences are in the inclusion reactive functionality and the way that the two functionalities are combined into a single molecule.

25.6.14 Organosilanes

These are the premier coupling agents in use today and so deserve pride of place in this section. Their success is largely due to the unique ability of silicon to stably connect polymer and inclusion functional groups and to do so in molecules that are low hazard liquids or low melting solids, soluble in most polymer types. An important, but often overlooked additional advantage is that precise coverage levels are not needed and excess coupling agent does not cause any problems. This is not true for many of the other organo-metallics, where a sharp peak in performance against loading is often reported and excess can be very detrimental. In these cases, precise control of addition level is essential.

As described earlier, the use of organosilanes grew from work sponsored by the US Air Force to find products that performed better than the original chrome complexes in glass fiber reinforced unsaturated polyester resin composites. The first success was achieved with vinyl trichlorosilane and its mixtures with allyl alcohol. The unsaturation provided the polymer reactive functionality while the chloro-groups provided the fiber reactive ones. The fiber reactivity comes about by hydrolysis of the chloro-groups to form silicon hydroxyls which are then able to condense with surface hydroxyls, as shown in the following simplified reaction sequence.

$$\mathrm{R{-}Si{-}Cl} + \mathrm{H_2O} \rightarrow \mathrm{R{-}Si{-}OH} + \mathrm{HCl}$$

$$\mathrm{Glass{-}OH} + \mathrm{HO{-}Si{-}R} \rightarrow \mathrm{Glass{-}Si{-}R} + \mathrm{H_2O}$$

While the chloro functionality is successful in achieving coupling to the inclusion, it has some limitations, notably the release of hydrogen chloride during the reaction. It was soon found that conversion of the chloro-groups to alkoxy ones (e.g., by reaction with a suitable alcohol, R—OH) produced more user friendly products of similar effectiveness. These liberate the corresponding alcohol rather than hydrogen chloride, when used. The first alkoxy-type silane coupling agent for commercial use was the vinyl trimethoxy one, still in significant use today. The surface coupling reaction still proceeds by hydrolysis to silanols and their subsequent condensation, as described above. The nature of the alkoxy group is important for a number of reasons. It determines the volatility and flash point of the molecule and also the rate of surface reaction. Potential toxicity issues related to alcohol also have to be considered. As an example, the use of methoxy-based organosilanes has been in decline due to the hazards associated with methanol release.

A frequently asked question is whether the silicon needs to have three surface reactive groups. The tri-functionality arose initially because the vinyl trichlorosilane (and hence the trialkoxy derivatives) was readily prepared. It is more difficult and expensive to make less functional molecules such as vinyl dimethyl mono-alkoxy silane. There is no definitive information on how such compounds might compare with the trialkoxy ones.

Once the vinyl functional product was established, attention moved to finding functionalities to suit other polymer systems. In quite a short period the following functionalities were developed.

Primary amine
Epoxy
Methacryl
Mercapto and polysulfide

The latter may seem rather exotic but are actually large tonnage products used in sulfur-cured elastomer systems. While many other functional types have been commercialized since, these five types still dominate the market and suit the majority of polymer systems.

For many years, product development and scientific research was focused on glass fiber applications, with particulate fillers being a relatively small segment. This changed significantly from the early 1980s when green (energy) tire technology began to appear. This technology is based on precipitated silica fillers and gives tires with lower rolling resistance and hence lower fuel consumption than the previous dominant carbon black technology. Despite the rolling resistance advantage, untreated silica gives very poor tread wear compared to carbon black, and it is the use of coupling agent technology that overcomes this and makes such tires a commercial reality. They have been so successful that virtually all new car tires in some parts of the world (notably Europe and Japan) are now silica based. The precipitated silicas have very high specific surface areas, which need virtually complete coverage if acceptable tread lives are to be achieved; this results in high silane addition levels (5−10 wt% on filler). As a result, the market is very significant and precipitated silica fillers, rather than glass fibers, have driven recent scientific understanding and commercial developments of coupling agent technologies.

One of the most important developments has been low volatile organic constituent (VOC) silanes. In the conventional trialkoxy products, about 50 wt% of the molecule is volatile alcohol which is released during reaction with the inclusion surface. The in situ addition method is widely used with particulates, especially in green tire technology and results in a very significant, uncontrolled, release of volatiles. Legislation is restricting such releases and has led to the commercialization of improved products. The reduction in volatiles is achieved by methods such as partially precondensing the silanes or by using alcohols which, while not volatile, still allow the surface reaction to take place and remain as inert materials in the final product.

25.6.15 Other Organo-Metallics

The main disadvantages of the organosilanes are their relatively high cost and their lack of activity on fillers such as calcium carbonate. Other organo-metallics have been extensively investigated in efforts to find alternative products. None has been wholly successful, although several have developed niche applications. The main types are briefly discussed below.

25.6.16 Chromium Salts

As mentioned earlier, these were the original coupling agents for use in polymer composites. Salts of trivalent chromium can be reacted with certain organic acids to produce cyclic complexes, such as shown in Figure 25.12. If the acid carries a polymer reactive functionality, this can be incorporated into the complex. The reaction between chromium chloride and methacrylic acid is particularly suitable, resulting in a complex with reactive unsaturation. This complex can react with inclusion surfaces through the chromium functionality and with suitable polymers through the unsaturation.

This technology has been developed by DuPont who market their Volan® products. It is technically very successful in its primary goal of producing strong, stable, interfaces, but there appear to be several limitations.

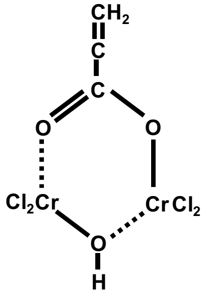


Figure 25.12 A chromium methacrylic acid complex.

The first is that the only polymer reactive functionality available appears to be unsaturation, and this limits the types of polymer composites that they can be used with.

The second relates to the need to prevent the self-condensation referred to earlier. This reaction proceeds readily and results in intractable solids with no utility for coating inclusion surfaces. The self-condensation is prevented by providing the agents in solution stabilized by low pH and by the presence of chloride. The pH is raised just prior to use in order to start the polymerization with the inclusion surfaces. In many cases, the coated product has to be washed to remove chloride. Scope for in situ addition is also very limited.

Finally, the coating solutions are somewhat hazardous, being acidic and containing a toxic metal. This latter is especially important in considering process effluents.

The main application today appears to be with glass fibers in unsaturated polyester composites. There is little or no reported use with particulate fillers.

25.6.17 Aluminates

References to aluminate coupling agents can be found in the literature. There is little structural information, but they seem to be derivatives of aluminum tri-isopropoxide, with one or more of the alkoxide groups being replaced by long-chain hydrocarbons. While often referred to as coupling agents, they are more likely to be dispersants, and this is borne out by the performance data available. Interestingly, they are claimed to be effective on calcium carbonate. As surface reaction (needed for coupling) with this filler would not be expected from the chemistry, this supports the mode of action as being dispersion rather than coupling.

25.6.18 Zircoaluminates

These chemicals were introduced in the early 1980s. Careful control of the reaction conditions allows aluminum and zirconium salts to be reacted with organic acids to produce low molecular weight, cyclic complexes of the generic structure shown in Figure 25.13. The alkoxy groups on the metals allow reaction with inclusion surfaces, while the organic acid allows the introduction of polymer reactive

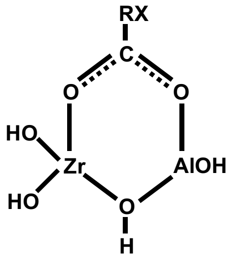


Figure 25.13 A typical zircoaluminate structure.

functionalities. Quite a wide range of functionalities are possible and have been offered commercially at some stage. Today only primary amine, carboxy, oleophilic, and mercapto functionalities appear to be commercial.

There is very little published information, but the main applications would seem to be as adhesives in the broader sense, rather than as coupling agents. The main use in our narrower sphere appears to be with siliceous fillers in elastomer compounds.

The principal limitations are again based around the need to stabilize the structures and prevent self-condensation prior to use. This means that they are not isolated as neat compounds, but sold as solutions in a polar solvent. They can be diluted with water before use, provided the solution is kept acidic. These issues mean that they can be tricky to use. They are most suited to liquid systems and not suited to in situ addition in most other systems.

25.6.19 Chartwell Adhesion Promoters

These proprietary products were introduced shortly after the zircoaluminates. Their structure is not revealed, but they are described as metal complexes. They are claimed to offer lower cost than organosilanes with similar polymer reactive functionalities and to overcome some of the difficulties of the aluminates and zircoaluminates.

Various polymer reactive functionalities are available including the following:

- Mercapto and sulfido
- Primary and secondary amine
- Hydroxy/carboxy
- Methacrylato

Like the chromates, aluminates, and zircoaluminates, the Chartwells cannot be isolated as neat solids (although dry powder forms on a carrier are available). They are claimed to need less aggressive stabilization, and their solutions are chloride free. The solutions can also have pH above seven.

Their main uses appear to be as adhesion promoters in inks and coatings, with only limited application as coupling agents.

25.6.20 Titanates

This is the area where there is most confusion over the use of the term coupling agent and indeed there has been considerable controversy. Potentially, titanate coupling agents can be derived from tetra-alkoxy titanate [$Ti(OR)_4$], where one or more of the alkoxides have been replaced by an organic moiety carrying a reactive functionality. The remaining alkoxides then provide the means of attachment to inclusion surfaces through hydrolysis and condensation reactions, as with the organosilanes.

Because of the instability of titanium to carbon bonds, any reactive functionality has to be attached through oxygen and even then, stability cannot be guaranteed. Many of the products available have long-chain hydrocarbon functionalities, and while they produce useful effects, these are more likely to arise from dispersion rather than coupling in the sense used in this chapter. The titanates appear to be effective with fillers such as calcium carbonate and carbon black, where it is difficult to envisage surface reaction mechanisms and weaker, dispersant-type interactions are more likely.

25.6.21 Unsaturated Acids

The success of organosilanes with unsaturation as the polymer reactive functionality suggests that unsaturated acids should be equally effective with fillers such as calcium carbonate. Despite a great deal of effort, there has been little commercial success with simple unsaturated acids. Long-chain ones, such as oleic, have not proved to have sufficient reactivity. Short-chain types such as maleic, acrylic, and methacrylic have been shown to be capable of producing coupling but are difficult to use on a commercial scale. A form of oligomerized unsaturated acid (Solplus™ C800) has recently been commercialized by Noveon with some success.

25.6.22 Acid-Functionalized Polymers

These are a growing class of coupling agents, their popularity being driven by the increasing use of cellulose-filled polymer composites, especially those based on wood flour. All the main types contain carboxylic acid or acid anhydride groups as the inclusion reactive species. This makes them very effective on basic fillers such as calcium carbonates and also on amphoteric ones like aluminum hydroxide. As mentioned above, they also function very well with cellulosic fillers such as wood flour.

The main polymer backbones in use are polyolefins such as polyethylene and polypropylene and the acid or anhydride is usually introduced by free radical grafting, although copolymerization is used in some instances. There are some specialized products based on low molecular weight polybutadienes reacted with maleic anhydride through the “ene” reaction and which are used in elastomers. In most instances the products can be regarded as one in which the actual coupling agent (e.g., an unsaturated acid) has already been incorporated into the polymer, and interaction with the matrix is by mechanisms such as entanglement or co-crystallization. The polybutadienes are slightly different, in that the starting polymers have relatively low molecular weight, and the grafted products are more like true coupling agents, reacting with the host polymer by sulfur or free radical curing processes.

The acid functional polyolefins are not suited to pre-coating because they are solids and are therefore predominately used by the in situ process. The polybutadiene types can be used by either pre-coating or in situ methods and water dispersible forms are available.

Table 25.5 Overview of dispersant versus coupling agent effects

Property	Dispersant	Coupling Agent
Flow (MFI/MVR)	↑↑	↑↑ or ↓↓
Modulus	=	=
Yield strength	=	↑↑
HDT semi-crystalline polymer	=	↑↑
Impact resistance	↑	↓
Elongation to break	↑	↓↓

↑ Increase in property; ↓ decrease in property; = no appreciable change.

25.7 Conclusions

We have seen that dispersants and coupling agents are powerful tools for tuning composites to give improved processability, and mechanical and aesthetic properties. The choice of either one or the other type of surface modifier will depend upon the type of enhancements sought (Table 25.5).

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26 Functional Fillers for Plastics

Chris DeArmitt
Applied Minerals Inc, 110 Greene St, Suite 1101, New York, NY 10012, USA

26.1 Introduction

Over the last several decades, thermoplastics have flourished, replacing traditional materials such as glass, metal, and wood. Today, they are a ubiquitous and irreplaceable part of modern day life. There are several different reasons why these materials have been so very successful. In some instances, they offer lower materials cost than the material they replace. Sometimes, they offer performance characteristics that cannot be attained using other competing materials. Finally, thermoplastics have facilitated part integration whereby several parts can be injection molded into one piece, thus reducing production time and enabling significant cost reduction through the elimination of assembly work.

As market penetration increased, people started to look for ways to reduce the cost of the plastic materials and for ways to extend the property spectrum, to allow plastics entry into new applications. Fillers were introduced and were readily accepted because they are easy to incorporate into plastics and offer myriad possibilities for product improvement and differentiation. The rather unglamorous term "filler" does not do justice to the essential role these additives play in tuning processability as well as mechanical, thermal, optical, electrical, and other key properties. Therefore, they are referred to as "functional fillers." As we shall see, these unassuming additives are a vital addition to the arsenal of the plastics formulator. Each type of filler lends a unique property set to the host polymer.

Fillers are an extremely diverse group of materials. They can be minerals, metals, ceramics, bio-based (e.g., plant matter), gases, liquids, or even other polymers. Minerals alone account for well over 4000 different distinct species. Any particulate material added to a plastic will behave like a filler. For example, anti-block, pigments, impact modifiers, nucleating agents, antioxidant crystals, and numerous other additives will affect the mechanical and other properties of polymers in the same way that filler particles do. Consequently, it is vital to understand how fillers alter properties even if no filler has been added per se.

Despite the almost limitless array of potential filler types, the numbers that have achieved wide-scale commercial adoption is far more limited (Table 26.1). A multi-billion-euro a year filler market is dominated by fewer than 10 fillers. Elastomers account for approximately 50% of filler usage followed by thermoplastics at 35% and thermosets with 15%.

Table 26.1 Fillers market in terms of volume and value

Filler	Millions of Tons	Billions of Euros
Carbon black	4.5	3.96
Natural $CaCO_3$	2.3	0.17
Precipitated $CaCO_3$	0.2	0.12
Precipitated silica	0.3	0.3
$Al(OH)_3$	0.3	0.17
Talc	0.3	0.14
Kaolin	0.2	0.03
Others	0.8	0.12
Total	8.9	5.01

Courtesy of Rothon Consultants

26.2 The Basics

There are numerous specialized texts devoted to fillers [1–3], polymers [4–6], and composites [7–14].

Before delving into the intricacies of filled polymer systems, it is prudent to begin with the following four fundamentals.

1. Filler concentration
2. Particle size and size distribution of the filler
3. Distribution and dispersion
4. Shape and aspect ratio

Note that the chemistry of the filler is not mentioned because that is secondary to the properties listed. To a large extent, the polymer does not "care" or "sense" what the chemistry of the filler is. The polymer only responds to the filler in terms of the criteria listed above. Consequently, one could add calcium carbonate, talc, mica, or glass, and the effect on properties would be largely the same provided that amount added, size, shape, and dispersion were equivalent.

Conversely, one could add three different grades of mica, each with a different aspect ratio and the effect on properties would be dramatically different even though the mica has the same chemistry in all the three cases.

There are exceptions to this rule, in particular when there is some specific interaction between the filler and the polymer, but for the most part, fillers and polymers are rather inert, so one should concentrate more attention on the four factors listed.

26.2.1 Filler Concentration

Usually, filler is dosed gravimetrically, that is to say the amount of filler added is measured and expressed as a weight percentage. When reporting the influence of filler on properties, it is common to plot property (y-axis) versus weight percentage of filler (x-axis). This practice is misleading, because there is no direct connection between the mass of filler added and properties. Rather, the properties all depend upon the volume percentage of filler in the polymer. Thus, one must plot results as property versus volume percentage of filler in order to gain any understanding.

Most people are astounded to learn that plotting composite density versus weight percentage of filler results in a pronounced curve (Figure 26.1). In contrast, when common properties such as density, modulus and yield strength are plotted versus the volume percentage of filler, straight lines result for commonly used filler levels.

Even when one knows that volume percentage is the appropriate parameter, it is still hard to understand conceptually why that is the case. The following example helps to clarify why it is that volume percentage is paramount. Imagine adding some very low density filler, such as air. Adding 1 wt% of air corresponds to adding 50 vol% of air filler. That means that even though only 1 wt% of filler was added, 50% of the polymer is now gone and replaced by air. It is clear that, with half of the polymer removed and replaced by voids, all the properties such as modulus, yield strength, impact resistance, and thermal conductivity will be markedly different.

26.2.2 Particle Size and Size Distribution

There is no one optimal particle size or size distribution. The ideal values depend upon the application and the properties desired. In general, though it is found that particles with a mean size of 1−10 microns are often well-suited as fillers. A specific example would be calcium carbonate for which a mean particle size of around 2 microns is often used in PP and PVC.

The distribution of sizes is at least as important as the mean size. Very large and very small particles both tend to be detrimental to the properties (Figure 26.2). Small particles result in high viscosity and therefore loss of processability as evidenced by poor mold filling and loss of extruder throughput. Large particles act as flaws. Stress concentrations are high around large particles and they lead to a dramatic reduction in impact resistance (especially unnotched) and elongation to break.

To complicate matters further, the very small particles are difficult to disperse and tend to agglomerate to form large particles which, as just described, are deleterious to some properties. This effect is one of the main reasons why the promise of nanoparticles has not been realized. They are so small as to be difficult or impossible to disperse so the excellent predicted properties are not seen in the real world. In addition, smaller particles are more expensive to produce, thus limiting the applications where they are cost-effective.

Usually, one attempts to correlate property changes with the size of the filler as shown on the manufacturers' datasheet. Often, no clear correlation exists because it is the size of the filler particles in the polymer that counts, not their size when they arrive in the bag. It is therefore important

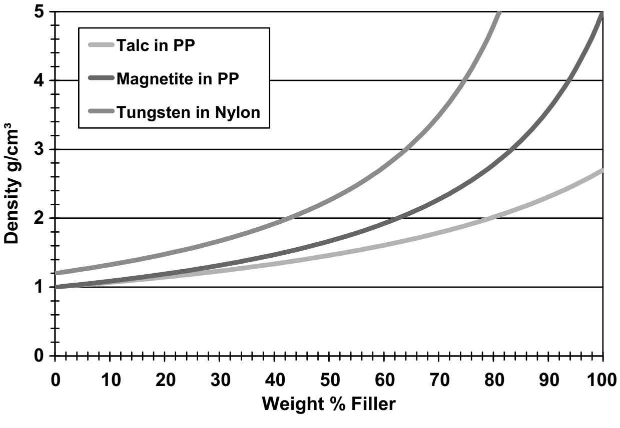

Figure 26.1 Density plotted versus weight percentage of filler.

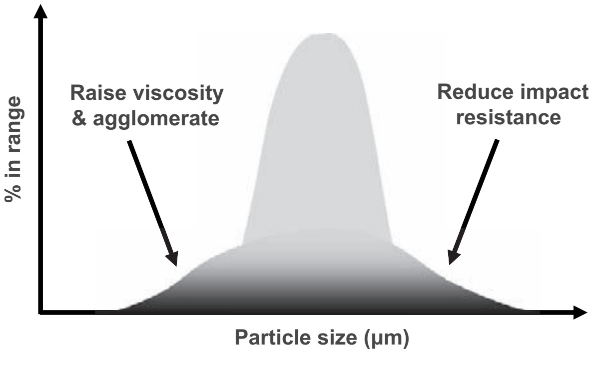

Figure 26.2 Particle size distribution and the effect on properties.

to measure the size of the filler particles in the final compounded material to ensure proper dispersion and wetting. Unfortunately, such measurements are seldom made.

26.2.3 Distribution and Dispersion

In order to obtain consistently good properties from a composite, it is vital to ensure an even concentration of filler particles throughout the material. The evenness can be viewed on different levels. Macroscopic measurements at low magnification are referred to as distribution. Microscopic measurements at higher magnification reveal the level of dispersion. Careful processing, for example extruder set-up and feeding are used to control distribution and dispersion. Use of dispersants is another way to facilitate good dispersion and is especially important when fine or nanoparticles are used. It has been shown that shear forces as found in typical extruders are not especially good for dispersing particles and elongational flow is needed instead. Therefore, new technologies have been introduced so that one can achieve elongational flow with a concomitant improvement in both dispersion and properties.

26.2.4 Particle Shape and Aspect Ratio

Different materials have a tendency to form particles of specific shape depending upon the crystal structure of the material and how it is processed. The shape is often described in terms of an "aspect ratio" which is defined as the ratio of the longest dimension to the smallest. Thus, for spherical and cubic particles the aspect ratio is one or thereabouts. For platy fillers like talc, kaolin, wollastonite, and mica, it is in the range ~5−50. For fibers and nanoclays aspect ratios of ~100−1000 are possible. A vital point to remember is that the datasheet value of aspect ratio is far less important than the aspect ratio of the filler in the final part. Compounding and subsequent steps such as injection molding can dramatically reduce the aspect ratio [9]. One should therefore measure the aspect ratio of the filler in the plastic, for example by ashing to remove the plastic and reveal the filler particles.

There is a perception that a high aspect ratio is always desirable. However, that is not true and may be misleading. Looking at the fillers market worldwide, it becomes clear that it is the low aspect ratio fillers like carbon black, silica, and calcium carbonate that dominate in terms of amount used. A look at the whole market shows that there is a place for every type of filler because each brings its own balance of properties (Table 26.1).

The effect of different fillers, with different particle shapes is outlined in Table 26.2. It is apparent that the each type of filler offers advantages and disadvantages. These pros and cons will be discussed individually.

Table 26.2 The influence of filler shape on properties

Property	Isotropic	Platy	Fibers
Modulus	↑	↑↑	↑↑↑
Yield strength	—	↑	↑↑
HDT amorphous polymer	—	—	—
HDT semi-crystalline polymer	↑	↑↑	↑↑↑
Impact resistance	↑ or ↓	↓	↑ or ↓
Elongation to break	↓	↓↓	↓↓↓
Permeability	↓	↓↓	↓

26.2.5 Mechanical Properties

Tensile testing gives rise to curves like those shown in Figure 26.3. The initial part of the curve is quasi-linear and its gradient is the modulus, i.e., the amount the polymer stretches under a small load. For short deformation times, the sample will return to its original length after the load is removed. Polymers are said to be viscoelastic meaning that they are elastic at short measurement times but for longer measurement periods the polymer slowly flows. A common material that behaves that way is Silly Putty® which, like thermoplastics, flows when you stretch it slowly but is brittle when stretched quickly. Not surprisingly, Silly Putty® is in fact a polymer.

Fillers are elastic and do not flow. Therefore, adding filler to a polymer raises its elastic response at the expense of the tendency to flow. Thus, adding filler tends to make polymers behave more like the curves shown on the left for brittle polymers and less like the curves on the right, which are for ductile polymers. So, one can expect filler addition to give rise to higher modulus, higher yield strength and lower elongation to break. This is exactly what is seen experimentally.

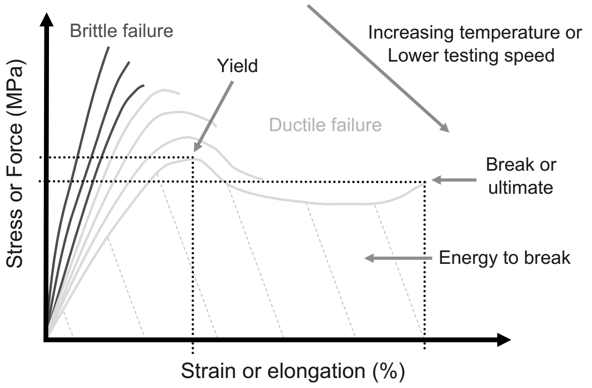

Figure 26.3 Tensile testing of polymers showing key properties.

26.2.6 Modulus

Nearly all common fillers are stiffer than, that is have higher modulus than, typical polymers. Therefore, adding filler tends to increase the tensile and flexural modulus of the polymer.

Isotropic fillers increase the modulus least but they do so equally in all three directions *x*, *y*, and *z*. As an example, adding 40 wt% calcium carbonate to PP homopolymer will increase the modulus from ~1.5 GPa to 3 GPa.

Platy fillers such as talc, clay, and mica increase the polymer modulus more strongly than do isotropic fillers such as calcium carbonate, dolomite, silica, and fly ash. The higher the aspect ratio of the filler is, the greater the increase in modulus.

Fibrous fillers such as glass fiber and carbon fiber have the highest aspect ratio and therefore are the most effective at increasing modulus. Nanoclays, although platy and not fibrous, have such high aspect ratios that they give similar increases in modulus as do glass fibers. However, nanoclays can only be used upto around 10 wt% whereas loadings of 10−60 wt% glass fiber are possible.

Modulus is not affected by the amount of adhesion between the filler and the polymer. This surprises many people who mistakenly believe that they can increase the modulus of a composite by adding a coupling agent to increase adhesion. The reason that modulus is not affected by the level of adhesion is that there is almost always significant adhesion between the filler and polymer to survive a test for modulus. The adhesion is caused by van der Waals interaction from close proximity of the filler and polymer. Additionally, as the polymer melt cools, it shrinks far more than the filler, so after cooling, there is a compressive force as the polymer clamps down around the filler particles. That ensures good contact and thus significant adhesion. Another reason why adhesion does not affect modulus is the way that modulus is measured. It is measured at very low stress and strain. In fact the strain is so low that the adhesion between filler and polymer, although relatively poor, is enough to survive the test intact. The modulus of elastomers is measured at 100% or 400% elongation, conditions which do challenge the adhesion between filler and polymer. Unsurprisingly, adhesion and therefore coupling agents do affect the modulus of elastomers.

26.2.7 Yield Strength

Yield strength is another important property that can be enhanced through the use of fillers. Similar to the trends seen for modulus, the higher the aspect ratio of the filler, the greater its ability to raise yield strength. Isotropic fillers have little or no influence on yield strength. A slight loss of yield strength may be observed when this type of filler is employed. Platy fillers enhance yield strength moderately and high aspect ratio fillers like glass fiber and nanoclay are most efficacious at elevating yield strength.

As mentioned, for the most part, fillers affect yield strength similarly to how they change modulus. However, there is an important difference too. Yield strength is affected by the level of adhesion between the filler and the polymer. Consequently, coupling agents can be successfully used to improve yield strength and also the retention of yield strength when the composite is exposed to water and/or elevated temperature. Furthermore, the surface area of the filler has an influence. High surface area fillers have more contact area to the polymer, thus adhesion and consequently yield strength are increased. The high surface area of nanoclays is one reason why they are effective at increasing yield strength. Even so, they are only about as effective as the equivalent loading of glass fiber. Furthermore, the nanoclay can only be used at low concentrations and are not cost competitive.

The effect of surface area on yield strength is often neglected. Isotropic fillers, which normally cause a slight decrease in yield strength, can actually reinforce if the particles are very fine and therefore of high surface area. Calcium carbonate can reinforce polymers when very fine or when used together with a coupling agent [11]. Once again, though the use of nano calcium carbonate limits the amount that can be added and increases the cost to the point where it makes no commercial sense. As with nanoclays, nano calcium carbonate can only be added in low concentrations below around 10 wt% because it causes a huge increase in viscosity and concomitant loss in productivity, for example the extruder throughput. In contrast, micron sized calcium carbonate is inexpensive and can be used at loadings of up to 80 wt%.

26.2.8 Heat Distortion Temperature and Vicat Temperature

The properties mentioned so far have been room temperature properties. Heat distortion temperature (HDT) and Vicat are both used to give an indication of the maximum temperature which a plastic material can withstand before unacceptably high deformation under load takes place. The effect of fillers is to increase the HDT and Vicat temperature, but because amorphous (non-crystalline) and semi-crystalline polymer respond so differently, they will be covered separately. HDT is often measured under flexural deformation and can be considered as a flexural modulus measured at elevated temperature. Thus, the effectiveness of fillers is as mentioned under the modulus section. Namely, isotropic fillers give least improvement in HDT, more anisotropic fillers such as talc, kaolin, mica, and wollastonite are better and very high aspect ratio fillers like glass fiber and nanoclay are best.

Vicat is measured by pressing a metal indenter into the polymer and measuring the temperature at which the penetration hits a pre-determined level. As Vicat is a surface measurement, one must be aware that anomalies can occur. Injection molded parts are often depleted of filler in the skin due to movement of filler away from the surface during flow. Thus, one may see a low Vicat temperature although the bulk polymer is actually still rigid at that temperature. Also, Vicat temperature is measured in an oil bath. If the oil plasticizes the polymer then unrealistically low Vicat temperatures will be recorded. Although, as shown, use of Vicat has some caveats, it normally follows HDT quite closely.

Unlike the case of modulus, where the adhesion between filler and polymer is irrelevant, good adhesion does help HDT and Vicat. The reason is that heating reduces the compressive forces exerted on the filler by the polymer so adhesion is lessened. Furthermore, weak adhesion between filler and polymer due to van der Waals interactions is not good enough to survive heating.

26.2.9 Amorphous Polymers (e.g., PS, SAN, PMMA, COC, PC)

Adding high aspect ratio filler will bring the HDT and Vicat temperature up to just below the glass transition temperature of the polymer. No matter how much more filler is added, the HDT cannot be further boosted because the polymer phase is soft and deforms. Fillers are therefore not so effective for raising HDT and Vicat in amorphous polymers [4].

26.2.10 Semi-Crystalline Polymers (PE, PP, PA6, PA6,6, PBT, PEEK)

Adding fillers, especially anisotropic fillers like glass fibers, is very effective at boosting HDT and Vicat [4]. Even low loadings, for example 5 wt% and upward of glass fiber or nanoclay can enhance the HDT nearly up to the melting point of the polymer. It is, therefore, common to add fillers to semi-crystalline polymers to extend the limits of their operating temperature. An example is the use of glass filled nylons in under the hood car applications where the high temperatures preclude the use of unfilled nylon. Another example is nylon cooking utensils which retain their rigidity thanks to glass fiber.

26.2.11 Elongation to Break

This property is critical in some instances. For example, wire and cable insulation and jacketing need to have high elongation to break to survive sharp bends during installation. Elongation to break is very sensitive to any flaws in the polymer which includes fillers, voids, or any other inhomogeneities. The larger the particles and the higher the concentration, the lower the elongation to break will be. Some polymers are very ductile, with elongation in the hundreds of percent and they can tolerate high filler concentrations before the elongation becomes unacceptably low. For example, polyolefin cable formulations can contain 60 wt% of ATH or $Mg(OH)_2$ flame retardant and still perform acceptably. High impact polystyrene (HIPS) and ABS, however, suffer a dramatic loss of elongation to break even upon addition of very low levels of fine, well dispersed filler.

Isotropic fillers and fine fillers are least deleterious to elongation to break. Highly anisotropic and coarse fillers are worst. Dispersants help prevent agglomeration, decrease the effective particle size and thereby help maintain good elongation to break. Coupling agents normally reduce elongation to break although exceptions do exist.

26.2.12 Impact Resistance

Impact resistance is often erroneously referred to as impact strength, when, in fact, it is not a strength at all. Strength refers to a force and impact resistance is an energy. It is the energy required to break the sample in two or more pieces. Like elongation to break, impact resistance is sensitive to any particles, voids, or other inhomogeneities that act as flaws. Stresses concentrate around filler particles. The larger the particle and the more sharp the edges, the greater the stress concentration. As impact takes place, the stress concentration exceeds the strength of the polymer and failure occurs in the form of micro-cracks which then rapidly spread and eventually lead to macroscopic failure. For fillers with poor adhesion to the polymer, impact leads to dewetting and formation of a void around the filler particle. In some brittle polymer/poorly bonded filler combinations this void formation actually helps impact resistance, examples are fine, well dispersed, stearic acid coated calcium carbonate in PP homopolymer or in PVC (Figure 26.4).

Normally, addition of filler reduces impact resistance and sometimes dramatically so. Even low levels of well dispersed, stearic acid coated calcium carbonate can lead to drastic reductions in impact resistance of ABS and to a lesser extent in HIPS. ABS and HIPS are impact modified using rubber particles whereby upon impact, the rubber cavitates and helps absorb the impact energy. When filler particles are present, the stresses concentrate around them instead of the rubber particles. Cracks form around the filler and spread before the rubber particles can come into effect. This leads to an interesting interplay between the size of the filler and the size of the rubber impact modifier particles. If the filler is significantly smaller than the rubber, then the stresses concentrate around the rubber, as intended and impact resistance is good. Use of filler of similar or larger size than the impact modifier particles leads to stress concentrations preferentially around the filler, so the effect impact of the modifier is nullified. This interplay between impact modifier and other particulates is not generally known.

Failure by impact can be thought of as two distinct processes. First is crack formation which occurs at the largest flaw, which may be a filler particle, pigment particle, or agglomerate thereof. Unnotched impact resistance measures both the energy to form the crack plus the energy to grow the crack and break the sample. Unnotched impact resistance is often the most relevant because real life parts are usually not

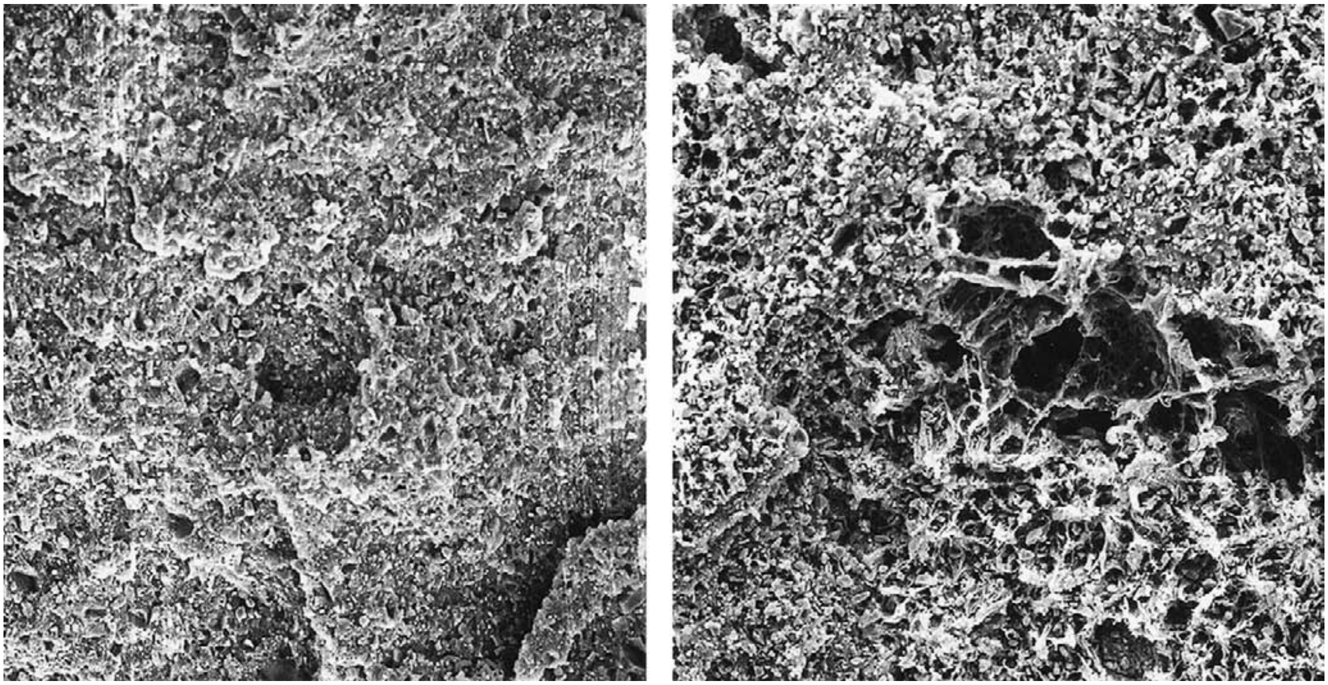

Figure 26.4 Impact fracture surface for 40 wt% of 2 micron d_{50} $CaCO_3$ in PP homopolymer non surface treated (left) and stearic acid coated (right).

notched. Unnotched impact resistance of a material may be one or two orders of magnitude higher than the notched impact resistance for the same material. Because the crack initiates at a flaw, which is often a filler particles or agglomerate, this test method is very sensitive to the filler type, amount, level of dispersion and adhesion between filler and polymer.

Notched impact resistance is performed on a sample with a large flaw introduced on purpose to ensure that the crack initiates from a predefined place, in a controlled manner. By introducing the defined flaw, one obtains experimental results with much lower scatter than those found when performing unnotched tests. This has led to the popularization of the notched test even though, as explained above, real life parts do not usually contain notches, so the results of notched testing while reproducible, are not relevant in most instances.

The ratio of the notched to the unnotched values gives an indication of how sensitive the material is to scratches or sharp features in the part design that may act like notches.

26.2.13 Creep

Creep is flow of the solid polymer over long periods. It is well known that all fillers increase the viscosity of molten polymers [14] and therefore it should be no surprise that they also increase the "viscosity," that is to say the creep resistance, of solid polymers [8,12]. The types of filler that are best at increasing viscosity and reducing creep are those that are highly anisotropic and also those that are well bonded to the polymer. Good bonding may be by virtue of high surface area like nanoparticles, or through intrinsic interaction between the polymer and the filler surface, or lastly, by use of appropriate coupling agents. Effective coupling is especially important to prevent creep at elevated temperatures and when moisture is present as those factors tend to interfere with filler to polymer adhesion.

26.3 Thermal and Electrical Properties

26.3.1 Conductivity

These two properties are covered together, because, they are related from a technical standpoint. The vast majority of polymers are excellent thermal and electrical insulators. Outstanding electrical insulation leads to extensive use in wire and cable insulation as well as numerous other applications. Although a few polymers are intrinsic conductors of electricity, for most polymers, conductivity must be induced through the use of conductive fillers. Similarly, plastics are superior thermal insulators and even more so when foamed. There are applications where plastic with exceptionally high thermal conductivity is called for. One notable example is heatsinks for laptop computers. Plastics allow complex, efficient shapes that fit within the strict confines of a laptop and when appropriate fillers are added. High thermal conductivity and performance rivaling metals is attainable.

Examples of electrically conductive fillers are carbon black, graphite (flake and fiber), and metal (copper, silver, steel, flake, and fiber). Metallized mica or glass beads offer high electrical conductivity but at lower cost than using pure metals.

Typical mineral fillers like calcium carbonate, talc, kaolin, mica, silica, and wollastonite all have thermal conductivities an order of magnitude higher than that of polymers. However, specialty fillers are used to achieve better thermal conductivities. Examples include alumina, beryllium oxide, boron nitride (cubic and hexagonal), graphite, carbon nanotubes, metals, and the best of all, diamond.

For the most part, the properties of composites vary smoothly as more filler is added (on a volume percentage basis). The properties of the composites are more or less a weighted average of the properties of the two constituent parts. Electrical and thermal conductivity are properties that do not follow that pattern. As more filler is added, there is virtually no increase in conductivity until the point at which a continuous pathway of touching particles forms. At that point, known as the percolation threshold, the conductivity increases dramatically and by several orders of magnitude. Further addition of filler leads to a leveling off of conductivity so that the overall curve is s-shaped (Figure 26.5).

Percolation occurs at lower concentrations for smaller filler particles, for fillers that tend to agglomerate and for highly anisotropic fillers. At a given filler concentration, one can achieve higher conductivity with a low conductivity filler that has percolated compared to a high conductivity filler that has not percolated [15]. Whereas one is usually striving for optimal dispersion, in the case of conductivity, dispersion means separation of particles and therefore an absence of percolation.

As conductivity is so dependent upon filler dispersion and also filler orientation, it is very sensitive to processing conditions and in particular flow. In applications where maximum conductivity is required, the sensitivity to processing is not such a problem, one just needs to ensure that the filler concentration is above the percolation threshold with some safety margin. However, in some cases, it is desirable to hit a target intermediate conductivity on the steep part of the s-curve. For example, anti-static and RF shielding require intermediate conductivity levels. It is very challenging to reproducibly hit conductivity values on the steep part of the curve because any variation in filler concentration, orientation, or flow pattern will result in a conductivity that is out of specification by a factor of ten or more.

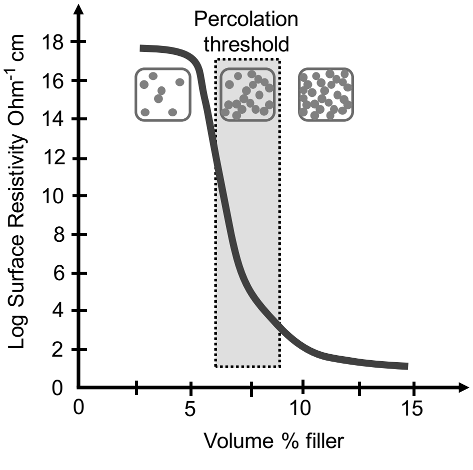

Figure 26.5 Percolation threshold.

26.3.2 Specific Heat Capacity

When processing polymers, the specific heat capacity is important because it is the amount of heat energy required to heat the polymer to melt and make a part. The reverse case is also important, namely the amount of heat that must be removed in order to solidify the part so that it can be removed and room made for the next part to be produced. Heating and cooling translates to energy costs and also productivity. Semi-crystalline polymers require more energy to heat and cool because of the specific heat of crystallization. That is, it takes extra energy to melt the crystals and then extra cooling to recrystallize them.

There is a lot of misunderstanding over the effect of fillers on specific heat capacity. In fact, some of the notable books in the field give erroneous advice in this regard. The confusion comes from a failure to take into account the units of specific heat capacity. The units for mass-specific heat capacity are J $kg^{-1}K^{-1}$ and values for mineral fillers are approximately three times greater than those for polymers. Therefore, it is often stated that minerals reduce the specific heat capacity of polymers thus aiding polymer processing. However, like all other properties, one must consider the property on a volume basis and not a weight or mass basis.

When one accounts for the density difference between polymers and mineral fillers, a factor of approximately 1:3, one arrives at the correct parameter, namely the volume-specific heat capacity with units of J L^{-1} K^{-1} which turns out to be the same for mineral fillers and polymers [8]. In fact, as a rule of thumb, all solid materials have similar volume-specific heat capacity. So, in conclusion, addition of fillers gives no advantage in terms of the energy required to heat and cool, although they do help speed of heating and cooling through their high thermal conductivity.

26.3.3 Coefficient of Thermal Expansion

Polymers have a much higher coefficient of thermal expansion (CTE) than metals or ceramics [12]. This means that when plastic parts are bonded to metals or other materials with dissimilar CTE, stresses build up at the joint leading to warpage or even failure of the joint. The CTE of fillers is approximately 10-fold lower than that of polymers so adding fillers reduces the CTE of polymers. The rule of mixtures approximates the behavior, but for high surface area, or well bonded fillers, the effect can be more pronounced than that predicted by the linear rule of mixtures [12].

26.4 Hardness, Friction, Scratch Resistance, and Wear

26.4.1 Hardness

Most fillers are harder than polymers, so filler addition increases the hardness of polymers. The trends are similar to those for modulus and yield strength, namely that more anisotropic fillers are more effective at increasing hardness. As hardness is a surface measurement, similar to a room temperature Vicat test, the filler will only affect the hardness if it is present at or near the surface. If the filler is depleted at the surface, for example due to flow effects during injection molding, then it may have little or no effect on the measured hardness.

26.4.2 Friction

The coefficient of friction (COF) may be adjusted upward or downward by the use of fillers [16]. Addition of low COF fillers such as graphite, hexagonal boron nitride, PTFE, paraffin wax, or molybdenum disulfide will reduce the COF. Often, only a low amount of low COF filler is needed because they are soft materials that become spread out across the polymer surface during use. In contrast, safety flooring is also made by adding fillers. Large, irregular particles of tungsten carbide are added to the PVC plastisol which hardens to leave the particles protruding upward. This type of surface has a very high COF and is used worldwide, for example in buses, trains, and staircases to prevent slipping. Thus, hard irregularly shaped particles are favored for achieving high COF.

26.4.3 Scratch Resistance

Scratch resistance is an important but difficult subject for many reasons. First, in most cases, people are focused on the physical scratch and the measurement thereof, whereas the consumer usually cares only about the visibility of the scratch. Secondly, it is the various test methods which may, or may not, be appropriate depending upon how the material will be exposed to scratch conditions in use. For the most part, the focus is on passing whatever test the customer specifies, rather than on making better materials. Thirdly, scratching occurs at speeds much higher than those of standard polymer tests. This means that mechanical properties from, for example, tensile tests do not correlate at all with scratch resistance. A material may be an elastomer at low testing speeds, but at the velocity experienced during scratching, it may behave in a brittle manner. This is because polymers have a time dependent response. These factors have held back progress in the field. It should be noted that Evans and Fogel showed an excellent correlation between the scratch resistance of elastomers and the energy to break from tensile tests once the effect of scratch speed had been accounted for using the WLF equation [17].

Fillers can help reduce the dimensions of the scratch by increasing the hardness of the surface leading to less deformation and by increasing the yield strength so that the plastic recovers elastically instead of irreversibly via plastic flow. However, in many cases, fillers increase the visibility of the scratch. An example of particular note is talc filled PP copolymer for car interiors where scratching debonds the talc particles which then lay on the surface scattering light and giving rise to a highly visible white line. Instead of talc, wollastonite is used, as it stays bonded in the polymer leading to less scratch visibility.

The best approach to scratch resistance is to find or create a test that models the real application closely and develop your material using that test.

26.4.4 Wear and Abrasion

Wear is a complex subject because there are many factors at work [16]. In general wear resistance of polymers is improved, and in many cases dramatically so, by the addition of fillers. For example, PTFE has very low COF but very poor wear resistance. Addition of virtually any kind of filler has been shown to improve the wear resistance of PTFE between one and several orders of magnitude.

Wear resistance is best improved through addition of small, well bonded particles, so use of coupling agents can be beneficial. When larger, poorly bonded particles are used instead, they are pulled out of the polymer under testing and act like an abrasive at the interface. So micron sized particles help, nanoparticles are better, and very coarse particles above 50 microns are detrimental [16].

Abrasion resistance is another complex area. One of the reasons for confusion is that the various test methods do not agree well with each other. There is a perception that hard surfaces lead to the best abrasion resistance, however that does not jibe with the facts. In actuality, it is elastomeric surfaces which have excellent abrasion resistance. Look, for example, at rubber car tires and PVC flooring which is always coated with a polyurethane elastomer layer to provide wear resistance. Elastomers deform and spring back undamaged, so scratch and wear resistance is good [17].

26.5 Barrier Properties

26.5.1 Permeability

Permeation through plastics is important for many applications, especially for food packaging where the goal is to prevent oxygen and water vapor from entering and spoiling the comestibles. Polymers provide some degree of barrier when used alone or in multi-layer structures. Addition of fillers can further improve performance. As gases and liquids can neither dissolve in, nor penetrate through, mineral fillers, such fillers impart barrier properties. For isotropic fillers, the effect is rather weak, approximating the linear rule of mixtures relative to the volume percentage of filler added. The best case is for highly anisotropic plates perfectly aligned perpendicularly to the direction of permeation. This arrangement increases the path length for diffusion, thereby slowing progress of the diffusant molecules. For conventional composites, this tortuosity effect is responsible for the barrier properties. In the case of nanocomposites, the tortuosity effect is augmented by the interphase (a layer of constricted polymer around the filler particles as described later).

It should be noted that fillers do not always improve barrier properties. If the filler is not wetted by the polymer, then the polymer-filler interface provides a pathway for easy diffusion and may even help wick liquid into the composite. This may be prevented by ensuring good wetting through careful processing or by using a surface treatment on the filler (see Chapter 25, Dispersants and coupling agents).

Fillers can also be used to intentionally increase permeability of polymers. Breathable films are prevalent in sanitary products as they allow permeation of gases but not liquids (e.g., in disposable diapers). Such films are made by compounding calcium carbonate into polypropylene. The calcium carbonate is surface treated with stearic acid to decrease adhesion between the filler and the polymer. A film of the material is made and then stretched whereupon the filler particles debond from the polymer to leave voids that permit permeation.

26.6 Optical Properties

26.6.1 Transparency/Opacity

Fillers affect the optical properties of plastics in two ways. First, because the filler and the plastic usually have different refractive indices and because the filler particles are often of similar size to the wavelength of visible light, filler addition leads to light scattering which manifests itself as opacity. In order to get high-light scattering and thus very white materials, pigments like titanium dioxide are used. Pigment grade titanium dioxide has a particle size chosen to maximize light scattering and has a very high refractive index, much greater than that of plastics, hence its ability to opacify effectively. Other more common fillers such as calcium carbonate, dolomite, and kaolin also lend opacity but to a much lesser degree because their refractive index is much closer to that of polymers. In rare instances, the refractive index of the polymer and filler are identical and in that case, the filler does not induce scattering so a transparent composite can result. One example is glass-filled PVC. In most cases, fillers have more than one refractive index due to asymmetry in their crystal structure and therefore transparency cannot be achieved because it is impossible to match the single refractive index of the polymer to the two or more refractive indices of the mineral filler.

Another point to note is that even the weak pigmentation arising from fillers limits the color palette achievable. For instance, calcium carbonate filled PP is noticeably white so it is impossible to achieve a true black, or other very dark colors, no matter how much pigment is added. Whitening from the filler also removes the possibility to achieve very vivid colors. It is not just fillers that lead to whitening of the plastic through light scattering. Impact modifiers are also particulates of different refractive index to the polymer. This is why HIPS, ABS, and ASA are white and the colors that can be achieved in those plastics are limited by the underlying whiteness. One can sometimes tune the refractive index of the polymer using miscible polymer blends (rare) or copolymerization to match the refractive index of the filler or impact modifier. This results in transparency and is how transparent ABS, known as MABS is made [17].

Nano-fillers are much smaller than the wavelengths associated with visible light (~350−780 nm) so they do not lead to scattering and can be used to make transparent materials, even when the refractive index of the filler and the plastic do not match. There are some caveats with this approach however. One is that the particles must be very well dispersed because agglomerates will act like larger particles resulting in scattering and concomitant opacity. Another aspect to be aware of is that although nanoparticles (or very large particles) may not scatter visible light, they are still scattering light of other wavelengths so the material may not be transparent to UV or IR light. This may be an advantage or a disadvantage depending upon the application. Lastly, because well dispersed nanoparticles lead to transparent materials, any coloration in the filler will be revealed. This occurs, for example, in the case of nanoclay composites where a yellow hue is often seen.

26.6.2 Color

Fillers may also impart color to the plastic. Even a filler that appears as a pure white powder may give significant color in the plastic. This is because dry filler powder scatters light intensely due to the large difference in refractive index between the filler and air. This intense scattering leads to such strong whitening that it can mask the underlying color of the filler. A quick test is to wet the filler powder with oil, preferably of similar refractive index to the target polymer, whereupon any color will be revealed. This test saves time and money compared to compounding the filler into the plastic to check color. White (colorless) fillers are preferred and carry a price premium compared to more colored grades. When the filler is to be used together with pigments to make a colored material, the consistency of filler color is more important than the degree of whiteness. If the filler were to vary in color, then consistency of color in the final material would be very hard to achieve because the pigment formulation would need to be continuously adjusted to compensate for drift in filler color.

26.6.3 Gloss

Fillers tend to reduce the gloss of plastics; however the extent of the reduction varies widely depending upon the filler and the type of processing. High gloss is a result of light reflecting from a surface unattenuated and without scattering. Hence smooth, homogeneous surfaces lead to high gloss and rough, inhomogeneous surfaces provide low gloss. There are applications for the whole range of possible gloss values to suit the preferences of a given market. Exterior car body parts, for example, mirror housings and bumpers, are normally of high gloss to match the painted metal body panels. In contrast, interior body parts, in particular the dashboard, must be very low gloss to prevent sunlight from reflecting and dazzling the driver.

Fillers can be used to deluster or reduce gloss of a polymer surface. The best effect is seen when using larger particles that help create surface roughness and scatter light at different angles. If a high gloss surface is desired, then smaller particles, preferably surface treated with a dispersant to ensure an absence of agglomeration is a sound approach. The observed gloss is highly dependent upon the angle of measurement. Low-angle measurements are more sensitive to loss of gloss than are high-angle measurements.

The processing route employed also affects gloss to a significant extent. For example, injection molding entails high shear rate which tends to make the filler particles move away from the surface. Thus the final part will often have a skin that is depleted in filler. As there is little or no filler at the surface, gloss can remain high. The same material processed, for example by compression molding, would not display a skin depleted in filler and gloss would be commensurately lower. Water and gas assisted injection molding can lead to low gloss in the area where the gas or water bubble is grown. As the bubble grows, the polymer skin is stretched, bringing filler up from the bulk and deglossing that region while the rest of the part surface retains high gloss.

26.7 Processing

There are many processing methods used to convert polymer pellets into parts or stock shapes to be machined. The main methods include injection molding, extrusion, compression molding, and rotational molding. In order to prepare samples for testing, injection molding dominates and that can lead to measured properties being rather different than those likely to be seen in actual parts. One must be aware of these differences in order to account for them in part design.

When test bars are injection molded, the high injection speed leads to alignment of the polymer chains, and more importantly, orientation of the filler particles. The long direction of platy or fibrous fillers orients itself preferentially along the flow direction, that is to say, the longest dimension of the test bar. This means that properties like modulus and yield strength are maximized and the benefits of anisotropic fillers like talc, kaolin, mica, wollastonite, glass fiber, and nanoclay are shown to best effect. The problem is that this ideal orientation of particles rarely occurs in production parts, so the properties seen on datasheets are not achieved in reality. It also leads to the perception that anisotropic fillers are better than they really are. Even when anisotropic particles are well oriented, this can lead to warping because the part shrinks unevenly. Ironically, one solution is to change the flow pattern in the mold to intentionally disrupt the flow and prevent the filler from orientating.

Another drawback of taking datasheet values from injection molded parts is that tensile testing is only performed in one direction. Very attractive modulus and yield strength values are seen when anisotropic fillers are used, but these values are misleading because the properties in the two perpendicular directions are completely different and, in some respects, inferior [9]. Fibers will reinforce strongly only in one direction, so the modulus and yield strength in the two perpendicular directions will be only equivalent to the case where the same volume percentage of isotropic filler had been added. Platy fillers reinforce strongly in two directions but only weakly in the third. Again the modulus and yield strength in the third direction will be that expected for an isotropic filler. The opposite is seen for other properties like elongation to break. So a fiber filled composite will have high modulus and yield strength, but low elongation to break in the usual tensile test direction. However, the other two directions will show low modulus and yield strength, but high elongation to break, as expected for an isotropic filler.

Other molding techniques such as compression molding and rotational molding do not orientate the particles in any particular direction, so lower modulus and yield strength are found, but these properties are equal in all directions. This leads to parts which show little or no tendency to warp, because the material is isotropic and shrinks equally in all directions.

26.7.1 Weld Lines

Weld line refers to the place where two polymer melt fronts meet and merge (Figure 26.6). This occurs, for example, for larger parts where more than one injection port per part is used. For unfilled polymers, the polymer chains meet and they entangle easily when the melt fronts meet, so good strength is attained at the weld line. This is not the case when any type of filler or impact modifier particle is present.

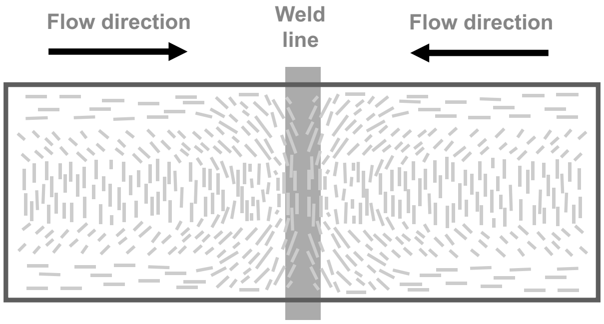

Figure 26.6 Orientation of filler particles within injection molded test bars.

Particles prevent good weld lines strength leading to a weak spot in the part where it will tend to fail under load. This is because fillers hinder optimal entanglement formation and because filler distribution at the weld line is uneven with areas of depleted and enriched filler. The results can be dramatic, in particular for anisotropic fillers with weld line elongation to break and yield strength far lower than for the rest of the part. Isotropic fillers are also deleterious to weld line strength but to a much lesser degree.

26.8 Extra Phase Effects

For the most part, when fillers are added to polymers, the polymer phase remains unchanged. That assumption is made in many of the equations used to predict composite properties. However, there are exceptions that occur and when they do, the properties of the final material deviate from the expected. When the properties found experimentally do not match theory, then look at these factors as the likely culprit.

26.8.1 Nucleation

Fillers and pigment can, in some cases, nucleate crystallization of semi-crystalline polymers including PE, PP, PA6, PA6,6, PBT, and PEEK. The effect is normally measured by differential scanning calorimetry (DSC) which detects crystallization. Nucleation results in crystals starting to form at higher temperature as the melt cools and this can be a great advantage because it can help lower injection molding cycle times, improving productivity, and saving money. Fine talc is often used to nucleate PP and nylon. Nucleating agents can have other effects too. Sometimes they lead to a different crystal phase (with different properties) and sometimes they lead to an increase in the overall level of crystallinity which will increase density, modulus, and yield strength. Nucleation also tends to give more and smaller crystallites so impact resistance may be improved and so may clarity. It should be noted that there is no satisfactory theory to predict which substances will induce nucleation so it must be determined by experiment [18].

26.8.2 Transcrystallinity

Transcrystallinity is an extreme case of nucleation whereby the polymer melt is cooled against a surface that nucleates so strongly that the spherulites immediately collide and a layer of crystals perpendicular to the nucleating surface is observed [11,19]. The effect can be seen for some types of fibrous fillers (e.g., glass, carbon, or Kevlar®) in certain polymers. A sheath of transcrystalline material forms around the fiber. Because the volume of the sheath can be greater than that of the fiber itself and its properties very different to those of the bulk polymer, the properties of the composite can be substantially altered [11].

26.8.3 Interphase

The interphase is a layer of constricted or immobilized polymer that forms on the surface of the filler particles. The influence of the interphase can be ignored for micron sized particles because their surface area is too low to cause significant amounts of interphase to form. However, nanoparticles have high surface area so that the interphase, typically 1−50 nm in thickness [10] can make up a significant volume percentage of the total composite. So, in the case of nanoparticles, the interphase can influence composite properties. In fact, many of the notable attributes of nanocomposites such as high modulus and yield strength together with low permeability are due, in part, to the contribution of the interphase.

Let us take as an example, a 5 micron particle surrounded by a 10 nm thick interphase. Calculation shows that the volume of the interphase is only approximately 1% of the particles volume. The influence of such a small amount of interphase can be neglected. However, if we take 100 nm particle, also surrounded by a 10 nm thick interphase, we find that the interphase volume is 70% of the particle volume. That is, the particle acts like it is 70% larger than it really is, so the viscosity is raised and the mechanical properties of the composites are altered because the interphase accounts for a significant volume percentage of the total material.

26.8.4 Voids/Foams

Voids may be caused by low-molecular-weight additives volatilizing during extrusion or by poor wetting of filler by the polymer melt. Such voids act as flaws where stresses concentrate, so impact resistance and elongation to break can suffer. Intentional introduction of voids, that is to say foaming, can be used to reduce weight and materials cost. It is achieved using foaming agents and the addition of filler helps nucleate formation of the bubbles leading to a fine cell structure and improved retention of mechanical properties. In particular, flexural modulus is retained to a large extent if the interior of the part is foamed, leaving a skin of unfoamed material.

26.9 Popular Fillers (Table 26.3)

A wide range of filler types enjoy commercial success providing mechanical and other benefits in a variety of polymers is shown in Table 26.3.

Table 26.3 Popular fillers and their properties

Filler	Shape	Density	Mohs Hardness	Uses
Calcite $CaCO_3$	Blocky	2.71	3.0	Mechanicals PP,PE
Talc $Mg_3(Si_4O_{10})(OH)_2$	Platy	2.7–2.8	1.0	Mechanicals PP,PE,nylons
Mica $KM(AlSi_3O_{10})(OH)_2$	Platy	2.7–2.9	2.0–2.5	Mechanicals PP,nylons
Wollastonite $CaSiO_3$	Acicular	2.9	4.5	Mechanicals PP
Kaolin Al_2O_3 $2SiO_2$ $2H_2O$	Platy		2.5–3.0	Mechanicals PE,elastomers
Dolomite $CaCO_3.MgCO_3$	Blocky	2.85	3.5	Mechanicals PP,PE
Glass fiber SiO_2	Fibrous	2.55	7	Mechanicals PP,nylons,PBT
Carbon black	Variable	2.26	2.0–2.9	Processing elastomers
Barites $BaSO_4$	Blocky	4.5	3.0–3.5	Sound
Magnetite Fe_3O_4	Blocky	5.1	5.5–6.5	Sound PP, nylons
Graphite	Platy	2.2	1–2	Conductivity lubrication
ATH $Al(OH)_3$	Platy	2.4	2.5–3.0	Flame retardant Elastomers, PE
Magnesium hydroxide $Mg(OH)_2$	Platy	2.4	2.5	Flame retardant PE,EVA,PP

26.10 Specialty Fillers

26.10.1 Flame Retardant Fillers

The main two primary flame retardant fillers are aluminum hydroxide (also known as aluminum trihydrate (ATH) and magnesium hydroxide [7,8]. Both operate by decomposing upon heating to give off water which is an endothermic process, taking heat from the fire. In addition, the decomposition liberates water vapor which also helps douse the fire. Both must be used at levels of around 60 wt% in order to be effective. At such high loadings, viscosity is high and mechanical properties, specifically, elongation to break and impact resistance, drop precipitously. ATH is the preferred alternative as it is the least expensive of the two. Magnesium hydroxide is employed in cases where ATH decomposes within the temperature range for processing on the polymer. So, for instance ATH is not used in PP, magnesium hydroxide is used instead. Precipitated grades are common because the particle size and morphology can be tuned through the precipitation process. Brucite, a natural form of magnesium hydroxide is less expensive but is more difficult to use because of a non-ideal particle morphology and transition metal impurities. As high filler loadings are needed, dispersants are often used to help reduce viscosity and agglomeration thereby boosting processability, throughput and mechanical properties.

Nanoclay is used as a secondary flame retardant/synergist, that is in combination with ATH or magnesium hydroxide. The clay promotes char formation and helps keep the char layer intact to help prevent oxygen from reaching the underlying material. The nanoclay enables reduction in the amount of ATH or magnesium hydroxide needed to attain a given flame retardancy rating. Other nano-fillers such as hydrotalcite are also attracting attention as viable flame retardant synergists. Use of filler type flame retardants is on the rise, partly because of legislation against the once popular halogenated flame retardants.

26.10.2 Natural and Renewable Fillers

For several decades, natural fibers have been proposed as fillers for thermoplastics [9]. They provide reasonable mechanical properties and have low density compared to mineral fillers. Fibers include sisal, jute, coir, flax, and wood. Chemically they are composed of lignin and cellulose where the lignin is rather unstable toward heating and begins to decompose near 200 °C in air as determined by loss in weight via thermogravimetric analysis (TGA). Moreover, the fiber may lose its strength at 160 °C [9]. This instability limits the use of natural fibers. Other problems include high and variable water content plus the inconsistency associated with fibers from plants, which change depending upon the weather and season.

If the use of such fibers had been compelling, then they would have enjoyed commercial adoption decades ago. Instead, the present interest in them is due to a perceived environmental advantage. In fact, it can be argued that using natural and renewable fibers may actually be harmful from an environmental perspective. Whereas unfilled or mineral filled thermoplastics can be recycled numerous times without degradation of properties, natural fiber filled plastics cannot be easily recycled due to thermal degradation of the fibers during extrusion. Only life cycle analysis (LCA) can conclusively determine whether such fillers are actually good or bad for the environment.

One area where natural fillers have attained commercial success is in plastic lumber for decking which is particularly popular in the USA. By filling PE or PP with wood flour one can achieve the look of wood but without the need to maintain the product, for example by varnishing. Often such plastic lumber is optimized through use of recycled polymer and via foaming to reduce materials cost.

26.10.3 Zeolites

Zeolites, also known as molecular sieves, are inorganic substances with a nanoporous structure [13] such that molecules preferentially adsorb within the pores depending on their size and polarity. A well-known example is the use of 4 Å molecular sieves to removes traces of water from solvents. More recently, they have been used commercially to adsorb bad odors or other unwanted volatile substances from plastic films and articles.

26.10.4 Dense Fillers

Dense fillers are used when heft, weight, or sound/vibration damping is required. Heft is the perception of quality associated with products that feel substantial in the hand. Dense formulations are used in washing machine counterweights to reduce vibration. Formulations include iron slag in polypropylene or epoxy. Dense fillers include barium sulfate (density 4.5 g cm^{-3}), magnetite (density 5.0 g cm^{-3}), micaceous iron oxide (density 5.0 g cm^{-3}) and metals (density 8−20 g cm^{-3}).

26.10.5 Expandable Microspheres

These specialty fillers are comprised of a polymeric shell surrounding a core of lower molecular weight substance [7], typically a member of the alkane family. Upon heating to a temperature near the boiling point of the encapsulated substance, the particles expand dramatically due to the high vapor pressure as the boiling point is approached. By expanding such beads within a polymeric matrix, a syntactic foam is created.

26.10.6 Nano-fillers

Nanocomposites and nano-fillers are covered in a separate chapter. The fundamentals as described here for traditional microcomposites all apply but allowance has to be made for the smaller particle size, added surface area and, in the case of nanoclays, the high aspect ratio.

26.10.7 Molecular Fillers

Polyhedral oligomeric silsesquioxanes are a family of molecules that consist of a silica-like core surrounded by a shell of organic groups. Conceptually, they can be considered to be the smallest possible particle of silica, which has been surface treated either with dispersant or coupling agent depending upon the type. The term “molicle” has been coined to describe these hybrid materials [7,20] which combine the solubility of organic molecules and the rigidity of inorganic particles.

Other molecular fillers include the fullerenes such as C_{60}, C_{70} and their derivatives. Like polyhedral oligomeric silsesquioxanes however, their commercial application is severely limited by high cost.

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27 Flame Retardants

Ann Innes and Jim Innes
Flame Retardants Associates, Inc., PO Box 597, Concrete, WA 98237, USA

> *…He walked slowly following the hoses toward the rig, inhaling with every labored breath the all too familiar smells of fiery destruction. His lungs ached from the heavy exertion. His throat felt swollen and burned with each dry swallow. He removed his helmet to wipe his face and head soaked with sooty sweat as he turned to look back toward the still smoldering, smoking remains. They had been home for a small family – young father with two little children. They didn't make it out. He fought back the feeling of guilt rising over the small gratitude he felt that night. One of his buddies upon entering first had been the one this night to find the bodies. As they stood momentarily together trying to regain themselves, his buddy remarked "if they only had about 15 more seconds, they might have made it…" How many times had they both been plagued by this same frustrating and futile thought? In this battle's aftermath, with time, his thoughts, moving in slow motion and chills assaulting his spine, he simply shrugged in response…*

27.1 Introduction—What Is a Flame Retardant (FR)?

Fire scenarios just like this one have sadly been happening for centuries. Fire is one of the most destructive forces on the planet. Hard to fight and often impossible to control, the loss of human life, injury, and damage to property are simply staggering, not quantifiable—although effort is made to assess monetary value. Statistics are gathered and reported in our modern societies by various agencies concerned with the issue and depended upon to provide justification for monies spent by numerous industries including forest safety, state and municipal building regulators, insurance companies, fire safety, federal disaster management, and chemical companies, to name a few. Many would argue, justifiably so, that we have made much progress in our ability to limit the hazards and threats from fire. Many of the industries just cited have been working for a long time to develop products, methods, processes all aimed at this single goal. Sprinkler systems, non-water fire extinction systems, smoke and fire detection devices, and thermal protection systems are valuable results of all of this dedication and hard work.

The subject to be presented herein, flame retardants, belongs to the chemical industry—or more precisely, to the polymer industry. The authors of this chapter will attempt to provide the reader with a broad review of a very complicated subject. Simply defined, flame retardants are chemical compounds added to or otherwise incorporated into plastic compounds to provide varying degrees of flammability protection. More technical details on this and related topics will be provided in the next sections. The focus will be on flame retardants for thermoplastic and thermoset polymers as used in a wide variety of applications to meet an equally wide array of flammability standards. First, it might be helpful to review some of the statistics recently reported, which try to assess the damage to humans and to property caused by structural and other types of fires.

27.2 Fire Statistics—Why Do We Use Flame Retardants?

Fire statistics are reported by a multitude of organizations in countries across the globe. Some of these include the National Fire Protection Association (NFPA) in the USA, the Center of Fire Statistics (CTIF) in Europe, China Fire Protection Association (CFPA) in China, and the Statistics Bureau of the Government in Japan. There are many, many more. Some charge fees to access their reports online, some require only registration, and some provide information free to the site visitor.

Dr Ing. Peter Wagner reports in 2006 that by 2000 there were about 6.3 billion humans on the planet with a collective experience of some 7–8 million annual fires accompanied by 70–80 thousand fire fatalities and a far great number of fire injuries. These fire incidents occurred in dwellings, other buildings, vehicles and other transportation systems, and forests and wildlands [1].

So large is the world's fire databank that sufficient volumes could not possibly be written to incorporate all the incident details. Indeed, just the locations of some fire incidents are enough to fill a multipage listing. See Table 27.1

Table 27.1 Selected worldwide fire incidents from recent history [2]

Year	Geographic Location	Fire Description/Incident	Fatalities
1927	Montreal, Quebec	Movie theater	78
1933	English Channel	Passenger liner	18
1946	Berlin, Germany	Restaurant fire	89
1947	Christchurch, New Zealand	Department store	41
1959	Massif des Aures, Algeria	Forest fire	48
1960	Pusan, Korea	Chemical plant	68
1963	Kobe, Japan	Rubber shoe factory	14
1970	Anchorage, Alaska	DC-8 post-crash	47
1974	Sao Paulo, Brazil	Office	179
1979	Saudi Arabia	B-707 in-flight	156
1986	Ukraine, USSR	Chernobyl nuclear power plant	31
1991	New Delhi, India	Shantytown hut fires	15
1993	Nakhon Pathom Province, Thailand	Toy factory	188
2000	Buenos Aires, Argentina	Nightclub	188

for a small sampling of worldwide fire incidents in recent history. The interested reader is encouraged to visit the NFPA Web site at www.nfpa.org to review the “Key Dates in Fire History” listing. A few of the entries there also reflect milestone accomplishments in fire safety such as the testing of a fire engine in 1853 and the issue of a fire extinguisher in 1863.

In the USA in 2007, NFPA reports that there were 1,557,500 fires with 3,430 civilian fire deaths, 17,675 civilian fire injuries and $14.6 billion in property damage. The most deadly fires were structural fires followed by vehicle fires. NFPA also reports major causes of home structure fires, which include cooking equipment, heating equipment, electrical distribution and lighting equipment, intentional, candle, smoking materials, and playing with heat sources. Of these, during 2003–2006, the deadliest causes were smoking materials, closely followed by heating equipment. In the US, one home structure fire was reported every 79 seconds, and one civilian fire death occurred about every 2½ hours [3].

In the UK in 2006, the total number of fires requiring fire and rescue service was reported in May 2008 by Communities and Local Government at 426,200 with 491 fire-related deaths. Dwelling fires accounted for 55,800 (or about 25%) of the total [4]. And in 2009, there were many civilian deaths in house fires in Japan, Spain, Canada, Russia, and the US [5]. For more information on fire statistics, the reader is encouraged to utilize web search engines such as Google. Further details on fire statistics are beyond the scope of this review. Suffice it here to conclude that there is plenty of justification for materials, processes, and tools aimed squarely at improving fire safety.

27.3 FR Applications—Where Are Flame Retardants Used?

The authors estimate the current global FR additives market at about 2 million metric tons and US $4.5 billion. Annual growth rates vary from 2–3% for the USA and EU to twice that rate or more for China and other Asian countries. There are a variety of applications where FR additives and FR technology are used. It is a good bet that most humans in modern societies are unaware of the abundant presence of this technology (and its potential benefits) in their daily lives. Electrical and electronic (E & E) applications include injection-molded wire nuts which can be found behind the electrical sockets on the walls in most dwellings and offices. Other E & E applications include components and parts used in ovens, microwaves, dishwashers, refrigerators, and dryers. Also included in the E & E market segment are components and parts in office/home automation equipment such as computer monitors, keyboards, telephones, and fax machines. Generally, whenever a plastic product or plastic product component is near or in contact with an electrical current (or electricity carrying element) a flammability standard is usually required to be met by that product or component. Compliance with the flammability performance established by the standard is used to assess fire safety of the product or component. Such standards and test methods are numerous, and some will be briefly reviewed in the next section.

Another sub-segment of the E & E market comprises wire and cable applications. Complicated and largely subjected to an entirely different body of flammability standards and testing methods (when compared to molded parts), this segment is sometimes considered as a major FR market segment all of its own.

A second major application market for FR products and technology is the building/construction market. Examples here include roofing materials, decking, structural products, and carpet backing. Other products include blown film and extruded shapes for window applications.

A third major FR application market is the transportation segment. Included here are components for under-the-hood and passenger compartments of automobiles, air ducts and seating for mass transit vehicles, floor coverings and furniture in marine vessels, and seating, toilet components, and waste containers in airliners.

A fourth major FR application market includes furnishings (such as plastic stacking chairs), FR thermoset laminates for countertops, walls, and floors in public institutions (schools, stadiums, civic auditoriums, etc.)

A fifth and final FR application market includes FR fibers and textiles. Examples here include items such as draperies, carpets, heavy duty apparel, and automotive interior fabrics [6].

Clearly, there are many, many plastic products and components incorporating FR technology. Not long ago in the US, there were well over half a dozen major injection molders supplying those plastic wire nuts (wire connectors) mentioned earlier. Just one of those suppliers produced upward of a dozen different wire nut sizes in different shapes and types with each of those in multiple colors. With not so careful consideration, it becomes easy to imagine then how quickly the number of FR products and components multiplies to produce an inestimable quantity. Most people would indeed be surprised at the prevalence of these items in their homes, schools, workplaces, and vehicles. Unfortunately, most also have no comprehension of the dangers posed by fire and how this very important FR technology can and does provide protection for humans and for their property.

27.4 Flammability Standards and Test Methods—How Is FR Effectiveness Measured?

Those lacking familiarity with the FR industry may find it surprising to learn that there are so many FR products virtually all around them. But this fact may pale in comparison to the sheer challenge involved in mastering the vast subject of FR standards and test methods. A full review is simply not possible here, but a few of the key standards and test methods in use today will be briefly reviewed along with some of the governing bodies issuing these FR requirements.

27.5 UL94 (Issued by Underwriters Laboratories) [7]

This relatively simple vertical flammability test has been in use for decades. It uses a small methane Bunsen burner with a specified flame applied in a particular way to injection-molded test bars of a specified size, shape, and thickness. The seconds of flame application are dictated by the standard, and the flame application to the specimen bars is done twice on 5 test specimens. The amount of burn time in seconds determines the ultimate classification of the material. Ultimately, the material tested is designated as UL94 V0, V1, or V2 at the tested thickness. Other test parameters important in this test include the test specimen's after-flame time in seconds, the total of the after-flame burn times, after-glow time, and the ignition by flaming drips of the cotton placed beneath the test specimen during the test procedure. This is only one of the testing methods incorporated in this standard. For example, an additional classification (harder to obtain as it requires even more flammability protection) is a UL94 5V designation. Additional but different flammability testing is performed on a dissimilar test specimen in addition to also requiring the previous testing of the five bars as just described.

27.6 Limiting Oxygen Index or LOI (ASTM D2863) [8]

Another workhorse in the FR testing business, this method measures the minimum oxygen needed to sustain combustion in an oxygen/nitrogen environment. The test result is expressed as a percentage and typically compared to the amount of oxygen in the Earth's atmosphere which is 21%. A value above 21% is considered to be an indication of a degree of flammability protection, presumably the higher the percentage, the higher the degree of protection. For example, a value above 30% would be interpreted as good or very good fire resistance. Such a value might be thought to also indicate good performance in the UL94 test (like V2 or V0) or in another FR test. However, drawing exact correlations between different FR test methods is generally not encouraged because such conclusions are frequently incorrect or inaccurate.

27.7 Steiner Tunnel (ASTM E84) [9]

A larger scale test, also commonly used in the FR industry primarily for building/construction market applications, is the Steiner Tunnel test or ASTM E84. A large (25 ft long and 2 ft wide) test specimen is installed on the ceiling of a long tunnel chamber and exposed to a specified fire at one end. The result obtained from this test is a flame spread index which indicates the flammability in relation to a calibration standard material (red oak).

27.8 Vertical Tray Cable Test (IEEE 383) [10]

This test for wire and cable applications is but one of many, many cable flammability test methods. This method, established by the Institute of Electrical and Electronics Engineers, measures the maximum length of cable burned after exposure to a 20 kW propane burner. The specimen cable is tested in a 10-ft vertical tray assembly.

There are many other wire and cable flammability standards including vertical wire, other vertical tray, riser cable, and plenum cable tests. In addition to these, another common type of flammability test is of the radiant panel variety where typically an inclined specimen is exposed to a specified radiant heat source. Rate of flame spread is used to determine a flame index test result. One example of this type of test is ASTM 162, Standard Test Method for Surface Flammability of Materials Using a Radiant Heat Source [11].

27.9 Smoke Measurement—What Is Smoke and How Is It Measured?

Closely related to flammability but yet with an entirely different set of testing methods is the field of smoke measurement. This body of test methods is aimed at measuring smoke parameters like density and composition. Smoke contains water, carbon, soot, ash, and other products of combustion. Development of test standards for its measurement is extraordinarily complicated due to the number of processes and variables involved in the production of smoke. Some of these include the measurement of smoke components just mentioned as well as the test material's ability to generate smoke, specifics of the fire situation such as propagation rate, and maximum temperatures. The measurements must somehow translate to a perceived amount of smokiness. One such test method is the ASTM E662 Standard Test Method for Specific Optical Density of Smoke Generated by Solid Materials. This test actually measures optical density of smoke in a test chamber using parameters including the volume of the chamber, the light path length through the smoke, and the light transmittance measured by a photo-sensitive instrument [12].

Another well-known smoke test is the cone calorimeter test. This method is standardized by ASTM 1354 and is also under ISO standard 5660 [13].

Many standards in the FR industry carry multiple test standard identifications. This situation sometimes causes confusion for formulators and users trying to comply with their requirements. For this reason, it is always mandatory and critical to first define for certain what flammability and/or smoke standards must be met by the formulation and its intended application or end-use.

27.10 FR Standards Issuing Organizations—Where Do All These Tests Come From?

Table 27.2 provides an incomplete listing of some of the governing bodies which issue flammability and smoke test standards. The interested reader and the FR formulator are encouraged to go directly to these organizations via the internet to obtain detailed and up-to-date information on the various test methods. Most of these bodies continually review and issue updates on these standards. It is especially critical to become very familiar with the most recent version of any applicable standard before beginning to assemble an FR formulation of any type for any end-use component or product.

In the European Union (EU), for some time now, an effort to harmonize test standards among various European countries has been underway. For this reason, only the CEN is listed in Table 27.2. However, most European countries had previously developed their own set of flammability standards. Many of these begin with FR-industry-recognized codes such as BS for British Standard, DIN for Germany, IBN for Belgium, etc. Each country has its own set of standards and they are numerous in most cases.

Table 27.2 FR test standards—selected major issuing organizations [14,15]

Acronym	Organization
ASTM	American Society for Testing and Materials
NFPA	National Fire Protection Association
UL	Underwriters Laboratories
CEN	European Committee for Standardization [16]
ISO	International Organization for Standardization [17]
IEC	International Electrotechnical Commission [18]
NBC	National Building Code of Canada [19]
ANSI	American National Standards Institute [20]
JISC	Japanese Industrial Standards Committee [21]
KATS	Korean Agency for Technology and Standards [22]
ICC	International Code Council [23]
FM	Factory Mutual Research Corporation [24]

27.11 Market Drivers—What Else Should Be Known Before Formulating an FR Product?

For the last three or four decades there has been a raging debate regarding the hazards and threats to human health and the environment associated with the use of certain types of flame retardant materials. These particular FR products belong to the class of FR technology called halogen. (Halogen refers to the group of chemical elements which includes bromine, chlorine, fluorine, and iodine. The different classes of flame retardants will be reviewed in detail in the next sections.) But prior to selection of FR materials any formulator should be informed enough to ask, understand, and answer questions stemming from this ongoing debate. Many would conclude after reviewing all the information on this debate that non-halogen FR technology is better than halogen FR technology. However, this is not always the case. First, there are many distinct FR products in each of three major FR technology groups. Only a few products in one of those groups are the subject of regulatory action limiting their usage. Second, the choice of FR additive or FR technology is largely determined by the base resin(s), other formulation additives, the physical properties required by the end-use product or component part, and the flammability standard(s) required to be met for the end-use application.

Nonetheless, the trend toward development and use of non-halogen FR technology has been and will continue to be the most important market driver in the FR industry. Therefore, the formulator must always define at the start whether or not the application and/or the customer can use halogen FR technology or must use non-halogen FR technology.

27.12 What is Wrong with Halogen FRs?

The short answer is "nothing!" Indeed many of the most cost-efficient and most performance-effective FRs are based on halogen technology. However, after many, many investigations by environmental groups and counter-investigations by industrial groups, certain halogen compounds have been identified (rightly or wrongly) as problematic. These have been voluntarily or through regulatory action selected for disuse by the industry. The specific FRs recently under scrutiny by regulators across the globe are of the polybrominated diphenyl ether (PBDE) type. A few years ago, the EU RoHSD (Restriction of Hazardous Substances Directive) specifically banned three FR PBDE compounds including polybrominated biphenyl (PBB), pentabromodiphenyl ether (pentaBDE) and octabromodiphenyl ether (octaBDE) [25]. Marketing and use of these compounds is outlawed by the RoHSD.

Certain states within the US as well as other countries are following suit. For example, the state of Washington announced a ban on the "use of toxic flame retardants in TVs, computers, and other household products by 2011" [26]. The National Oceanic and Atmospheric Administration (NOAA) issued a report dated April 1, 2009, which confirmed that "evidence of toxic chemicals used as flame retardants has been found in all US coastal waters, including throughout Puget Sound [WA]"[27]. California has a "Green Chemistry Initiative" and Canada has its "Chemical Substances Plan." [28]

In addition to regulation limitations, many producers are voluntarily discontinuing the use of other PBDE-type FRs not yet banned. The most important of these, Deca (decabromodiphenyl ether) is arguably the most performance-effective FR additive and has been widely used in a variety of resin systems and applications for many decades. Producers of this compound have developed a substitute offering for users so interested. Such new compounds as well as many non-halogen FR compounds have been the focus of much research and development effort within the FR industry during the past decades, and this work will continue into the future.

27.13 Flame Retardants—What Compounds Are Used?

To this point, we have briefly reviewed the reason for flame retardants, where they are used, how they are measured for performance, and what types of regulations direct their usage. These topics are frequently dismissed by novice formulators. In fact, full knowledge of all of these topics is equally as important as selecting the right FR material for the job at hand.

We now turn to a discussion of flame retardant technology starting first with what the authors call "FR101," a sort of introductory discourse on FR technology, how it works, which types work in which resin systems, etc. Following this, in-depth product details for each of the major FR technologies will be reviewed.

27.14 FR 101—What Are the Major FR Technologies and How Do They Work?

There are three elements required for a fire, and they are fuel, oxygen, and energy or heat. These three elements comprise the classical "fire triangle" (Figure 27.1). This simplified representation of the combustion process has been used throughout the FR industry literature for many years. It may help to envision a burning candle. When one asks why the candle continues to burn once lit, the answer can be found in the fire triangle. Wax, the material of which the candle is made, is the fuel. The wax, which is melted by the flame heat, migrates up the wick and is burned or pyrolized at high

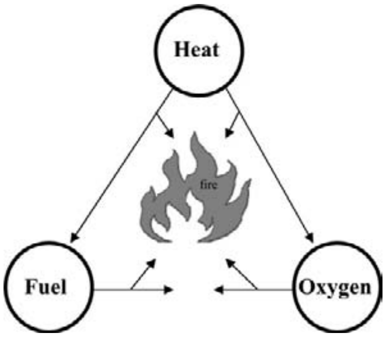


Figure 27.1 The classical fire triangle.

temperatures. The gases which result continue to undergo chemical reactions in the flame, components of which eventually interact at even higher temperatures with oxygen at the outer edge of the flame. As long as the fuel (candle wax) remains and the air (oxygen) is present at the candle flame, burning will continue.

So the three elements of the triangle are actually the critical determining parameters for fire. Fuel is contributed to any fire by the article or articles being burned. Important factors for fuel in the real world would include aspects such as types of furniture and position in the room, other furniture characteristics such as size, shape, density, surface properties, and other physical or chemical properties including heat of combustion, thermal conductivity, ignition temperatures, etc. Oxygen is a required element for combustion. If one pinches the burning candle wick with fingers or uses a candle snuffer, the oxygen is removed from the candle burning scenario and the flame goes out. Energy or heat is generated during the chemical reactions occurring in the flame and at the flame−oxygen interface and by interaction with the fuel continues the burning process. Important factors include the proximity to the fuel and the chemical components generated from the combustion and decomposition of the fuel [29]. Combustion or burning continues as long as the three triangle elements are present in sufficient quantity. If any one of these elements is removed or interfered with, the combustion process is disrupted. This removal or interference is the practical objective of flame retardants. Researchers in the FR industry have over several decades developed a large portfolio of FR products which in essence attack one or more of the three triangle elements.

27.15 The Three Major FR Technologies

There are many FR products under development and in commercial use today. Most of the older commercial FR products can be classified into three major FR technologies. The first of these technologies is also the oldest and could be described as the "workhorse" FR technology. Halogenated FR technology includes a large number of products each of which typically contains bromine, chlorine, or sometimes both. Specific product examples include Decabromodiphenyl oxide (DECA), Tetrabromobisphenol A (TBBA), and Hexabromocyclododecane (HBCD). These and other products will be presented in more detail in the following sections. The action of halogen flame retardants during combustion is complicated. They are known to act mostly in the gaseous or vapor phase. During the combustion process, a persistent supply of chemical free radicals (elements such as hydrogen and/or carbon−hydrogen with free electrons [30]) is generated. The flame retardant decomposes during the combustion process to generate halogen acid gas. It is this gas which interacts with the chemical radicals, essentially "trapping" them and thereby interrupting the combustion process. This mechanism is sometimes referred to as radical trapping and corresponds to the disruption of energy (or heat) on the fire triangle. This is a simple explanation of a complex reaction. Additional details including alternative explanations are available in the literature [31].

Halogen FR products are almost always used in conjunction with other products called synergists. A synergist is defined as a product which when used in combination with a FR product boosts the FR performance to a level that is greater than that achieved if the respective FR performance of the two products were simply added together. Synergists are used in specific ratios with the FR product to maximize the FR performance. The most well-known and widely used halogen FR synergist is antimony trioxide. There are other synergists also used, and these will be presented in a section to follow. Synergists are thought to boost flammability of the FR system by ultimately generating antimony trihalide, which also acts as a radical trap. Again, this is a simple explanation of what actually is a much more complex series of actions, all of which interfere with the combustion process [32]. Halogen FR products are used in a wide variety of resins including polyolefins, polystyrenes, polyamides (nylons), polyesters, and more.

The second major FR technology is also currently the fastest growing segment and comprises products called metal hydrates. The most well-known FR metal hydrate is aluminum trihydrate (ATH). Another fast-growing metal hydrate FR is magnesium hydroxide or $Mg(OH)_2$. The growth of the magnesium hydroxide FR product can be attributed at least in part to the current industry focus on environmentally friendly FRs. These metal hydrate FRs function by releasing water vapor in product-specific temperature ranges. That reaction leads to several effects which interfere with the combustion process. The release of water vapor acts to cool the substrate, an insulating metal oxide layer is formed on the substrate, and a dilutive effect is also produced in the flame front. Metal hydrate FRs interfere with at least two of three triangle components, including oxygen and fuel. Again the interested reader is referred to the literature for further details [33]. Metal hydrate FRs are also used in a variety of resins including polyolefins, olefinic elastomers, EVA (ethylene-vinyl acetate), PVC, and some epoxies.

The third major FR technology includes products containing phosphorus. Common FR products include ammonium polyphosphate or APP, red phosphorus, and other phosphates and phosphonates. Well-known and well-used products of the phosphate ester type include resorcinol diphosphate or RDP, and bisphenol A diphosphate or BDP. Details on these and additional products will be presented later. The FR mechanism for phosphorus-based products is largely perceived to be a char-forming mechanism following the decomposition to phosphoric or polyphosphoric acids during the combustion process. However, depending on the specific phosphorus FR product and the resin substrate type, the actual FR mechanism can be multifunctional and may also include vapor phase activity (like that of the halogen FRs) and/or crosslinking mechanisms. Consult FR industry references for further details [34].

Phosphorus-containing FR products are used in resins including PVC, ABS, PC/ABS, polyamides, and PPO (polyphenylene oxide). Depending on the polymer resin, the amount of phosphorus needed to achieve flammability performance controls the loading of the phosphorus FR product.

Although the above are considered to be the three major FR technologies, there are of course a number of FR products which do not fit into those groups. These include products based on nitrogen, sulfur, boron, graphite, and silicone to name a few. Specific examples will be presented in a later section.

Smoke suppressants are a separate class of products often discussed with flame retardants. Smoke is composed of water, carbon particles, ash, soot, and other combustion by-products which are contained in combustion gas and air. This collection of components is perceived by the human eye as smoke. Smoke suppressants are compounds which work to suppress the production of smoke during the combustion process. Metal hydrate and char-forming FR products can be considered smoke suppressants in and of themselves. The metal hydrate products by their nature and mode of action produce lower smoke and the char formers effectively retain carbonaceous material in the solid phase (preventing the otherwise subsequent contribution to smoke production). There is another type of smoke suppressant which essentially works in FR systems containing halogen FR compounds. These include products based on molybdenum and zinc compounds. Molybdenum oxide and ammonium octamolybdate or AOM are among the older, more widely recognized products. Such products work in the solid phase through crosslinking and other modifications to the pyrolysis process all of which work to keep the fuel in the solid phase [35]. Specific products and details will be presented later.

Finally, to finish up this FR101 summary, mention should be made of today's leading focus of FR technology development. Nanotechnology is seen in a variety of industries and applications, not just in flame retardants. Nano in English is defined as one-billionth (or 10^{-9}). In FR technology, nano does not mean one billionth. Nano composite polymers are polymers with a different internal structure such as alternating nanometer-thick layers of organic and inorganic materials. These frequently impart flame retardancy to the systems in which they are incorporated. The exciting aspect of this nanotechnology in FR technology is the improvement in physical and mechanical properties often found in addition to possible improvement in flammability. These improvements are highly valued as the use of flame-retardant additives in thermoplastic formulations frequently adversely affects physical and mechanical properties of the formulation. Indeed one of the tricks in successfully using FR additives is knowing how to balance the opposing effects of increased flammability performance and decreased physical/mechanical properties.

27.16 Halogen FRs—Selected Products

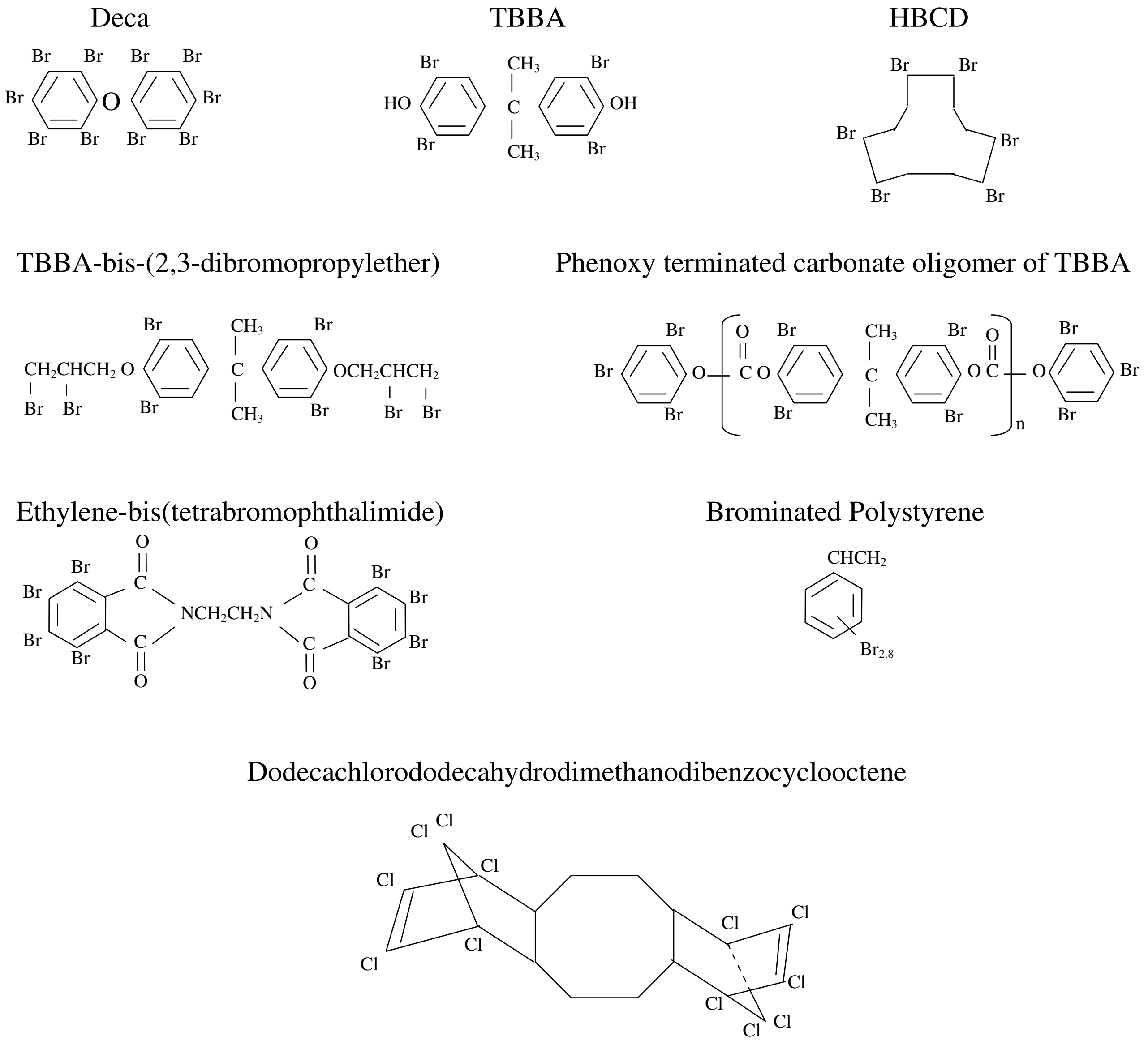
Bromine and chlorine containing FRs comprise the largest (by dollars) segment of all FR compounds. Many of the specific FR products in this segment are classified as commodity products within the FR industry. These products are mature, and their pricing has moved downward on their respective pricing curves. Selection of each of these mature products for a specific formulation or application is determined largely by the resin system into which they will be incorporated as well as by the desired flammability and physical property characteristics. Most, but not all, of these mature halogen FR products are typically accompanied by one of several synergist compounds to be discussed in the following section, Halogen FR Synergists.

Decabromodiphenyl oxide or Deca is arguably the most cost- and performance-effective halogen FR product available today. Deca is a benzene ring (or aromatic) compound containing approximately 83% bromine contributed by its ten bromine molecules (Deca = 10). It has over the past decades been widely used to flame retard polyolefin, polystyrene, ABS (acrylonitrile-butadiene-styrene), polyamide (nylon), polyester, PVC, and other resin systems. Its decomposition temperature of 300–310 °C makes it suitable for higher processing temperatures, hence its applicability in a variety of resins. Deca is frequently added together in a specific ratio with a synergist such as antimony trioxide.

An example formulation using Deca in HIPS (high impact polystyrene) would incorporate Deca at a 12% loading with antimony trioxide at a 4% loading (a 3:1 ratio). The remaining 84% of the formulation comprises the HIPS resin and any other additive components including colorants, stabilizers, process aids, etc. Such a formulation would be suitable for an electronic housing or cabinet used in a television or computer monitor and would most likely achieve a rating of V0 in the UL94 flammability test. In LDPE (low density polyethylene), Deca at 6% loading with 2% antimony trioxide can achieve a UL94 V2 flammability rating. A UL94 V0 rating in PE (polyethylene) resins could likely be achieved with 22% Deca and 6% antimony trioxide [35]. Many other formulations with Deca as the FR have been studied and used in commercial applications. See Figure 27.2 for the chemical structures of Deca and several other halogen FR additives and Table 27.3 for a list of current suppliers of Deca and other FR products.

Decabromodiphenyl ethane is a comparatively newer FR quite similar to Deca, except Deca's oxide linkage is replaced with ethane. With 82% bromine and a melt temperature around 360 °C, it performs similarly to Deca but appears to have less blooming tendency than Deca. (Blooming is a term used to describe the migration of the additive to the surface of a component or substrate. Deca blooming in some applications actually manifests as a whitish dust on the surface of the product. This is acceptable in some applications and not in others.) The newer product was developed in response to the tremendous pressure to discontinue the use of Deca by the environmental groups concerned with adverse effects on human health and the environment. See Figure 27.2 and Table 27.3 for chemical structure and suppliers.

Hexabromocyclododecane or HBCD is an aliphatic (no benzene rings) FR containing six bromine molecules (Hexa = 6) and about 75% bromine. Its melt temperature of about 190 °C limits its processing temperature and usage to applications including expanded and extruded polystyrene foam, textiles, coatings, and adhesives [35]. FR foam



Deca

TBBA

HBCD

TBBA-bis-(2,3-dibromopropylether)

Phenoxy terminated carbonate oligomer of TBBA

Ethylene-bis(tetrabromophthalimide)

Brominated Polystyrene

Dodecachlorododecahydrodimethanodibenzocyclooctene

Figure 27.2 Chemical structures of selected halogenated FRs.

Table 27.3 Major suppliers of selected halogen FRs

FR Product	Albemarle	Chemtura	ICL
Decabromodiphenyl oxide	Saytex® 102E	DE83R	FR 1210
Decabromodiphenyl ethane	Saytex® 8010	Firemaster® 2100	
HBCD	HP-900P	CD75P	FR 1206
TBBA	CP2000	BA 59P	FR1524
TBBA-bis(2,3-dibromopropyl ether)		PE68	
Ethylene-bis(tetrabromophthalimide)	Saytex® BT93		
Brominated Polystyrene	Saytex® 7010 PyroChek® 68PB		

applications include electronic goods packaging and thermal insulation used in the building market. Incorporated at relatively low loadings (<5%), HBCD is often accompanied by thermal stabilizers to counter its thermal instability. See Figure 27.2 and Table 27.3 for chemical structure and suppliers.

Another FR product which like Deca could be considered a mature product is TBBA or Tetrabromobisphenol A. TBBA is different from Deca and HBCD in that this FR is not just an additive FR but is also a "reactive" FR. This means that the FR is actually chemically reacted into the resin matrix. TBBA is often reacted into unsaturated polyester and epoxy resins. It is used as an FR additive in ABS, PC/ABS, and as a reactive FR in polycarbonate or PC.

Several halogenated FR products could be considered specialty products (rather than commodity) as their applicability is usually narrower than that of the commodity FRs. Most of these specialty products have also been in use for many years. Some are briefly discussed below and some can be found in Figure 27.2 and Table 27.3.

Tetrabromobisphenol A bis(2, 3-dibromopropylether) is another aromatic FR containing about 68% bromine and is primarily used in polyolefin (polypropylene or PP) resins. Melting point is relatively low and can range from 100−115 °C. As little as 2% loading with appropriate synergist can achieve UL94 V2 flammability with loadings of 12% increasing flammability performance to the V0 rating. Applications include various electrical connectors, light sockets, and other components.

Phenoxy terminated carbonate oligomer of TBBA (also known as BC58) is another TBBA derived product. Primarily used to flame retard PBT (polybutylene terephthalate) and PC resins, it is typically incorporated at about 6% loading to get the best flammability performance from its 59% bromine content.

Ethylene bis(tetrabromophthalimide) is another specialty FR used in polyester resins such as PBT as well as in HIPS, ABS, and polyolefin resins. Colored appliance components, electronic equipment enclosures, and wire and cable applications are examples of end uses. Its bromine content is about 67% and it has a relatively high melt point around 455 °C. Add to this the additional benefits of non-blooming, excellent UV stability, and decent wet electrical properties, and it becomes easy to understand its popularity with formulators looking to flame retard higher temperature resin systems and for cable applications.

Brominated polystyrene is still another specialty halogen FR, and this product also has the distinction of being a polymer itself, unlike the other FR additives. This product contains about 67% bromine and is used primarily in polyamide 6 and 6/6 resin systems. End-use applications are again largely found in the electrical and electronic connectors and components market.

Although the prior halogen FR additives are all based on bromine, mention should be made here of a chlorine-containing product, a specialty and very long-lived, called Dechlorane Plus®. Chemically, Dechlorane Plus® is dodecachlorododecahydrodimethanodibenzocyclooctene (Figure 27.2). This one is produced and marketed by OxyChem (Occidental Chemical Company) and is largely used to flame retard nylon and in low smoke polyolefin applications. This FR contains 67% chlorine and has a melt temperature of about 350 °C. Loading levels are formulation specific and depend on desired flammability performance and can range below or above 10−15%. This product provides flammability protection via a char-forming mechanism in addition to the standard halogen vapor phase flame retardance.

Finally, not often considered as a flame retardant, but actually quite true to fact, the resin PVC could be considered a halogen flame retardant product. Its chlorine content makes it intrinsically flame retardant without the addition of FR additives. PVC formulations often include a synergist like antimony trioxide added to boost PVC's natural flame retardant characteristic.

27.17 Halogen FR Synergists

Synergists are frequently used to enhance the flammability performance of halogen FRs. Addition of the synergist also counters the degradation in physical properties inevitably resulting from the addition of FRs to the resin system, thus allowing the flammability performance to be achieved with less loading of the FR additive. The long-time standard is antimony trioxide. Alone, antimony trioxide shows virtually no flame retardant action. However, there is a significant synergistic effect when used with halogen FRs. Much study has been done over the years, and several mechanisms are apparently thought to be responsible for this effect. One mechanism is that antimony trioxide generates oxyhalide and trihalide compounds which can function as a source of halide radical interceptors in the vapor phase and over a wide temperature range. Additional FR mechanisms include endothermic cooling and solid phase reactions like charring [36]. Antimony is principally sourced today from China and supplied by a large number of Chinese and other trading companies.

Antimony like some of the halogen FRs is presently under scrutiny by regulators and is a suspected carcinogen. Therefore, non-antimony synergists getting some attention from researchers and formulators include metal oxides based on tin, molybdenum, and zinc. Zinc stannate, zinc borate, zinc molybdate, and zinc phosphate are sometimes used as synergists, especially when a customer requires something other than antimony trioxide. These products can also be used as a partial substitute for antimony trioxide. Some provide other benefits such as smoke suppression in addition to the FR synergistic effect.

27.18 Halogen FRs and REACH

The human health and environmental debate regarding a specific few halogen FR products was mentioned earlier. In addition to country and/or local regulations and voluntary actions to remove or restrict a few halogen products, perhaps the most complex outcome of the broader safety debate can be found in Europe. A new system has been enacted there for registration and evaluation of new and existing chemicals. REACH (registration, evaluation, and authorization of chemicals) essentially calls for a central database of information (publically available) on chemicals imported into Europe above a certain small volume. The process is underway but is not yet completed.

Possible outcomes of the evaluation under REACH include the need for authorization or restriction of the tested chemical. For example, authorization might be required for products that are carcinogenic, mutagenic, persistent, and bioaccumulative, or otherwise hazardous to human health or the environment [37]. This system applies to all chemical products and includes flame retardant products. Due to the globalization of the flame retardant and other industries, most producers worldwide will find it necessary to comply with the REACH system (hence, it does not just apply to European producers). More details on REACH can be found at the European Chemicals Agency (ECHA) Web site at echa.europe.eu/reach.en.asp.

27.19 Metal Hydrate FRs

This is the largest volume FR additive product group in the FR industry. ATH and $Mg(OH)_2$ were mentioned earlier and are the principal FR products in this group which also includes brucite, hydromagnesite, huntite, and mixed metal hydroxyl carbonates. Brucite is essentially magnesium hydroxide in a naturally occurring form. Hydromagnesite is a natural mineral usually found with huntite ($3MgCO_3 Mg(OH)_2 3H_2O$) + $Mg_3Ca(CO_3)_4$. Mixed metal hydroxy-carbonate compounds are like hydrotalcite with varying amounts of magnesium and aluminum interspersed in layers [38]. These less frequently used types of metal hydrate FRs have been studied, but their commercial usage is small in comparison with ATH and $Mg(OH)_2$.

ATH is the largest volume flame retardant and has been so for many, many years. It is an extracted component of bauxite ore. ATH is a low cost FR and is easy to use. ATH begins its endothermic breakdown in the range of 180–200 °C releasing its chemically bonded water. Current producer suppliers of FR grade ATH include Albemarle, Almatis (Alcoa), Showa Denko, and Huber. At loadings ranging up to 70%, ATH is used in a variety of thermoplastics and thermosets including PVC, EVA, PE, unsaturated polyesters, acrylics epoxies, and phenolics. Applications include wire and cable, bathroom ware, wall panels, conduit and pipe, laminated countertops, and many electrical and electronic components.

Like ATH, $Mg(OH)_2$ or magnesium hydroxide is also used at loadings of 60% or more in thermoplastic resins including polyolefins, EVA, and elastomers. It is likewise used in some thermoset resins including epoxies. Applications include wire and cable, building products like laminates, roof membrane, plastic lumber, and some appliance components. Suppliers include Martin Marietta Magnesia Specialties, Kyowa, ICL (Dead Sea Bromine), Albemarle and others.

$Mg(OH)_2$ functions in the same way as ATH by the release of water of hydration which cools the combusting system, and $Mg(OH)_2$ also provides an insulating oxide. One significant advantage of $Mg(OH)_2$ over ATH is the higher temperature at which it begins to function, 300 °C and above versus about 200 °C for ATH. This allows processing at much higher temperatures using FR grade $Mg(OH)_2$ and therefore allows a wider range of resin systems to use $Mg(OH)_2$ as the metal hydrate FR. See Table 27.4 for a list of selected metal hydrate FR suppliers and their metal hydrate FR product trade names.

There are no toxicity problems identified with either ATH or $Mg(OH)_2$. However, both of them share the disadvantage of higher loading levels for FR efficacy which typically interferes with physical properties of the system. This can often be overcome with careful formulation development.

Table 27.4 Suppliers of metal hydrate FRs and product trade names

Supplier	ATH Trade Name	$Mg(OH)_2$ Trade Name
Albemarle	Martinal®	Magnifin®
Almatis Gmbh	Hydral®	
Huber	Hymod®	Zerogen®, Vertex®
ICL		FR20
Kyowa		Kisuma®
Martin Marietta Magnesia		MagShield®

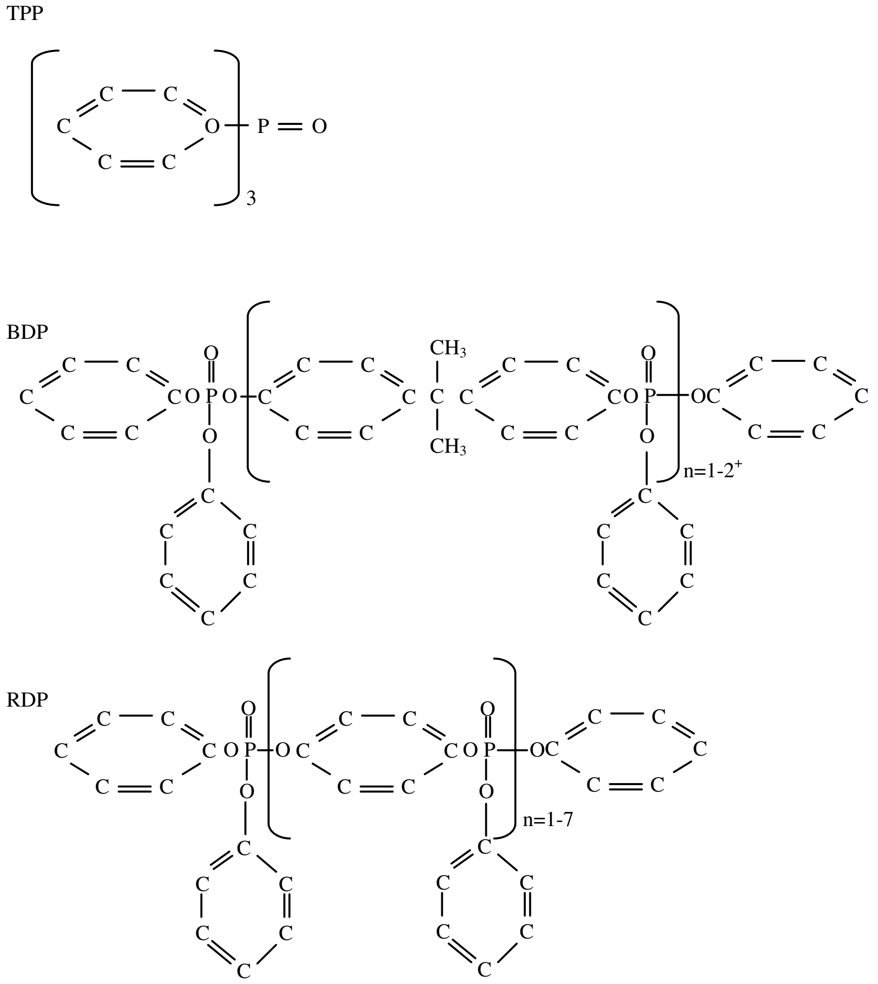
Examples include the use of surface treatments, especially for $Mg(OH)_2$ and/or the selection of proper base resin starting melt flow index. Processing conditions should also be properly adjusted to ensure a good result. Indeed successful formulations are being developed often enough to propel $Mg(OH)_2$ into arguably the fastest growing FR additive in today's global FR market.

27.20 Phosphorus FRs

The phosphorus FR product group includes many phosphorus containing compounds including organic phosphates, phosphonates, phosphate-and-halogen containing compounds, ammonium polyphosphate or APP, and red phosphorus. The FR mechanism for phosphorus FRs is complicated and is believed to often include (depending on the phosphorus product) char formation (solid phase) as well as possible vapor phase activity.

Phosphate ester FR products include triphenyl phosphate or TPP, resorcinol bis (diphenyl phosphate) or RDP, and bisphenol A bis (diphenyl phosphate) or BDP. These three phosphorus FR products contribute the largest volume share of this FR product group. Frequently used in PC/ABS blends, loadings of 8−1.5% by weight can achieve UL94 V0 flammability performance. Such formulations often include an anti-drip agent such as PTFE (polytetrafluoroethylene or Teflon) at 0.5% or less. Similar FR performance can also be achieved in PPO (polyphenylene oxide)/HIPS blends at approximately similar loadings of 10−20% [39]. See Figure 27.3 for FR phosphate ester chemical structures.

Figure 27.3 Chemical structures of selected phosphorus containing FRs.



Applications for these types of FR resin blends include housings or enclosures for electrical and electronic products such as computer monitors, printers, copiers, household appliances, fan, and pump motor housings. Suppliers of phosphate ester FRs include Chemtura, Lanxess, Supresta (now ICL), and Daihachi.

Red phosphorus has been in the phosphorus FR product portfolio for a long time. It is used in nylon electrical components like connectors of all sorts, in olefin wire and cable, in PU (polyurethane) rigid foams, and in some polyester (PBT) applications. Suppliers include Clariant, Italmatch Chemicals, and Rinkagaku Kogyo.

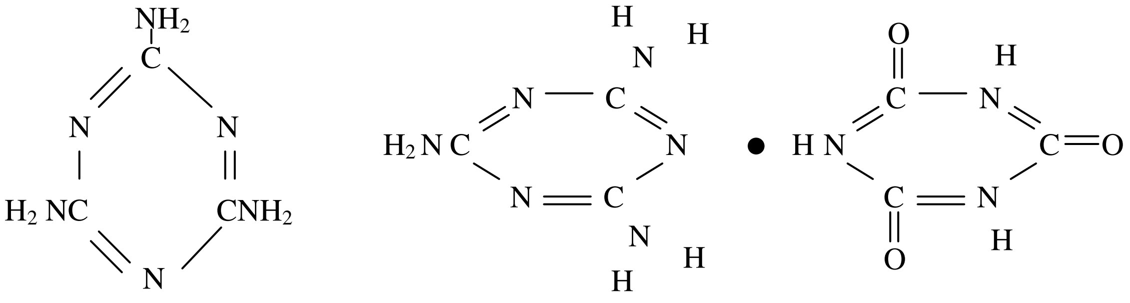
Metal phosphinates and melamine polyphosphate are often found in glass reinforced nylon and if used in proper formulations can deliver UL94 V0 flammability performance in multiple types of connectors, switches, and other components. Some suppliers include Clariant, Budenheim, and BASF (Ciba).

APP, also sometimes used in polyolefin formulations for similar E/E component applications, can be found on the product lists of Budenheim and Clariant.

Phosphorus-containing FR products will be subject to the same REACH requirements as other FR product types and as all other chemical products. Although some specific phosphorus products seem to occasionally find mention in the discussions on environmentally not-so-friendly products, phosphorus containing FR products have not been banned or restricted in any way to date. Their use and continued evaluation as effective non-halogen FR products is assured for the foreseeable future.

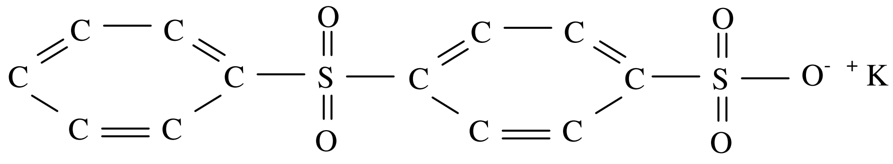
27.21 Other FRs

Flame retardant products based on chemistries not yet presented are available for specific applications. Some of these like those including and/or based on melamine have been available for many years. Others are relatively more recently developed products and of course research continues on these non-halogen, non-phosphorus, non-metal-hydrate types of FRs. See Figure 27.4 for chemical structures of a few of these FR products.

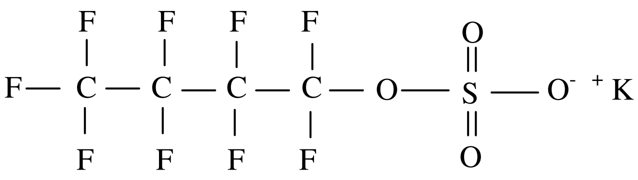


Melamine

Melamine Cyanurate



Potassium diphenylsulfonesulfonate



Potassium perfluorobutylsulfonate

Figure 27.4 Chemical structures of selected other FRs.

Melamine can be found in specific polyurethanes, including polyurethane foam in home furnishing applications. Melamine cyanurate can be used to achieve UL94 V0 flammability performance in unfilled nylon.

Zinc borate is an inorganic FR (often used as a synergist) under continuing development in a variety of resins, including PVC, polyolefins, polyesters, and others. In some cases, it is used in combination with other FRs (like metal hydrates) to boost flammability and/or smoke suppressant performance.

Expandable graphite is another FR that is long-lived. Development efforts so far seem to point to possible applications in various polyurethane foams. Graphite's FR mechanism is thought to be more mechanical in nature in that it tends to produce crosslinked carbon char when under combustion conditions. Of course, graphite applications are limited to black color.

Sulfur-based FR compounds are used today for polycarbonate or PC transparent and translucent applications. Potassium diphenylsulfonesulfonate is one such product. The largest supplier of this FR product is Arichem LLC. The sulfonate product (often designated as KSS) is used in PC at fractional loading levels to achieve UL94 V0 flammability performance. Potassium perfluorobutylsulfonate is a competitive product based on fluorine which is supplied by 3 M, Bayer, and Matini. Its use appears to be limited by its relatively higher formulation component cost. The use of these sulfonate products is limited to PC and high PC alloys (Figure 27.4).

There are many other elements and compounds continually being researched and evaluated for potential flammability performance. As an example, many compounds based on silicon are under study. These include siloxanes, silanes, and silsesquioxanes.

Of particular interest recently are polymer-layered silicates as nanocomposites which will be reviewed in more detail in the section, Nanotechnology and Flame Retardance.

27.22 Smoke Suppressants

Smoke suppressants are a group of specialty additives separate from flame retardants. They can be considered an extension of flame retardants, as they are frequently used in concert with FR additives and especially in PVC formulations to reduce smoke generated during combustion. PVC formulations produce smoke when burning, and if antimony trioxide has been added as a synergist, smoke production is increased even further.

The solution to suppressing smoke in any burning situation is to move the fire suppression mechanism from the vapor phase to the solid phase. The first step then is to not use vapor phase (halogen) flame retardants. Char-forming FRs (phosphorus types) and endothermic FRs (metal hydrate types) are the better choices for lower smoke. Some smoke suppressant products have already been mentioned. These include ATH and $Mg(OH)_2$. Zinc borate has been shown to reduce smoke in specific formulations. Its action is that of first cooling through water release and then forming borate glass to protect the substrate [40]. These approaches are usually, however, not sufficient to meet the most stringent smoke release standards.

Table 27.5 Selected smoke suppressant suppliers and products

Sherwin-Williams Chemicals*	R.J. Marshall	Polymer Additives Group
Kemgard® 911C	C-Tec™ LS	Charmax® LS
Kemgard® 911A	C-Tec™ ZST	Charmax® LS ZST
Kemgard® 911B	C-Tec™ ZHS	Charmax® LS ZHS
Kemgard® MZM	C-TEC™ AOM	Charmax® AOM
Kemgard® HPSS	C-TEC™ MO	Charmax® MO

**Kemgard is now part of Huber Corp.*

For the most stringent smoke standards and in particular with PVC applications, compounds based on transition metal chemistry are used to move the fire suppression to the solid phase. These compounds are usually molybdate based and can substitute as synergist replacements for antimony trioxide synergist.

Historically the use of molybdenum compounds started with molybdenum oxide. This compound worked well as a substitute for antimony trioxide but caused blue color formation in PVC compounds. The next step in development was the use of ammonium octamolybdate (AOM). This product works well as a smoke suppressant but is a costly option. Also, the molybdenum contained in the interior of the AOM particle is not available to participate in smoke suppression.

Supported molybdenum compounds were subsequently developed to more effectively utilize molybdenum's smoke suppression capability. Sherwin-Williams Kemgard® smoke suppressant products like KG 911C and PAGs Charmax® products like Charmax® LS are examples. Higher efficiency products came thereafter with much better stability in PVC formulations. There are several suppliers that have introduced such products. See Table 27.5 for a listing of selected smoke suppressant products and suppliers.

27.23 Nanotechnology and Flame Retardance

By definition, nano as related to flame retardance is a material whose particle size is less than 100 nm (0.1 microns). This size particle is 10−100 times smaller than

Table 27.6 Suppliers of selected nano FR type products

Supplier	MMT	LDH	CNT
Southern Clay	Cloisite® Nanofil®*		
Nanocor	Nanomer®		
Elementis	Bentone®		
Akzo Nobel		Perkalite®	
Hyperion			Fibril™
Nanocyl			Nanocyl™
Arkema			Graphistrength™

**Southern Clay acquired SudChemie Nanofil in 2008.*

typical particulate flame retardants. Additionally, nano flame retardants are a filler material and do not dissolve in the polymer resins.

Initial publication in 1997 by NIST (National Institute of Science and Technology) pointed to a new flame retardant approach [41]. This was an extension of 1993 work done at Toyota Central R&D laboratories on an inorganic–organic hybrid polymer of nylon 6 and nanoclay. Over the last 10 years, much has been learned about the application of nanotechnology to flame retardance. Three such products that have been successfully applied as flame retardants are organo-modified montmorillonite clay or MMT, organo-modified layered double hydroxides or LDH, and carbon nanotubes or CNT.

MMT clays are of the cationic type and are typically modified with fatty acid quaternary ammonium compounds. LDH clays are of the anionic type and are typically modified with fatty acids. Carbon nanotubes are available in two types, including single wall or multi-wall. Surface modification on these seems to be proprietary to the supplier. See Table 27.6 for a listing of selected nano FR products and suppliers. In application, nano fillers are used at 2–6% by weight into the polymer matrix to provide flammability performance. Note that nanotechnology is almost always used in combination with other FR compounds or technologies as their effectiveness is not sufficient to meet many required flammability standards. The flame retardant effect of nano fillers is exhibited in two ways. The first is the reduction of heat release, and the second is a reduction in the tendency of polymers to drip and transmit flame.

As an example of the reduction of heat release, Figure 27.5 presents cone calorimeter results showing the reduction in heat release with the different levels of organo-modified MMT [42]. Similar results can be observed for

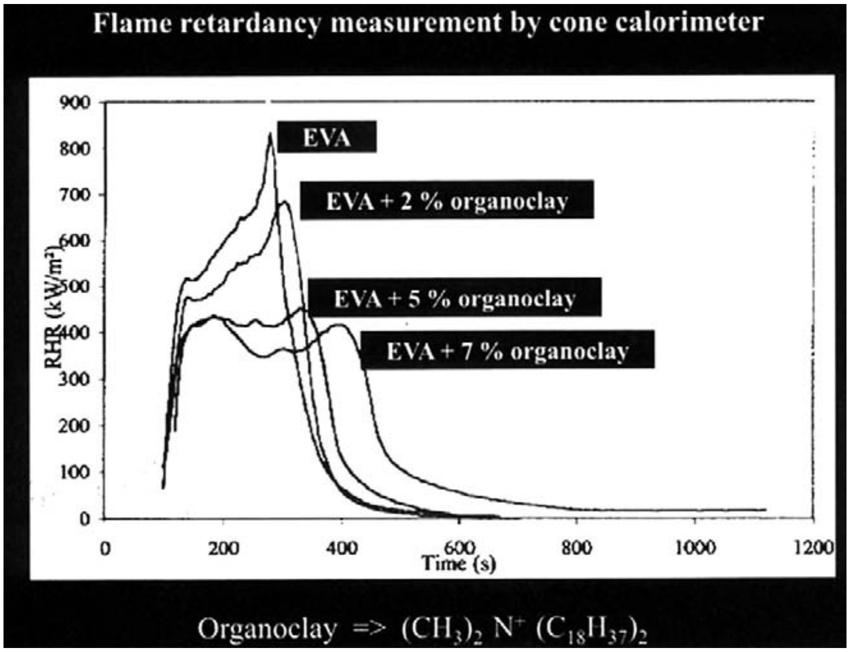
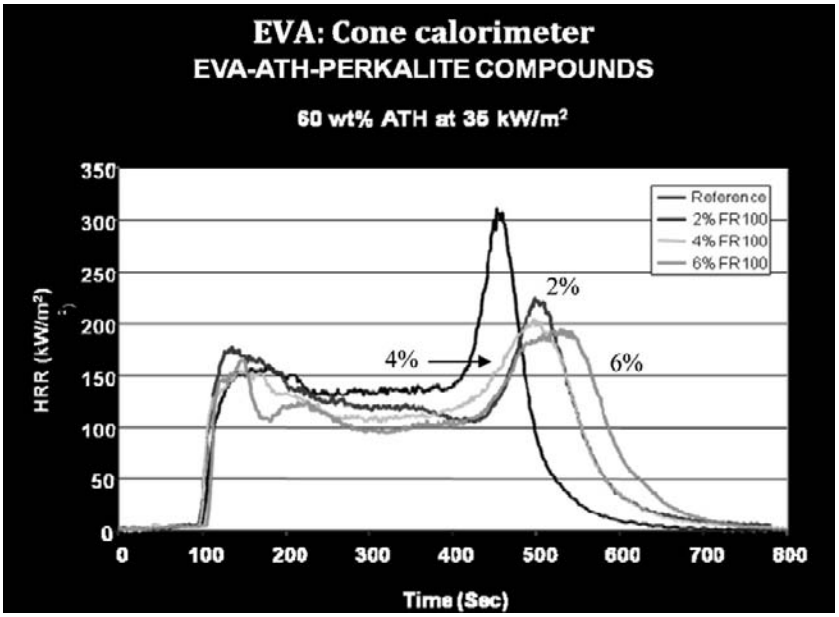


Figure 27.5 Reduction in RHR with different levels of organo-modified MMT [42].

Figure 27.6 Heat release rate for varying loadings of LDH [43].



LDH (Figure 27.6) [43]. CNT demonstrates a similar effect (Figure 27.7) [42].

Combinations of nano fillers and conventional flame retardants have demonstrated that the two FR mechanisms are effectively combined to meet many flammability standards. See Table 27.7 for an example [43].

The application of nano FR technology is not simply one of adding the nano filler to the formulation. Careful application of compounding technology is necessary to adequately delaminate the clay and disperse it into the matrix. The nano filler must be dispersed through the polymer matrix [44].

Commercial applications today include low smoke zero halogen or LSZH polyolefin wire and cable as well as conductive compounds utilizing nanotubes. Current commercial products using organo-modified MMT have a temperature limitation of about 210 °C. New modifiers are being developed. Current commercial products using organo-modified LDH have a temperature limitation of about 260 °C. There may be water release below that temperature which can be removed by vacuum during compounding. CNT-based products need to be handled carefully due to suspected health-compromising properties.

Figure 27.7 Rate of heat release for various carbon nanotube formulations [44].

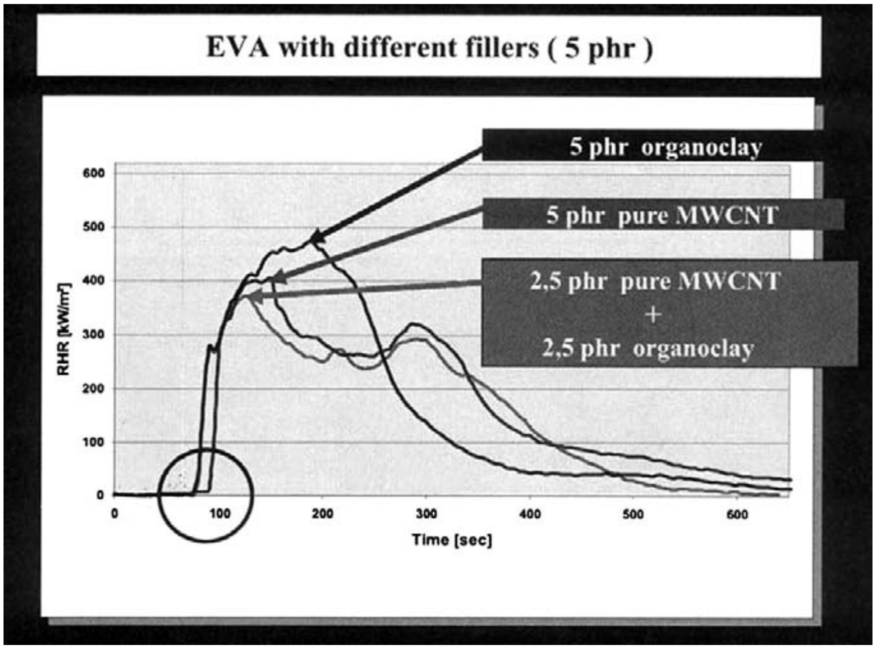


Table 27.7 Combination FR system—MDH plus LDH*

Formulation Component	Formulation 1 (Control)	Formulation 2	Formulation 3
PP (Ineos H2OH-00)	33	34	42
MagShield® UF NB10	65	60	52
Perkalite® F100		4	5
MA-PP, Polybond 3105	1	1	1
Ca Stearate	1	0.6	0.5
UL 94 (3.2 mm)	V0	V0	V0
UL 94 (1.6 mm)	V2	V2	NR/V2†

**Data provided by Martin Marietta Magnesia Specialties.*
†NR = No rating (repeat test obtained V2 rating).

This aspect is under evaluation by various medical and safety authorities.

Organo-modified clays, either the MMT or LDH type, can contain from 40–65% organic modifier. This to a user is an important consideration as when the nano particle acts as a flame retardant, its modifier has been burned off. Hence, the flame retardant effect of a nanoclay depends specifically on its amount of mineral and not the total amount of modified clay in formulation.

This nanotechnology area of research and development is clearly of significant interest to the FR industry as well as other industries. Much study is underway to determine viable means of improving flammability performance in various resins and for various end-use applications. This focus of research and development resources is expected to continue for some time to come.

27.24 Conclusion

Let us revisit our fire scene at the start of the chapter and the fireman's frustration at the victims' need for just a little more time in order to escape. Starting in the middle of the last century (and some would say even earlier than that), an entire industry rose up around trying to address this need and to find means to limit the devastating effects of uncontrolled fire. It has grown into a global industry comprising many companies and organizations which employ many dedicated researchers, technologists, and professionals from many fields all striving to develop FR products that if used properly and in a sufficient quantity of applications will buy the victims of fire more time to escape. These products are intended to delay ignition, or retard the burning process once it starts, and/or suppress the development of smoke. The ultimate purpose is to help the victims of fire escape by providing just a few more precious seconds than they would otherwise have, to limit the loss of life and injury to humans, and to protect property. FRs are a highly valuable class of products and when properly used go a long way toward accomplishing their noble purpose.

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28 Plasticizers

Allen D. Godwin
ExxonMobil Chemical Company, 4500 Bayway Drive, Baytown Texas 77520, USA

28.1 Introduction

A plasticizer is an additive that when added to another material makes that material softer or pliable. Although this definition can be applied to a variety of products, the word "plasticizer" generally refers to materials used in plastics. The Council of the International Union of Pure and Applied Chemistry (IUPAC) adopted the following definition of a plasticizer: "A plasticizer is a substance or material incorporated in a material (usually a plastic or elastomer) to increase its flexibility, workability, or distensibility."

Early plasticizer technology focused on nitrocellulose materials. In the mid-1850s Alexander Parkes developed new nitrocellulose-based plastics where various oils were used to make the brittle polymer more pliable. Parkes and later one of his colleagues, Daniel Spill, attempted to create a new plastic industry with their technology. Unfortunately they were unable to produce affordable materials with acceptable quality. A few years later, John Wesley Hyatt was able to develop a new process [1] for plasticization of nitrocellulose, leading to the successful commercialization of his plastic materials which he called celluloid and the start of the plastic industry.

As this technology developed and expanded, the search for new and improved plasticizers began. The early work by Parkes and Spill used solvents together with castor oil, but their manufacturing process and the use of castor oil led to compatibility problems and exudation. Hyatt's technology focused on a new manufacturing process that significantly reduced volumes of solvent and used camphor as a plasticizer. This technology created a variety of quality products which spread to new markets.

Natural product-based materials dominated the plasticizer innovations throughout the remaining part of the nineteenth century, but in the early 1900s new chemicals such as phthalates and phosphates were beginning to be proposed as plasticizers. In the 1920s, the increasing demand for plasticized nitrocellulose paints led to the successful commercialization of two important plasticizers, that is, tricresyl phosphate and dibutyl phthalate. Many of the important polyvinyl chloride (PVC) plasticizers that we see today were first tested with nitrocellulose and other cellulose polymer applications in this period.

Although, PVC was first synthesized in the nineteenth century, it was Waldo Semon's vision of the usefulness of plasticized PVC that initiated the growth of the flexible PVC industry. In 1933, Semon's patent [2] on the use of PVC with solvents such as *o*-nitrodiphenyl ether, dibutyl phthalate, and tricresyl phosphate to produce a "rubber-like composition" having many different uses was granted. At about the same time the patent on the composition of di-2-ethylhexyl phthalate or DEHP (DOP) was granted [3] (describing the application as a plasticizer for nitrocellulose plastic compositions) and soon after it was evaluated as a PVC plasticizer. In the period that followed, thousands of products were tested and evaluated as plasticizers. DEHP became commercially available in 1940 and since then has remained one of the more important plasticizers for PVC worldwide. A report published in 1943, mentioned that as many as 20,000 different chemicals had been proposed or tested as plasticizers [4]. Based on that number, it is expected that today, the total number of chemicals described with potential usage as a plasticizer may approach 30,000.

Presently, there are about 100 different plasticizers produced worldwide, although only about 50 of these are classified as commercially important. Approximately 90% of these plasticizers are used in the production of plasticized or flexible PVC products. For this reason, the majority of the information discussed in this chapter will focus on PVC plasticizers. Other polymer systems that use small amounts of plasticizers include polyvinyl butyral (PVB), acrylic polymers, poly(vinylidene chloride), nylon, polyolefins, polyurethanes, and certain fluoroplastics. In 2009 it was estimated that worldwide production of plasticizers was about 12 billion pounds [5], with the majority of the plasticizer consumption taking place in Asia Pacific, predominately China. About 85% of this volume are phthalate ester plasticizers.

28.2 Mechanism of Plasticization

For a plasticizer to modify the properties of the base polymer, it must be thoroughly mixed and incorporated into the polymer matrix. This is typically performed by heating the polymer and the plasticizer together with mixing until the

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resin dissolves in the plasticizer. The material is then formed into the desired product and cooled. Different plasticizers will exhibit different characteristics in both the ease with which they form the plasticized material and in the resulting physical properties of the flexible product.

Plasticization does not create chemical bonds. Within the polymer matrix, the plasticizer must be able to move to be effective, for if the plasticizer molecules are attached to the polymer, the ability to plasticize is greatly diminished. Navarro et al. [6], in their attempt to make a non-migrating plasticizer, showed that when a phthalate such as DEHP is chemically attached to the PVC polymer, the T_g of the PVC composition changes from -40 °C for a 12 mole% DEHP plasticized system to about $+40$ °C for a 12 mole% attached plasticizer product. This plasticizer mobility restriction changes a very flexible PVC system with very good low-temperature properties to a non-flexible, fairly rigid plastic, which is brittle at room temperature.

When the PVC polymer and the plasticizers are mixed and heated, the plasticizer begins to solvate portions of the PVC polymer. Initially, this occurs only in the amorphous region of the PVC polymer but with additional heating, the polymer in the crystalline regions begins to interact with the plasticizers and is solvated. When the plasticized PVC product is molded and then cooled, the PVC crystallites will again slowly reform, but the polymer in the amorphous region will remain closely associated with the plasticizers due to transient, but significant, attractions caused by secondary chemical bonding forces.

Several theories have been developed to account for the observed characteristics of the plasticization process; Daniels has recently published a review of plasticization mechanisms and theories [7]. Although most mechanistic studies have focused on PVC, much of this information can be adapted to other polymer systems. According to the lubricating theory of plasticization, this theory holds that plasticizers act as lubricants to facilitate polymer chain movement when a force is applied to the plastic. It starts with the assumption that the unplasticized polymer chains do not move freely because of surface irregularities and van der Waals attractive forces. As the system is heated and mixed, the plasticizer molecules diffuse into the polymer and weaken the polymer—polymer interactions. Portions of the plasticizer molecule are strongly attracted to the polymer while other parts of the plasticizer molecule can shield the polymer chain and act as a lubricant. This reduction in intermolecular or van der Waals forces among the polymer chains increases the flexibility, softness, and elongation of the polymer.

The gel theory considers the plasticized polymer to be neither solid nor liquid but an intermediate state, loosely held together by a three-dimensional network of weak secondary bonding forces. This network or gel could be formed by permanent intermolecular ties or by ties which form in a dynamic state, as plasticizers associate and disassociate with the polymer. In effect the plasticizer provides the role of a bridge between two polymer chains. The bonding forces acting between plasticizer and polymer are easily overcome by applied external stresses allowing the plasticized polymer to flex, elongate, or compress.

Free volume is a measure of the internal space available within a polymer. As free volume is increased, more space or free volume is provided for molecule or polymer chain movement, making the polymer system more flexible. In the unplasticized polymer, free volume arises from movement of polymer end groups, polymer side chains, and internal polymer motions. Free volume can be increased through modifying the polymer backbone by adding more side chains or end groups or by incorporating smaller molecules with flexible end groups, which can move and rotate. The free volume theory builds on both the lubricity and gel theories of plasticization.

The mechanistic explanation of plasticization looks at the interactions of the plasticizer with the polymer. It assumes that the plasticizer molecules are not permanently bound to the resin molecule but are free to self-associate and to associate with the polymer molecule at certain sites and then disassociate. As these interactions are weak, there is a dynamic exchange process whereby as one plasticizer molecule becomes attached at a site or center it is rapidly dislodged and replaced by another. Different plasticizers will yield different plasticization effects because of the differences in the strengths of the plasticizer—polymer and plasticizer—plasticizer interactions. At low plasticizer levels, the plasticizer—PVC interactions are the dominant interactions while at high plasticizer concentration ranges, plasticizer—plasticizer interactions can become more important.

For a plasticizer to be effective and useful in PVC, it must contain two types of structural components, polar and apolar. The polar part of the molecule must be able to bind reversibly with the polymer while the apolar or non-polar portion of the molecule adds free volume and contributes shielding effects at other polar sites on the polymer chain. The balance between the polar and non-polar portions of the molecule is essential. If a plasticizer is too polar it will tend to act more as a solvent at room temperature and yield a product with overall poor performance. If it is too non-polar, compatibility problems can arise with high levels of plasticizer exudation. Useful tools in estimating plasticizer compatibility are the Ap/Po Ratio method developed by van Veersen and Merelaenberg [8] and the solubility parameter methods [9,10].

In another plasticization study Howick [11] examined the interactions of plasticizers with PVC using ^{13}C NMR spectroscopy coupled with computer modeling and minimum energy configurations. The molecular modeling calculations led to his summary of plasticization where he describes the interactions of the polar regions of the plasticizer molecule with the CH_2 of the polymer backbone leading to a lowering of the overall energy of the system. This interaction creates a change in the conformation of the alkyl side groups of the plasticizers which creates additional free volume and provides the plasticization effect. These conclusions tend to reinforce the Ap/Po ratio methods, where the importance of both polar and non-polar groups is noted.

In Howick's solid state ^{13}C NMR studies, no evidence was gained for specific interactions between the carbonyl carbons with the PVC polymer. However, the strongest effects were observed on the resonances of the aliphatic side chains. In general, Howick is proposing that the polarity differences between the PVC and the plasticizer create attractive forces. As the plasticizer molecules "move" around to find their lowest energy state, aligning with the PVC molecule, the non-polar or alkyl group of the molecule will also be able to rotate and move to their lowest energy state. In this state, the more successful plasticizers will be those molecules that once aligned with the PVC polymer to have alkyl groups that provide the greatest contribution, the overall free volume of the system. Those offering low or limited amounts of free volume contributions will be poorer performing plasticizers.

One important requirement for plasticization noted by Howick is an even distribution of the plasticizer throughout the polymer matrix, which again maximizes the potential free volume contributions. Other studies involving infrared spectroscopy and NMR techniques found that in plasticized PVC products, the plasticizer molecules interact with the PVC polymer only in the amorphous region while the polymer in the crystalline region is typically free of plasticizer. They also found little evidence of "pools" of plasticizers [12] with the majority of the plasticizer molecules associated with the PVC polymer.

28.3 Types of Plasticizers

In discussions about plasticizers, there are many different classification schemes and proposals. One of the highest level approaches is to classify plasticizers based on their molecular weight.

Monomeric plasticizers are those products that can be represented by a single, often unique structure. Generally, these are higher boiling liquids, with good solvency for the polymer, relatively low viscosity, showing good heat and chemical stability, and in a molecular weight range of 300−600 g/mol. Almost all plasticizers are esters. Many plasticizer reviews have focused strictly on monomeric plasticizers [13] while others have reported on polymeric plasticizers [14].

Polymeric plasticizers are characterized by many repeating units. These are typically polyesters which do not have a single discrete molecular weight and are characterized by an average molecular weight and molecular weight distribution. The molecular weight of most polymeric plasticizers range from 1,000 to over 10,000, with somewhere around a 3,000 molecular weight average representing a typical product. Polymeric plasticizers offer lower volatility and greater permanence as compared to monomeric plasticizers, but they are more difficult to use and are more expensive. Consequently polymeric plasticizers are used in those applications where greater permanence is an absolute requirement and the use of these plasticizers creates added value that can be realized in the price of the final product.

Plasticizers are also characterized by the concentrations in which they are used. *Primary plasticizers* are the products which are either used as the sole plasticizer in the system, or the major plasticizer that is used in plasticizer blends. *Secondary plasticizers* are used in smaller quantities in a blend with a primary plasticizer, and are generally added to improve on some specific property such as improved low-temperature flexibility, reduced flammability, improved processing, or reduced costs. For instance, in shoe soles, it is common practice to incorporate a small amount of the plasticizer di-2-ethylhexyl adipate (DEHA) as a secondary plasticizer together with a primary general-purpose (GP) plasticizer such as diisononyl phthalate (DINP) to give improvements in low-temperature flexibility. Often a plasticizer can be considered a secondary plasticizer in one system, while when used at higher levels in another formulation it is a primary plasticizer. For example, DEHA can also be used as the primary plasticizer in certain types of PVC food films in addition to the secondary plasticizer role with shoe soles.

Plasticizers can also be classified by their primary functions. The most common classifications are as follows:

GP plasticizers
Low-volatility/permanent plasticizers
Low-temperature plasticizers
Fast-fusing plasticizers
Specialty plasticizers

Examples of some of the more common plasticizers and their classifications are listed in Table 28.1. Often a plasticizer can be placed in multiple classifications. For example linear phthalates are recognized for both their low-temperature performance and low volatility. In addition, some specialty plasticizers could also be classified under the fast-fusing plasticizers.

GP plasticizers are those which offer the best balance of performance in a variety of applications and are generally available at the lowest price. These plasticizers are usually the first plasticizers considered in developing a new formulation. Although the GP classification represents about 80% of the volume of all plasticizers used today, it usually includes only four plasticizers: DEHP, DINP, diisodecyl phthalate (DIDP), and di-2-propylheptyl phthalate (DPHP). This list can change a little depending on specific applications. For example, today in many parts of the world DEHP is no longer considered a GP plasticizer because of labeling issues impacting marketing and use of DEHP. Often

Table 28.1 Properties of selected plasticizers [13,15,17] [f]

	Mol. Wt.	Viscosity[a]	Sp. Gravity[a]	Efficiency Factor[b]	Final Gelation Temp.[c]	Low Temp. Flexibility[d]	Weight Loss, wt%[e]
General-purpose plasticizers							
Di-2-ethylhexyl phthalate (DEHP)	390	80	0.986	1.00	71	−25	10.6
Diisononyl phthalate (DINP)	418	102	0.973	1.06	80	−24	5.4
Diisodecyl phthalate (DIDP)	446	129	0.968	1.10	80	−24	3.0
Di-2-propylheptyl phthalate (DPHP)	446	127	0.963	1.10	81	−34	3.5
Fast solvating plasticizers							
Butyl benzyl phthalate (BBP)	312	49[f]	1.119[f]	0.93	58	−11	15.0
Diisoheptyl phthalate (DIHP)	362	51	0.994	0.96	70	−24	19.3
Dipropylene glycol dibenzoate (DPGDB)	342	215	1.13	0.96	61	−7	15.1
Acetyl tributyl citrate (ATBC)	402	43	1.05	0.97	61	−18	>30
Low-temperature plasticizers							
Di-2-ethylhexyl adipate (DEHA)	370	15	0.927	0.94	70	−53	27.5
Diisononyl adipate (DINA)	398	22	0.922	1.16	89	−51	9.2
Di-n-nonyl phthalate	418	54	0.969	0.99	78	−34	3.1
Low-volatility plasticizers							
Ditridecyl phthalate (DTDP)	530	322	0.957	1.26	108	−24	1.9
Di-n-undecyl phthalate (DUP, L11P)	474	77	0.954	1.14	88	−34	1.4

Nonyl undecyl phthalate (L911P. 119P)	446	74	0.962	1.09	83	−33	1.3
Tri-2-ethylhexyl trimellitate (TEHTM)	546	310	0.992	1.11	85	−19	<1
Triisononyl trimellitate (TINTM)	588	430	0.978	1.24	99	−19	<1
Polymeric plasticizers (variety, typical)	~3000	>1000	>1.0	1.0−1.3	85−90	−10	<1
Other/specialty plasticizers							
Di-2-ethylhexyl terephthalate (DEHTP)	ca 390	65	0.984	1.04	82	−28	5.5
Alkyl sulfonic acid ester of phenol	~ 360	115	1.05	0.99	69	−21	12.0
Cyclohexanedicarboxylic acid ester of isononanol	424	60	0.948	1.09	83	−29	7.5
Isodecyl diphenyl phosphate	390	22	1.07	0.97	N.R.[g]	−22	5.7
Acetylated glycerol mono12 hydroxy stearate	500	110	1.07	1.0	N.R.	N.R.	3

[a] *At 20 °C.*

[b] *Efficiency ratio or substitution factor versus DEHP [13,17].*

[c] *Determined by dynamic mechanical analysis, onset of 70 phr plastisol gelation [17].*

[d] *Clash-Berg T_f, °C, calculated at 50 phr [15].*

[e] *Weight loss after heating for 7 days at 100 °C, air flow at 150 changes/hr, calculated at 50 phr [15].*

[f] *For additional information, see J.K. Sears, J.R. Darby, The Technology of Plasticizers, John Wiley and Sons,1982, pp. 893−955.*

[g] *N.R. not reported.*

processing requirements restrict this definition even further, as with plastisols where the higher processing temperature requirements might exclude DIDP or DPHP from GP considerations. Additionally, some applications with less demanding requirements may be able to use the terephthalate DEHTP (DOTP) as a plasticizer with GP performance potential, assuming that it is priced competitively and there are no processing or compatibility limitations that often are present with terephthalates. Today, the use of DEHTP is very small relative to the usage of other GP plasticizers; thus DEHTP falls within the specialty plasticizer category.

The *low-volatility plasticizer* category includes those plasticizers which offer greater permanence and longer service lives. This category includes the higher molecular weight (HMW) monomeric plasticizers such as TEHTM (TOTM), TINTM, and DTDP, but in some applications DIDP and DPHP are used for their greater levels of permanence versus other GP plasticizers. The linear phthalates L11P or DUP and 911P are also low-volatility plasticizers.

Low-temperature plasticizers are used in applications where improvements in the low-temperature flexibility limits are desired. Applications can include automotive interiors, weather stripping, outdoor cables, hoses, and vinyl roofing. Low-temperature plasticizers include the linear phthalate esters L9P, L911P, and L11P or DUP plus dibasic acid esters such as DEHA (DOA), DINA, and DEHZ (di-2-ethyl azelate).

Fast-fusing plasticizers enable the PVC material to be processed faster or at lower temperatures, sometimes functioning more as a processing aid as opposed to a plasticizer. Generally, it is in the area of plastisol applications where the uses of faster fusing plasticizers are preferred. Examples of fast-fusing plasticizers include BBP, DIHP, alkyl sulfonic acid esters of phenol, lower molecular weight phthalates and terephthalates, and several dibenzoate esters and ester blends.

The class of *specialty plasticizers* includes a variety of different products which share two things in common: they are used in relatively few applications and are usually available at price premiums over GP plasticizers. Consequently, they are used in those applications where the added performance benefits are required and the ultimate customer is willing to pay extra for that performance. Examples of plasticizers in this classification would include polymeric plasticizers, phosphate esters, citrates, cyclohexanoate esters, brominated phthalate esters, alkyl aromatic sulfonic acid esters, and vegetable oil-based plasticizers.

Plasticizers can also be classified according to chemical type. Phthalate esters continue to represent the major class of PVC plasticizers as they have done for almost 70 years. The non-phthalate plasticizers are present in small amounts with very little distinction in market size among them. Table 28.2 includes an approximate distribution of global plasticizer consumption [16]. In the United States, with a long history of a variety of different plasticizers available, the phthalate usage would be lower and may represent about 75% of the market. With fewer plasticizer selections available in Asia, the phthalate plasticizers there make up more than 90% of the market. Although epoxy plasticizers are listed in this table, this consumption is predominately epoxidized soybean oil (ESO). Although ESO is used in some regions as a cheaper alternative to GP plasticizers for markets with no concern about product quality or how long a product lasts, the majority of this consumption is as a component in PVC heat stabilizers.

Table 28.2 Estimates [16] of global plasticizer consumption, 2009

Plasticizer Type	Percent
Phthalate esters	85
Dibasic acid esters	3
Trimellitate esters	2
Epoxy plasticizers	2
Polymeric plasticizers	2
Benzoate esters	1
Cyclohexanoates	<1
Phosphates	<1
Terephthalates	1
Citrates	<1
Others	2

28.4 Phthalate Esters

Phthalate esters represent the largest chemical class of plasticizers, with DEHP and DINP being the most important plasticizers globally. Phthalate esters are prepared by the esterification of phthalic anhydride with two molar equivalents of an alcohol or an alcohol blend. Although almost any alcohol can be used to make a phthalate ester, it is usually only the esters of the C6 to C13 alcohols that are useful as PVC plasticizers. Esters made with C4 or C5 alcohols produce plasticizers with high-volatile losses, while phthalate esters made from alcohols with carbon numbers greater than C13 are not compatible with PVC. Performance of the plasticizer can vary greatly with changes in carbon number.

Improvements in plasticizer performance can be obtained through the choices in the level of branching of the alcohol used to make the phthalate esters. Krauskopf has examined this relationship with plasticizer performance [17] and has developed a number of correlations that can be used to predict plasticizer performance in flexible PVC as the molecular weight and the linearity of the alcohol is varied. These observations are shown in Table 28.3. As plasticizer alcohol linearity is increased, it yields plasticizers with improved performance in reduced volatility, lower plastisol

Table 28.3 Generalized effects of alcohol structure on performance of plasticizers [17]

Characteristics	Increasing Mol. Wt.	Increasing Branching	Increasing Aromaticity
Compatibility	Decreases	Independent	Increases
Solvency	Decreases	Independent	Increases
Efficiency (Shore A hardness)	Decreases	Decreases	Decreases
Low-temperature flexibility			
at equal concentrations	Independent	Impaired	Impaired
at equal hardness	Improved	Impaired	Impaired
Permanence			
Migration resistance	Improves	Improves	Improves
Volatilization losses	Improves	Impaired	Improves

viscosities, better outdoor or UV aging resistance, and improved low-temperature flexibility. Increased plasticizer alcohol branching is associated with improved plasticizer compatibility, decreased plasticizer mobility, and increased plasticizer electrical resistivity. As plasticizer molecular weight is increased, plasticizer volatility losses improve, migration resistance to many materials improves, and low-temperature flexibility at equal hardness comparisons improves slightly. HMW plasticizers are deficient in their ability to soften the PVC resin and are more difficult to process.

With flexible PVC processing, an almost linear relationship between alcohol carbon number of the phthalate ester and the fusion or processing temperature [18], where the fusion temperature requirement increases by about 7−8 °C per increase in carbon number of the alcohol, has been observed. Phthalate esters prepared from HMW C10 to C13 alcohols are used to prepare plasticizers for low-volatility applications, such as those required for electrical cable insulation and sheathing or automotive interior materials. Additional data on the relationships of phthalate performance versus carbon number can be found in Wypych's text, *Handbook of Plasticizers* [19].

28.5 Dibasic Acid Esters

Aliphatic dicarboxylic acid esters are prepared by the esterification of diacids such as adipic or azelaic acid with C6 to C10 monohydric alcohols. This class of plasticizer is usually used to help extend the useful temperature range of plasticized PVC products, by providing increased flexibility at lower temperatures. DEHA, which is prepared by the esterification of one mole of adipic acid with two moles of 2-ethyl hexanol, is the most important plasticizer in this class. Another important adipate is diisononyl adipate (DINA) which offers greater permanence over DEHA. Di-2-ethylhexyl azelate (DEHZ), di-2-ethylhexyl sebacate (DEHS), and diisodecyl adipate (DIDA) are used for extremely demanding low-temperature applications or low-temperature applications requiring lower volatility over that of DEHA. The adipate and azelate esters may be used as primary or as secondary plasticizers.

28.6 Trimellitate Esters

Trimellitate esters are used as primary plasticizers in those applications where greater permanence is required. These esters, prepared by the esterification of trimellitic anhydride with three molar equivalents of alcohol, are similar in structure to the phthalic acid esters, except the third ester functionality on the aromatic ring gives HMW and improved compatibility with PVC. Trimellitate esters offer advantages with greater permanence, either by reduced volatility losses or losses attributed to lower migration rates into other materials. Plasticized PVC electrical wire insulation prepared from either tri-2-ethylhexyl trimellitate (TOTM) or the more permanent plasticizer, triisononyl trimellitate (TINTM), will survive longer periods of high-temperature service versus those products prepared from more volatile phthalate plasticizers. Trimellitate esters prepared with linear alcohols in the C6 to C8 range show improved resistance to outdoor weathering and are in automotive instrument panels.

28.7 Terephthalate Esters

Terephthalate plasticizers are very similar in structure to phthalates except the substitution of the aromatic ring is at the 1,4 position versus the 1,2 position of the aromatic ring. Terephthalates are prepared by the esterification of terephthalic acid or the transesterification of dimethyl terephthalate with aliphatic alcohols such as butanol or 2-ethyl hexanol. In general, terephthalate esters are not as compatible in PVC and are more difficult to process when compared to other phthalates of the same carbon numbers. Terephthalate esters prepared with C10 and higher carbon number alcohols will have high levels of exudation and are poor plasticizers. Today, there is essentially only one important terephthalate plasticizer commercially available, DEHTP (DOTP), although another terephthalate ester based on C4 alcohols is being introduced for use in plasticizer blends to help improve processability [20] of DEHTP. Some HMW terephthalate esters are also being test marketed in Asia Pacific, but the expected compatibility and processing problems will greatly restrict their acceptance.

28.8 Cyclohexanoate Esters

Cyclohexanedicarboxylic acid esters or hexahydrophthalate esters have been used as plasticizers for many years, first being prepared in Germany by the hydrogenation of lower molecular weight phthalates, dimethyl phthalate, diethyl phthalate, and possibly dibutyl phthalate. These were offered as nitrocellulose plasticizers in the 1930s [21]. In the 1970s Union Carbide offered as a PVC plasticizer, their cyclohexanedicarboxylic acid ester Flexol™ CC55, which was prepared by an alternative route: esterification of hexahydrophthalic anhydride with 2-ethyl hexanol. In the 1990s a further extension of the 1920s hydrogenation technology was developed, by hydrogenating the plasticizer DINP to produce the cyclohexanedicarboxylic acid ester of isononyl alcohol. This product is now available as Hexamol™ DINCH and has some popularity as a phthalate alternative in toys and food contact products.

28.9 Citrate Esters

Citrates have been used as PVC plasticizers in specialty applications for many years. Citrate esters are prepared by the esterification of citric acid with three molar equivalents of *n*-butanol or *n*-hexanol. As this step does not convert the hydroxyl group of the citric acid, and the free hydroxyl group can create long-term compatibility problems, the hydroxyl group needs to be converted to an ester in a separate step. This is accomplished through esterification with acetic acid or acetic anhydride.

Citrates are relatively fast-fusing plasticizers, especially when compared to many of the phthalate alternatives. Unfortunately, citrates are not as permanent and will migrate into other materials. Citrates are often used in blends with the harder-to-process terephthalate or cyclohexanoate plasticizers. They also find uses with other plastics such as acrylics, cellulosic polymers, and vinyl acetate.

28.10 Benzoate Esters

Benzoic acid-based plasticizers have been commercially available for more than 50 years. Although there are a variety of different types [22], most can be classified as dibenzoate esters or monobenzoate esters. Dibenzoate esters are prepared by the esterification of two molar equivalents of benzoic acid with a glycol such as ethylene glycol, propylene glycol, diethylene glycol, triethylene glycol, or dipropylene glycol. They are relatively faster fusing plasticizers and find a variety of applications in plastisol processes like spread coating, especially when used in blends with plasticizers such as DINP or DEHTP or in custom or proprietary blends with other benzoate esters. The advantages benzoate plasticizers bring are improved processability, improved stain resistance, and better UV stability; unfortunately, they have higher densities, reduced low-temperature flexibility, and do give higher plastisol viscosities.

Monobenzoate esters are prepared by the esterification of benzoic acid with one molar equivalent of alcohol, usually 2-ethyl hexanol, isononanol, or isodecanol. Monobenzoates are not used as primary plasticizers but as secondary plasticizers where they help reduce plastisol viscosities, lower the fusion or processing temperatures, and give a boost to stain resistance in formulations based on GP plasticizers. Mono and dibenzoate esters are used in non-PVC materials such as acrylic films and caulks, latex coatings, polysulfide sealants and coatings, and polyurethanes.

28.11 Phosphate Esters

One of the very first plasticizers proposed for PVC was the phosphate ester, tricresyl phosphate. This plasticizer was later used for its flame-resistant properties in the first commercial PVC electrical wire insulation materials. Today, the majority of the phosphate esters used as plasticizers are the alkyl diaryl phosphates, prepared with mixtures of various phenols and alcohols, often used in combination with GP plasticizers such as DINP or DIDP. Phosphate esters provide significant improvement in flame retarding properties and for some products, reduced smoke generation. This property helps enable flexible PVC materials to be used in plenum cables, data and communication cables, and electronics. Phosphates such as isodecyl diphenyl phosphate can also be used in transportation fabrics and wall coverings where some level of flame retardant properties is required.

28.12 Modified Vegetable/Plant Oil Esters

Vegetable oils and modified vegetable oils have been used for plasticizers for over 150 years, starting with nitrocellulose plastics and coatings. For plasticization of PVC, some of the early plasticizers were acetylated esters of ricinoleic acid, which is obtained from castor oil. ESO was at one time promoted as primary plasticizer for PVC and a potential DEHP replacement. Although the products produced with this plasticizer had acceptable initial qualities, after a few months, exudation and incompatibility problems developed. Today, the use of ESO in PVC is limited to relatively low concentrations, where it serves as a PVC costabilizer.

To improve the use of soybean oil as a raw material to produce a GP plasticizer, Battelle Institute developed their soyate technology [23] where they isolated the soyic acids, prepared the epoxides, and converted these to selected esters which have utility as PVC plasticizers. Others have expanded this technology, looking at mono and di-glycerol esters and various monoesters of the epoxidized soyic acids [24].

In Europe, a new modified castor oil plasticizer is being produced, similar in structure to the ricinoleic acid esters. Instead of taking castor oil and isolating the acids, the technology leaves one of the acid groups attached to glycerol molecule. In the final step, the hydroxyl groups of the glycerol and on the ricinoleic acid are all reacted with acetic anhydride, giving in effect a tetra ester [25]. Although this product has some performance properties in the GP range, the high-price premiums for this product limit it to only a few applications.

28.13 Polyester Plasticizers

The largest class of polymeric plasticizers is the polyesters which are prepared by the reaction of differing diols, dibasic acids (such as adipic acid or phthalic anhydride), and an aliphatic primary alcohol or an aliphatic acid acting as a chain stopper to help control the molecular weight. These products typically range from high viscosity liquids to gels or semisolids at room temperature. Polymeric plasticizers offer improved performance in resistance of plasticizer extraction by solvents or oils, resistance to migration to coatings or other plastics, and reduced volatility. However, they are more expensive, more difficult to process, and have serious limitations in plastisol applications because of the high viscosity. Polymeric plasticizers are sometimes blended with a low-volatility plasticizer such as DIDP to help improve processability and to reduce costs. Applications for polymeric plasticizers include vinyl decals, vinyl electrical tape, gaskets for refrigerators, extraction-resistant hose, and non-migrating inks.

28.14 Plasticizer Characteristics and Performance of Flexible PVC

A change in both the type and the level of the plasticizer concentration will affect the properties of the finished flexible article. In most cases, the choice of plasticizer or plasticizer blend is a compromise between meeting the minimum performance requirements and achieving the lowest product cost. Some of the more important properties that should be considered when choosing a plasticizer include low-temperature flexibility, flammability, volatility, automotive fogging performance, UV resistance, water or oil extraction resistance, processability, plastisol volatility, migration resistance, regulatory approval status, final product color, and, of course, overall costs.

Plasticizers are added to materials to make them softer and more flexible; the efficiency at which this is accomplished varies from plasticizer to plasticizer as shown in Figure 28.1, where the Shore A hardness values of several plasticizers are reported at various plasticizer concentrations. The term *plasticizer efficiency* is used to describe the ability of a plasticizer to make the product softer and can be reported as a ratio of the slope of the hardness versus concentration for one plasticizer relative to the slope of that found for DEHP. The efficiencies for some of the more important plasticizers are included in Table 28.1. By convention, the efficiency of DEHP is defined as 1.00. DINP, being less efficient than DEHP, requires additional plasticizer to achieve the same level of hardness. To substitute DINP for DEHP with an equal hardness formulation, one would multiply the concentration in phr of DEHP by the efficiency of DINP which is 1.06. Therefore, in most formulations, DINP would require about 6% additional plasticizer to achieve the same hardness as the DEHP formulation. More efficient plasticizers such as DEHA or BBP would require lesser amounts of plasticizer to achieve the same Shore A hardness.

An important performance requirement with any plasticizer is that it must be compatible with the polymer. *Compatibility* is the ability of two or more substances to mix with each other and form a useful product; when a PVC system has compatibility problems, exudation or spew will occur. This can also be aggravated by stress, prolonged exposure to high humidity or high temperature, or through UV exposure. Plasticizers with solubility parameters and polarity and hydrogen bonding characteristics similar to that of the polymer would be expected to have good compatibility. Plasticizers with greatly differing solubility parameters would have poor compatibility. It is important to note that in most cases of exudation involving the more common

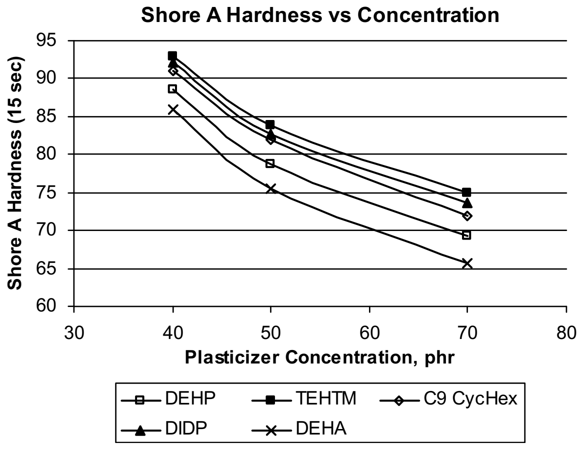

Figure 28.1 Shore A hardness of plasticized PVC.

plasticizers, the causative agent is not the plasticizer itself but rather other factors such as poor choice of stabilizer or partially decomposed stabilizers, excessive use of lubricants, certain organic dyes, pigments, and other additives. These all impact the overall compatibility of those additives as well as the plasticizers.

Plasticizer volatilization is directly related to the vapor pressure of the plasticizer. Volatilization losses will occur during processing and during use at elevated temperatures. Changes of as little as one carbon number of the alcohol group in a common series of esters can lead to significant reductions in losses as shown in Figure 28.2. For example, by substitution of DEHP in a flexible PVC formulation with DINP, the amount of volatile loss will be reduced by more than 50%. A C10 phthalate will have about one-third the losses of a DEHP formulation. If very low volatility losses are required, trimellitate plasticizers and polymeric plasticizers are used.

Plasticizers can be extracted from PVC in contact with water or other solvents. Plasticizer molecular size and plasticizer solubility in the extractant are the most important factor in providing resistance to plasticizer migration or extraction. Water extracts plasticizers from PVC very slowly while hydrocarbon solvents are very aggressive. As the plasticizer molecular size increases, the tendency for plasticizer migration or extraction is reduced, especially into water. Polymeric plasticizers are very effective in providing migration or extraction resistance. Within a given series of esters, branched plasticizers offer better extraction and migration resistance than linear plasticizers.

The addition of plasticizers to a PVC product extends the lower useful temperature limit of the finished product. Generally, the lower temperature performance is enhanced as the plasticizer concentration is increased. Some plasticizers are more efficient in providing low-temperature flexibility than others. Aliphatic diesters of adipic, azelaic, and sebacic acids are the preferred plasticizers for very low temperature requirements. In addition, the linear phthalates based on linear C9 alcohols, linear C11 alcohols, and the linear C9/C11 blends offer enhanced low-temperature performance over the corresponding branched esters. The low-temperature flexibility for PVC plasticized with several esters is shown in Figure 28.3.

Rigid PVC is inherently fire resistant and self-extinguishing; however, the addition of plasticizers such as phthalates, adipates, and trimellitates contributes to flammability. The triaryl and alkylaryl phosphates and brominated phthalate plasticizers inhibit burning of plasticized PVC. These products are often blended with other plasticizers to achieve a balance of flame resistance, physical properties, and cost. Chlorinated paraffins can also be used as secondary plasticizers, to help reduce flammability and smoke; however their high volatility, chlorine content, and potential compatibility problems restricts their use to but a few end-uses. Flame resistance or smoke suppression may also be gained through addition of various additives into the flexible PVC formulation. These additives include antimony trioxide, alumina trihydrate, molybdenum ammonium octanoate, and zinc borate.

In the processing of plastisols, plastisol viscosities at shear rates associated with the manufacturing process technology

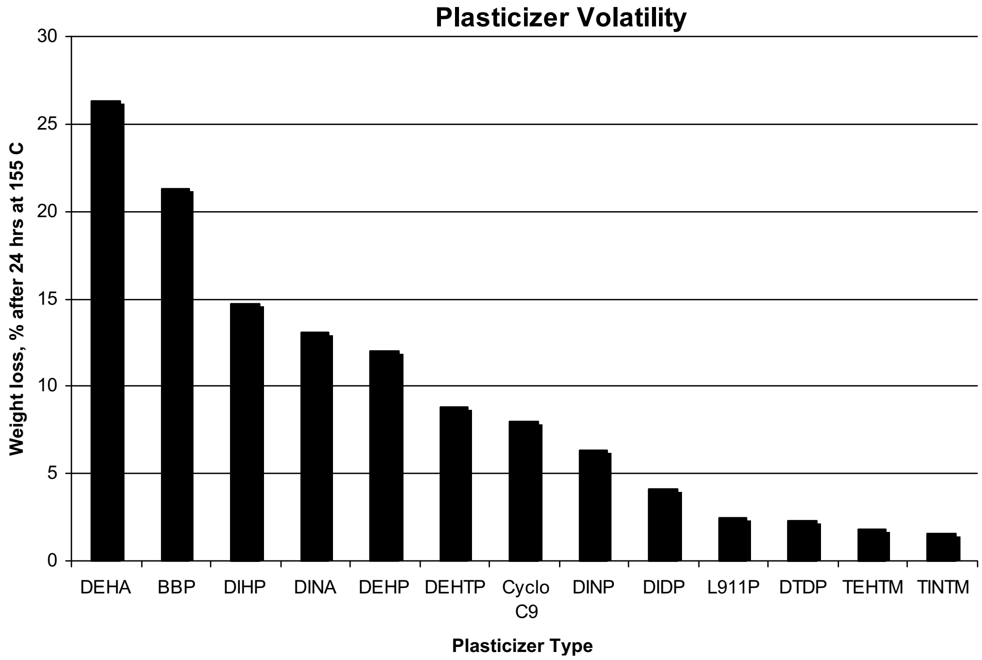

Figure 28.2 Volatility of selected plasticizers.

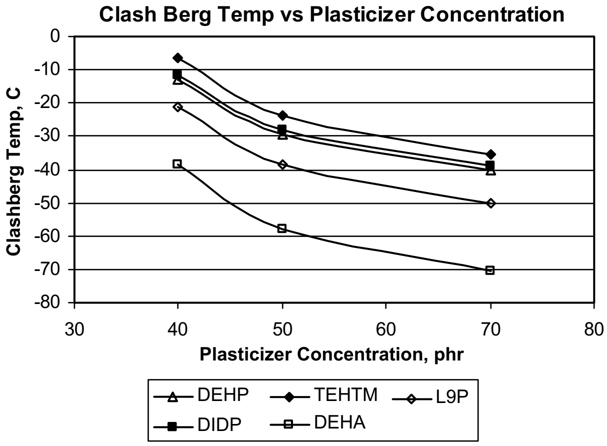

Figure 28.3 Low temperature flexibility of flexible PVC.

is important. Using lower molecular weight or linear plasticizers will yield lower plastisol viscosities when compared at equal concentrations. However, once the formulations are adjusted for equal hardness by taking into account the efficiency differences of the plasticizers, less-efficient plasticizers will often yield equal or lower plastisol viscosities. For example, even though DEHP gives a lower plastisol viscosity than DINP at the same concentration, at equal hardness formulations, the DINP-based plastisol has lower viscosity.

Most finished plastic products or articles are sold by the unit or by volume; however, the raw materials used to prepare the product are purchased and formulated by weight. Thus when the costs to prepare the product are calculated, it should be determined on a cost per unit or cost per volume basis. Ingredients with lower specific gravities will give an increase in the number of units and thus plasticizers with lower specific gravities will often yield lower costs per unit or lower volume costs. Plasticizer efficiency is also important in determining volume costs. Often, but not always, the volume costs for PVC polymer can be higher than the volume cost of the plasticizers because of the high specific gravity of the polymer. Thus, as more of the lower-volume-cost plasticizers are added to the polymer, the volume cost of the finished product decreases. Less-efficient plasticizers will require higher levels of addition to achieve the same degree of hardness which leads to additional savings.

28.15 Plasticizer Selection for Specific Applications

Plasticizer selection involves trying to meet a combination of end-use performance requirements, processing needs, cost, and in some cases, specific regulatory requirements. Products produced from flexible PVC are used in a wide range of applications and industry market segments. Table 28.4 lists a breakdown of the usage of plasticizers by different market segments.

Table 28.4 Plasticizer market segments and flexible PVC applications [5]

Share, %	Segment
35	Film, sheet and coated substrates
19	Wire and cable
12	Extruded and molded
8	Floor coverings
7	Adhesive, sealants and caulks
5	Regulated, food and medical
14	Miscellaneous

The largest market sector for plasticizers is the film, sheet, and coated fabric market sector. These products are manufactured by calendering, extrusion, cast films, and spread coating processes and are used to produce a wide variety of products including table cloths, packaging films, swimming pool liners, tarpaulins, agriculture films, wall coverings, office products, awnings, shower curtains, upholstery fabrics, and shoe fabrics. The majority of these products will use the GP plasticizers DEHP, DINP, DIDP, and DPHP although some products may incorporate specialty plasticizers to improve performance attributes. Linear phthalate esters such as linear dinonyl phthalate (L9P) or linear diundecyl phthalate (L11P or DUP) are used for improved UV resistance. The faster fusing plasticizers (BBP, DIHP) are added to help improve the processability in spread coating. Plasticizers such as DIDP or DPHP are used for products needing greater permanence; automotive interior trim applications will focus on DIDP, DPHP, L9P, L911P, L11P, and trimellitates to meet fogging requirements. Adipate esters (DEHA, DINA) can be added to the phthalate esters in other film and sheet products to improve the low-temperature performance.

Another large end-use for flexible PVC is wire and cable. With electrical cables, plasticizer selection is dependent upon the performance specifications of the insulation material and the jacketing. Higher temperature rated products require more permanent plasticizers, while lower temperature rated materials can use GP plasticizers. In the United States, building wire insulation is typically formulated with trimellitate plasticizers such as TOTM or TINTM blended with the heavier molecular weight phthalates such as DTDP or DUP to help reduce costs and improve processing. Jacketing compounds can use DINP, DIDP, DPHP, and in some cases DEHTP.

Cushioned vinyl flooring is prepared by coating a substrate with various layers of plastisols. These products generally use a mixture of plasticizers such as DIHP, DEHP, DINP, and DEHTP often in blends with faster fusing plasticizers such as monobenzoates, dibenzoates, or BBP. Vinyl floor tiles and other sheet flooring are produced by calendering; again GP plasticizers, often used in blends with fast-fusing plasticizers, are commonly used. Plasticized PVC is also a major component of some types of carpets and carpet tiles, either as an adhesive or as a backing material. Faster fusing plasticizers such as DIHP offer advantages over DINP or DEHTP because of the lower fusion temperature, which is desirable to protect the carpet fibers.

Many molded and extruded products are prepared from GP plasticizers with DINP offering the best compromise between price and performance. Products designed for outdoor applications will often use more permanent plasticizers such as DIDP, DPHP, L9P, or L911P. Many medical devices still continue to use DEHP because of its very long history of safe use and product approvals. In the toy market, the industry has moved using non-phthalate plasticizers such as citrates, benzoates, DEHTP, and the C9 cyclohexanoate ester. Because of the processing problems with DEHTP and C9 cyclohexanoates versus the traditional GP plasticizers, blends of these esters with citrate plasticizers, dibenzoate plasticizers, and lower molecular weight aliphatic diesters are becoming popular [26].

In addition to these major market segments, plasticizers are used in a variety of smaller segments. Adhesives and sealants generally use lower molecular weight phthalate esters because of improved solvency and lower fusion temperatures. One major use of plasticized PVC is automotive underbody coatings; these products are highly filled plastisols that are commonly based upon GP plasticizers often with a fast-fusing plasticizer added to improve processability.

28.16 Plasticizers for Other Polymers

Polymers other than PVC account for $<10\%$ of the current worldwide plasticizer usage. While the combination of PVC polymer, plasticizers, and other additives can yield an extensive range of flexible products with varying performance characteristics, plasticizer usage with other polymers does not produce the same level of versatility. More often plasticizers are used with other polymer systems for processing improvements rather than for producing flexible products.

Plasticizers can be used with acrylic polymers to produce flexible coatings, caulks, and sealants, sometimes serving a role as a coalescing agent instead of plasticizer. Most of the common phthalates and adipates have been described as having some compatibility with acrylic systems, although the number of plasticizers having acceptable performance is smaller than those listed for PVC. The most common plasticizers used are BBP, DIHP, and dibenzoate esters and benzoate ester blends. Dibutyl phthalate was used in these applications for many years, but its use is rapidly declining.

Polyvinyl acetate (PVAc) emulsion polymers are used for adhesives, sealants, and paints. PVAc homopolymer is too brittle for most end-uses, so much of the PVAc used in the paint industry is internally plasticized through the incorporation of comonomers into the polymer backbone. However, there are some uses of externally plasticized PVAc in adhesives. The most common plasticizers used with adhesives are a variety of benzoate esters.

Nylon is a highly crystalline material and, as such, plasticization can only occur at very low levels. Plasticizers used with nylon are typically sulfonamides, as these products are significantly more compatible with nylon than phthalates. Sulfonamides can be used as nylon flow aids, to retard degradation and to speed up processing.

Many rubbers and elastomers are comprised of long hydrocarbon segments, and thus can accept petroleum oils and other predominately hydrocarbon products for use as plasticizer or extenders. These products are available at a significantly lower cost than the synthetic ester plasticizers. Phthalates and adipates of linear alcohols are used to enhance low-temperature properties of certain rubber applications, which cannot be met using the hydrocarbon extenders. Polar elastomers such as nitrile rubber and polychloroprene have low compatibility with hydrocarbons and require more polar products such as phthalates or adipates.

Plasticized PVB is used as a laminating film between layers of glass to provide strength and shatter resistance. This forms the "safety" glass used in automobile windshields and architectural glass. PVB can be plasticized with a variety of esters, but in practice only a few products are used as the plasticizer selection is a complicated process. The most common plasticizers used in safety glass film are the di-2-ethylhexanoic acid esters of tri- or tetra-ethylene glycol. These esters give excellent compatibility, clarity, and resistance to sunlight.

Many cellulosic materials, including cellulose nitrate, are compatible with relatively high levels of plasticizers. Plasticizers are used to reduce processing temperatures, improve impact resistance, and to increase flexibility and resistance to cracking in these materials. Cellulose acetate can be plasticized with more polar esters such as dimethyl and diethyl phthalate. Cellulose nitrate, on the other hand, shows better compatibility with many of the PVC type plasticizers including BBP, DBP, DINP, dibenzoates, terephthalates, and cyclohexanoate esters.

Plasticizers can be used to reduce both the viscosity and the cost of polyurethane and polysulfide automotive and construction sealants. HMW phthalate esters such as DINP, DIDP, and DUP or L11P are generally suitable for most polyurethane sealant applications. Polysulfide sealants require more polar plasticizers such as the alkyl benzyl phthalates, alkyl sulfonic acid esters, or dibenzoate esters.

Diluents or plasticizers for epoxy resins lower the viscosity of the uncrosslinked resin for greater ease in application of surface coatings and adhesives. Non-reactive plasticizers such as phthalates and phosphates will reduce the viscosity but lead to poor impact resistance and lower the extraction resistance. Reactive plasticizers are low molecular weight epoxy compounds, typically having one reactive epoxy group per molecule. These contribute to lengthening the polymer segments between crosslinks and produce a slight softening and flexibility effect with impaired impact strength. The products used include a variety of glycidyl esters or ethers.

28.17 Human Health Aspects of Plasticizers

The increased attention in recent years about the safety and risks associated with phthalate ester plasticizers can be attributed to the restrictions initially imposed in Europe on the use of 6 phthalates in toys. Since this ban was temporarily placed in 1999, it has expanded to include several other countries and in 2008, it was applied toward toys and childcare articles sold in the US. With the passage of the Consumer Product Safety Improvement Act (CPSIA), three plasticizers DBP, DEHP, and BBP are now banned from all toys for children up to age twelve and childcare articles for children up to age three. Three other plasticizers, DINP, DIDP, and DnOP (a component of the phthalate plasticizer blend 610P), have a temporary restriction for childcare articles for children up to age three and for toys intended for the mouth up to age twelve.

The Consumer Product Safety Improvement Act (CPSIA) also required that the risks associated with the use of DINP, DIDP, and DnOP be evaluated by a Chronic Hazard Advisory Panel (CHAP); this panel must also evaluate the risks from non-phthalate alternative plasticizers that are presently being used in toys. The restrictions in toys for the HMW phthalates DINP and DIDP occurred in spite of very favorable and positive outcomes from very extensive reviews by various government agencies around the world. It is expected that this CHAP will follow sound scientific principles with a risk assessment and arrive at the same conclusion as a previous CHAP [27] and other review panels [28], concluding that the HMW phthalates DINP and DIDP are safe for use in all applications including toys.

The concerns with phthalates were originally raised in 1982 with the report by the National Toxicology Program [29] (NTP) that rats and mice when fed diets with high levels of DEHP for almost a year, developed liver tumors. The high doses of DEHP used in this test were excessive and equivalent to a human drinking about a cup of liquid plasticizer per day, every day, for many years. Ironically, this high dosing level was only made possible by the extremely low acute toxicity of DEHP. Based on these results, the International Agency for Research into Cancer (IARC) agency listed DEHP as “probably carcinogenic to humans”. (The IARC has since reclassified DEHP to “not classifiable” as to its carcinogenicity to humans after careful review of all the data on DEHP.)

Since this study was published, the health aspects and associated risks with phthalates have continued to be tested, evaluated, and debated by various governmental organizations globally. The consensus developing from studies and scientific reviews suggests that rats seem to have problems when eating large amounts of lower molecular weight phthalate esters made with alcohols containing a carbon backbone length of four to six carbons (e.g., DBP, DEHP, DIHP). Upon eating large amounts of HMW phthalate esters prepared from alcohol having backbones of seven or greater carbon numbers, rats and mice show much reduced effects. It must be noted that the potential hazards identified for rats with the lower molecular weight phthalates do not necessarily mean that these particular phthalates present human health concerns, for the effects observed occur at very high levels in only rats and mice, and far exceed typical exposure levels.

In Europe, after publication of several extensive analyses and risk assessments for several of the more important phthalates, several phthalates with the C4−C6 backbones were listed with a Category 2 or Category 3 CMR (Carcinogenic, Mutagenic, or Reproductively-toxic) label, while the HMW phthalates made with alcohols having backbones ≥ 7 carbon numbers were not classified (Table 28.5). In fact, the EU DINP and DIDP risk assessments [30,31] were favorable, reporting that the sources of exposure to these products are unlikely to pose a risk for workers, consumers, or human health following inhalation, skin contact and ingestion, and that there is no need for further risk reduction measures beyond those already being applied.

In more recent news, the plasticizers DINP and DIDP were two of the first plasticizers to be registered under the EU’s REACH legislation. These early REACH registrations have been facilitated by the comprehensive toxicological and environmental data on these substances, as well as the EU Risk Assessment Reports that have demonstrated safe use. The registration was also facilitated by DINP’s and DIDP’s status as non-classified substances without PBT (persistent, bioaccumulating and toxic) or vPvB (very persistent, very bioaccumulating) properties.

28.18 Future of Plasticizers

The future of plasticizers and plasticized PVC is tied very closely to the future of phthalates. The top performing and lowest cost plasticizers are the GP phthalate esters, and of all the thousands of non-phthalate ideas proposed, nothing to date has been developed to equal the attributes offered with phthalates. As formulations change to non-phthalate systems, the flexible PVC products obtained with those alternatives will not perform as well and will often be more expensive. If phthalate deselection accelerates, anticipated non-phthalate plasticizer shortages will create even higher product costs. Thus, with poorer performing, more expensive plasticizers, the opportunities for intermaterial substitution to replace flexible PVC with other polymer systems will increase.

Table 28.5 European union CMR classification of phthalate esters

	Alcohol Carbon	EU Classification and Labeling		
Phthalate	**Backbone Length**	**Cancer**	**Fertility**	**Development**
DBP	4	None	Cat 3	Cat 2
BBP	4	None	Cat 3	Cat 2
DIHP	5–6	None	None	Cat 2
DEHP	6	None	Cat 2	Cat 2
DINP	7–8	None	None	None
DIDP	8	None	None	None
DPHP	7	None	None	None
911P (slightly branched)	7–11	None	None	None

Cat 2 = Category 2, suspicion of human effects based on animal studies.
Cat 3 = Category 3, some evidence of effects in animals but insufficient to presume a link in humans.

There have always been phthalate alternatives available to anyone who wanted to use them, although in limited volumes. Of perhaps more than 300 different plasticizers that went into some sort of commercial production or test marketing in the past 70 years, $<20\%$ were phthalate esters; the rest were non-phthalate plasticizers, a fact that is missed by many critics. The reasons that phthalate esters represent the most important class of plasticizers is that they continue to offer the best performance at the lowest cost and are available in sufficient quantities to meet market demands. Non-phthalate plasticizers have traditionally been used in situations were a phthalate ester could not meet the performance requirement, and the application could support an increased price premium to offset the higher costs of the non-phthalate plasticizer. Additionally, many of these non-phthalates are actually used in blends with other phthalates. Nevertheless, active research continues to look for new plasticizers, with the goal that the next idea generated will possibly offer general-performance potential and competitive pricing, a goal that has yet to materialize.

Meanwhile, the phthalate producers and the major phthalate users continue to test, evaluate, and promote the virtues and safe use of the HMW phthalates, DINP, DPHP, and DIDP, with the ultimate goal being that any future legislative action involving the use of phthalates will be based on sound scientific principles.

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29 Adhesion Promoters: Silane Coupling Agents

Peter G. Pape
Peter G Pape Consulting, 3575 E. Marcus Drive, Saginaw, MI 48603, USA

29.1 General Concepts

Adhesion promoters, or coupling agents, are chemicals that act at the interface between an organic polymer and an inorganic surface to enhance adhesion between the two materials. Organic and inorganic materials are very different in many ways, e.g., compatibility, chemical reactivity, surface properties, and coefficient of thermal expansion, such that it is very difficult to form a strong adhesive bond between these two dissimilar materials. An adhesion promoter, in its optimal sense, will act effectively at the organic/inorganic interfacial region to chemically and physically wed these dissimilar materials into a strong cohesive bond structure. Other surface modification approaches to improve adhesion can involve chemical modification of the polymer surface via oxidation with ozone or plasma and physical and chemical abrasion of the inorganic substrate to increase the bonding surface area by altering the surface roughness. While the latter approaches can enhance adhesion, the use of adhesion promoters, or coupling agents, will not only alter physical and chemical forces at the interface but also provide a "glue," or compatibility bridge, to give a much greater level of adhesion. Additionally, adhesion promoters can impart resistance to environmental and other destructive forces, such as heat and moisture, that often act on the bonded site to destroy adhesive strength. The inherent chemical and physical nature of organosilane coupling agents are such that they are the predominant chemical type that are used as adhesion promoters and, therefore, will be the main focus of this chapter.

29.2 Nature of Silane Adhesion Promoters

29.2.1 Typical Silane Coupling Agents

A silicon-based chemical that will function as an adhesion promoter, or a coupling agent, has a general structure of four substituents attached to a single silicon atom. The most common structure has three inorganic-reactive alkoxy groups, methoxy or ethoxy, and one organic group (see Figure 29.1), although sometimes it may contain only two alkoxy groups and two organic groups. The organic group can be either reactive (amino, epoxy, methacrylate, etc.) or unreactive (methyl, butyl, octyl, phenyl, etc.). Coupling agents with many different organofunctional types are commercially available. Typical commercial coupling agents are listed in Tables 29.1 and 29.2.

29.2.2 Silane Chemistry

Silicon is in the same family of elements as carbon in the periodic table, but silicon compounds exhibit significant differences in chemical reactivity compared to analogous carbon-based compounds. Similar to carbon, silicon will conveniently bond to four substituents in its most stable state, but silicon is more electropositive than carbon, does not form stable double bonds, and is capable of very special and useful chemical reactions. A silicon molecule can be synthesized which has dual reactivity, i.e., one silicon molecule can contain both organic and inorganic reactivity. The unique nature of silane chemistry to have both inorganic and organic reactivity in one molecular structure gives rise to the use of silane chemicals as coupling agents and adhesion promoters.

Monomeric silicon chemicals are known as silanes. A silane has the chemical formula 1 in which R_2 | $R_1{-}Si{-}R_4$ **1** | R_3. R_1, R_2, R_3, and R_4 can be the same substituent or four different substituents. The electropositive nature of the silicon atom causes certain atoms or groups attached directly to silicon to be very reactive and exhibit inorganic rather than organic reactivity. Silane substituents such as chlorine, amine, methoxy, acetoxy, or hydroxyl are reactive with inorganic materials that contain hydroxyl groups, such as

General Structure : $R_xSi(OR')_y$ $x + y = 4$

- R= alkyl, aryl, or organofunctional group
- OR'= methoxy or ethoxy
- Examples:

$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2Si(OCH_2CH_3)_3$
(n-Octyltriethoxysilane)

$H_2NCH_2CH_2NHCH_2CH_2CH_2Si(OCH_3)_3$
(Aminoethylaminopropyltrimethoxysilane)

Figure 29.1 General structure of silane coupling agents.

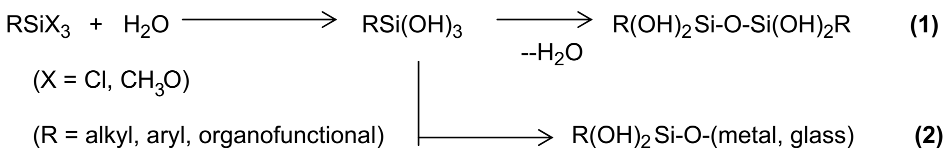
Table 29.1 Silane coupling agents: Part 1. Match organic group to polymer type

Chemical Type	Chemical Name	Polymer
Amine	Aminopropyltriethoxysilane	Acrylic, Nylon, Epoxy, Phenolics, PVC, Urethanes, Melamines, Nitrile Rubber
Diamine	Diaminopropyltrimethoxysilane	Acrylic, Nylon, Epoxy, Phenolics, PVC, Melamines, Urethanes, Nitrile Rubber
Methacrylate	3-Methacryloxypropyltrimethoxysilane	Unsaturated Polyesters, Acrylics, EVA, Polyolefin
Epoxy	3-Glycidoxypropyltrimethoxysilane	Epoxy, PBT, Urethanes, Acrylics, Polysulfides
Methyl	Methyltrimethoxysilane	Hydrophobing agent for mineral surfaces
Isobutyl	Isobutyltrimethoxysilane	Hydrophobing agent for mineral surfaces, Masonry water repellent

Table 29.2 Silane coupling agents: Part 2. Match organic group to polymer type

Chemical Type	Chemical Name	Polymer Type/Application
Phenyl	Phenyltrimethoxysilane	Hydrophobing, dispersing aid for mineral surfaces, blends, hydrophobe, thermal stability
Octyl	Octyltriethoxysilane	Hydrophobing for mineral surfaces; Dispersion of minerals in polyolefins; Masonry water repellent
Vinyl	Vinyltrimethoxysilane	Graft to polyethylene for Moisture crosslinking, EPDM Rubber, SBR, polyolefin
Chloroalkyl	3-Chloropropyltrimethoxysilane	Urethanes, epoxy, nylon, phenolics, polyolefins
Chloroalkyl	3-Chloropropyltriethoxysilane	Urethanes, epoxy, nylon, phenolics, polyolefins
Vinylbenzylamino	Vinylbenzylaminotrimethoxysilane	Epoxies for PCB's, polyolefins, all polymer types

—Si—OH, —Al—OH, or metal—OH in glass, minerals, or metals. A silanol, —Si—OH, or silylamine, $—Si—NH_2$, is generally not stable and will condense rapidly to siloxane, —Si—O—Si—, or silazane, —Si—NH—Si—, respectively. A chlorosilane or a methoxysilane, $RSiX_3$, X = Cl or CH_3O, reacts with water (hydrolyzes) to give unstable silanetriol, $—Si(OH)_3$, which in turn will condense with a second silanetriol to form a siloxane, —Si—O—Si—, structure (reaction 1) or will react with available metal hydroxyls on a metal or glass surface to form a silicon—oxygen—metal bond with the inorganic substrate (reaction 29.2).



In order to be classified as an *organo*silane, one of the silane substituents must be an organic (carbon-based) group that is directly attached to silicon via a Si—C bond. Organic substituents attached to silicon can be either nonreactive, such as methyl, ethyl, butyl, octyl, and phenyl or can be organofunctional, i.e., contain an organic reactive group, such as amino, epoxy, methacrylate, sulfido, and isocyanato. An organic spacer group usually separates the organofunctional group from the central silicon atom. If the spacer group is at least three carbons in length, e.g., $—CH_2CH_2CH_2—$, then the organic reactivity of the organic group in the silane will be similar to organic analogs in carbon chemistry; if the spacer group is one or two carbons in length, then the silicon atom may influence the reactivity of the organic group. Other reactive silanes, particularly vinyl silanes, $—Si—CH=CH_2$, and silicon hydrides, —Si—H, are useful reactive groups in silicon chemistry; however, a silicon hydride is not classed as an organofunctional chemical.

29.3 Mechanism of Adhesion Promotion

29.3.1 The Interphase Region

Silane coupling agents will act in the interphase region, the area between an inorganic substrate (such as glass, metal, or mineral) and an organic substrate (such as an organic polymer, coating, or adhesive), and act as a bonding, or bridging, agent to improve the adhesion between the two dissimilar materials [1,2] (see Figure 29.2). Modification of the interphase region can produce other desirable changes: improve wet-out of the inorganic substrate by the polymer; improve dispersion of fillers in liquid polymers; reduce the viscosity of the uncured polymer/filler mixture; protect minerals against cleavage and heal flaws in the surface; and strengthen the polymer layer at the interface by interdiffusion with the coupling agent to form interpenetrating polymer networks (IPN) (see Figure 29.3).

The interface, or interphase region, between a polymer and an inorganic substrate involves a complex interplay of physical and chemical factors related to adhesion, physical strength, and retention of properties of the product. Adhesive bonds can be destroyed by migration of water into this interface to hydrolyze bonds and cause physical detachment. Silane coupling agents have unique chemical and physical properties to not only enhance bond strength, but also, more importantly, prevent debonding at the interface. In composites, often a 40% increase in flexural strength is obtained by the use of a silane coupling agent. Silane coupling agents give coatings and adhesives significantly increased bond strength and resistance to humidity and other adverse environmental conditions.

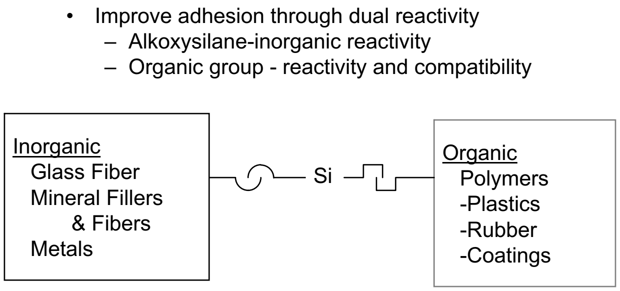

- Improve adhesion through dual reactivity
  - Alkoxysilane-inorganic reactivity
  - Organic group - reactivity and compatibility

Figure 29.2 Silane coupling agents—dual reactivity.

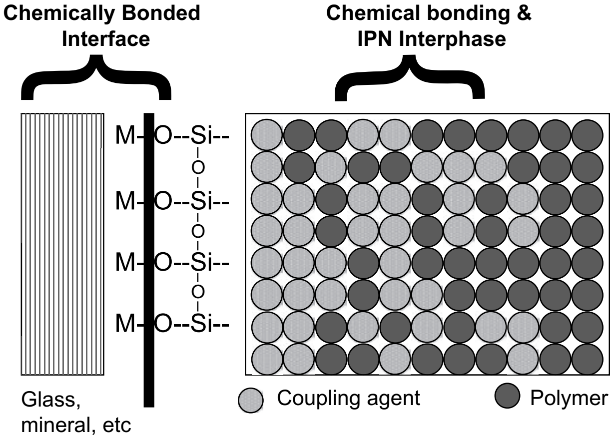


Figure 29.3 Interpenetrating network theory—bonding to polymers.

29.3.2 Bonding to the Inorganic Substrate

Silane coupling agents contain inorganic reactive groups on silicon and will bond well to most inorganic substrates, especially if the substrate contains silicon, aluminum, or most heavy metals in its structure. The alkoxy groups on silicon can hydrolyze to silanols, either with added water or from residual water on the inorganic surface (reaction 29.1). The silanols coordinate with metal hydroxyl groups on the inorganic surface to form an oxane bond with elimination of water (reaction 29.2). Studies of the mechanism of bond formation of silane coupling agents to inorganic substrates show covalent oxane bonds with silica and glass reinforcements [3]. Hydrolysis and reformation of siloxane bonds of silane coupling agents are in true equilibrium [4]. These bonds are hydrolyzed by water, but they reform rather easily. Acids and bases catalyze the rates of both hydrolysis and condensation. It is estimated that a trisilanol, $R'Si(OH)_3$ (the intermediate generated by a trialkoxysilane coupling agent), has an equilibrium constant 10^3 more favorable toward bonding to a silica substrate than the corresponding monoalkoxysilane. Trialkoxysilanes have approximately a tenfold equilibrium constant relative to dialkoxysilanes toward bonding to the inorganic substrate. So it is fortuitous that the original silane coupling agents were based on trialkoxysilanes rather than mono- or dialkoxysilanes since the equilibrium toward retention of bonding to the inorganic substrate is much greater with trialkoxysilanes.

The condensation of the silane silanols with other silanols at the interface gives a multimolecular structure of crosslinked siloxane on the inorganic surface. The crosslinked structure exists as multiple layers of siloxane with a very tight siloxane structure existing close to the inorganic surface and a more diffuse structure away from the surface. This "grid" type of structure allows organic coatings to interpenetrate, or diffuse, into the siloxane structure to allow electrostatic forces of interpenetration, very powerful adhesive forces, to become part of the bonding mechanism. A representation of this type of IPN structure is shown in Figure 29.3.

Once a silane coupling agent is attached to an inorganic surface, that surface takes on the surface chemistry and/or surface reactivity characteristics of the organic group attached to the silane coupling agent. The treated surface will exhibit the surface energy of the organic group, and the surface can become a reactive surface as determined by the reactivity of the organofunctional group in the silane coupling agent. A silane coupling agent or silane surface modifier can be selected to give the surface whatever property is desired to transform the nature of the surface into whatever is needed to allow optimization of the inorganic material for the intended use.

29.3.3 Bonding to the Organic Polymer

The interaction of the silane coupling agent with the organic polymer can be very complex. For a thermoset polymer the silane bonds to the polymer through chemical reactivities of the silane and polymer. The most important consideration is to match the reactivity of the silane coupling agent with the reactivity of the thermoset polymer [5]. Coupling agents have been shown to be optimum when the organofunctional group can participate in the curing mechanism or has some way of reactively attaching to the polymer structure in the final composite. For example, an epoxysilane and aminosilane can participate in the curing mechanism of an epoxy resin and are excellent coupling agents for epoxy resins; a methacrylate silane will bond through silane crosslinking to an unsaturated polyester resin and is the optimum choice for polyester composites; phenolic resins have multifunctional reactivity, so therefore it is not surprising that several types of silanes, e.g., amino, epoxy, and chloroalkyl, all impart good properties to phenolic composites.

For thermoplastic polymers, especially polyethylene and polypropylene, the lack of reactivity on the polymer backbone minimizes the potential for covalent bonding to the polymer. Yet, unexpectedly good property improvements are often obtained with silane coupling agents in thermoplastic systems. In those cases, bonding is best explained by interdiffusion of the polymer into the layered siloxane network at the inorganic surface and formation of an IPN in the interphase region. Interdiffusion and crosslinking of silane adhesion promoters, as depicted in Figure 29.3, were identified as the mechanism of adhesion of polyvinylchloride plastisols to silane-treated glass [6]. Such interdiffusion is recognized as important in adhesion of thermoplastic elastomers to primers comprising silane-modified tackifying resins [7], primers used for bonding polyolefins [8], silane-modified melamine resin primers for bonding engineering thermoplastics [9], and silane-modified epoxy primers for bonding crosslinkable ethylene/vinyl acetate copolymers to surfaces in solar cell modules [10]. An IPN structure can give strong bonding between the silane structure and the organic polymer via physical and electrostatic effects. Matching the solubility parameters of the silane with that of the polymer can give beneficial effects of enhancing the interpenetration of the polymer.

Thermoplastic polyester resins, such as polyethylene terephthalate (PET) and polybutylene terephthalate (PBT), can contain residual phenolic or carboxylic reactive sites that make epoxysilane coupling agents effective. The use of a nonreactive organosilane, such as an octyl- or phenylsilane, on a mineral filler surface can improve wet-out and dispersion of the filler and give electrostatic bonding between the resin and the filler. Alkyl and aryl silanes can also be used in combination with organofunctional silanes for thermoset applications to improve dispersion of the resin (by matching solubility parameters), increase hydrophobic character, give greater resistance to attack of water in the interphase region, and often give increased heat resistance to the composite structure.

29.4 Optimizing Coupling Agent Performance

A very destructive force of adhesion is migration of environmental moisture to the interface and attack of agglomerates of water on the adhesive bond. Silane coupling agents have unique chemical and physical properties to not only enhance bond strengths but also, more importantly, prevent debonding at the interface, even in hot, humid environments.

The bond between a silane coupling agent and an inorganic substrate forms very rapidly and dynamically in most situations. The chemical structure of the organic group in the silane coupling agent has a large effect on its effectiveness as an adhesion promoter in composites or coatings. The “wet strength,” the strength of the bond between an inorganic substrate and a polymer in a humid-aging environment, is most often studied to evaluate the effectiveness of silane coupling agents. Physical properties, such as flexural strength of composites or a peel adhesion test for coatings and adhesives, can be measured before and after a wet aging test. Usually a test specimen is aged in warm or boiling water for 2 hours, 4 hours, 24 hours, 72 hours, or a week. The length of time that a bond survives, or the coupling agent that gives the strongest bond in the wet environment, will determine the effectiveness of various silane coupling agents.

The effect of the organic structure of the coupling agent on improving the flexural strength of a silica-reinforced unsaturated polyester composite is shown in Figure 29.4.

Significant increase in dry and wet strength of the composite is seen when a silane coupling agent is used. The choice of a coupling agent with optimum reactivity and chemical structure makes it possible to optimize the retention of flexural strength. For each application two or more possible

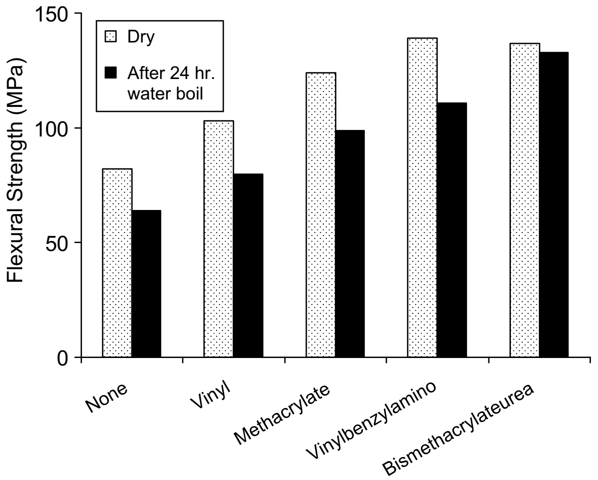


Figure 29.4 Silane organic group—effect on flexural strength of a silica/polyester composite.

coupling agents can be effective, but often one will give the best combination of properties in the final bonded material.

Adhesion can also be improved by using blends of silanes in a coupling agent system. A hydrophobic silane in combination with a hydrophilic silane will often improve bonding and improve retention of "wet" strength compared to use of the hydrophilic silane alone. Blending a hydrophobic silane, phenyltrimethoxysilane, with a hydrophilic diaminosilane gives significant improvement in adhesion of a urethane polymer to glass even though the aminosilane adhesion promoter alone is a good coupling agent for urethane polymers [11]. The data in Table 29.3 show that the bond of urethane to glass fails in boiling water after 2 hours if the aminosilane alone is used, but total bonding is retained even after 5 hours in boiling water when 90% phenylsilane is blended with the aminosilane coupling agent.

Table 29.3 Silane blends: Adhesion of urethane to glass

Ratio of Silanes	**Adhesion to Glass (N/cm)**		
I/F in Primer	**Dry**	**2 hr Boil H_2O**	**5 hr Boil H_2O**
Control	3.0	nil	nil
0/100	C	nil	nil
50/50	C	nil	nil
80/20	C	C	C
90/10	C	C	C
95/5	C	C	C
99/1	C	C	C

C = Cohesive failure > 20 N/cm;
I = Phenylsilane Z-6124;
F = Aminosilane Z-6020

Silane blends also can be used to increase the thermal stability of a silane for use in high temperature polymers. Many reinforced plastics, such as polyimides, are fabricated at temperatures up to 400 °C or higher. Standard aliphatic silane coupling agents have adequate heat stability for fabrication temperatures up to 250 °C but may decompose at higher temperatures. Certain aromatic functional silanes, such as an aminophenylsilane imidized with an aromatic anhydride, have outstanding heat stability, but they are not commercially available.

The thermal stability of several commercial silanes was determined by isothermal weight loss studies of the hydrolyzed silanes, $RSiO_{3/2}$ at 300 °C [11]. Figure 29.5 shows that phenylsilane (from phenyltrimethoxysilane) has very good thermal stability but the diaminosilane (from diaminopropyltrimethoxysilane) has poor thermal stability. The aminosilane based on vinylbenzylaminosilane has surprising good thermal stability.

Phenyltrimethoxysilane blends or vinylbenzylaminosilane is recommended for high temperature applications. A blend of 90% diaminosilane and 10% phenylsilane was used in a fiberglass/polyimide laminate, processed at 400 °C, and then aged for 1000 hours and 200 hours at 260 °C. Flexural strength data in Table 29.4 show the improved thermal performance of the phenylsilane blend compared to a monoaminosilane coupling agent, the standard coupling agent that had been used in that application. In an analogous system, proprietary sizes were formulated with vinylbenzylaminosilane and applied to a silicon carbide fiber/polyimide composite. The composite was aged at 315 °C for up to 1000 hours (see Table 29.5). The proprietary size gave improved flexural strength after 1000 hours compared to an epoxy-organic size that was normally used in such systems.

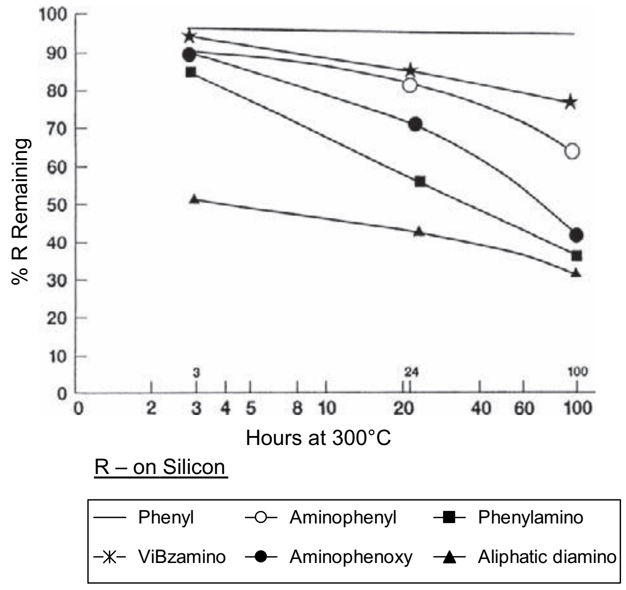


Figure 29.5 Stability of $RSiO_{3/2}$ in air at 300 °C.

Table 29.4 Thermal stability: S-glass/polyimide laminates

	Coupling Agents on Glass	
Properties of Laminates (MPa)	**Blend 9/1 Phenyl/Diaminosilane_**	**Monoaminosilane**
Flexural Strength, initial	544	476
1000 hrs @ 260 C	409	258
2000 hrs @ 260 C	306	134

Phenylsilane = $PhSi(OMe)_3$
Monoaminosilane = $(EtO)3Si(CH_2)3NH_2$
Diaminosilane = $(MeO)_3Si(CH_2)_3NH(CH_2)_3NH_2$

Table 29.5 Si−C fiber/polyimide laminates retention of strength at 315 °C

Silicon Carbide	**Flexural Strength (Mpa)**			
Fiber Size	**Initial**	**100 hrs**	**500 hrs**	**1000 hrs**
Epoxyorganic	1480	1320	1000	610
DCC-1	2350	2320	1660	890
DCC-2	2120	2060	1670	980

DCC-1 and DCC-2 are proprietary − based on vinylbenzylaminosilane

An increase in siloxane crosslinking in the interphase region can also improve performance. The theory is based on a silicate "rock" as a very durable material, so any way that the siloxane structure can be modified to give a rocklike structure, should increase durability at the interface. The organic bonding requirement still has to be met, and diffusion of the polymer in the interphase region must not be impeded, but promising crosslinking systems have been developed which have successfully substantiated the "increased crosslinking" theory.

A multifunctional crosslinking additive can be added as an adhesion enhancer [12]. A hexafunctional methoxydisilane additive, $(CH_3O)_3SiCH_2CH_2Si(OCH_3)_3$, sometimes called hexabis, was blended with conventional silanes. The data in Table 29.6 show that the crosslinking additive improves the adhesion of an epoxy film to glass compared to either a diaminosilane or an epoxysilane alone. Similarly, two silane coupling agent pairs, if the two organic functional groups can react with each other, can be used to give increased crosslinking. Blends of aminosilane and epoxysilane, aminosilane and methacrylate silane, or chloroalkyl silane and an aminosilane can each coreact in properly formulated amounts to give in situ formation of multifunctional alkoxy reactivity. Also, addition of tetraethoxysilane in a coupling agent formulation can increase crosslinking.

29.5 How to Choose a Silane Coupling Agent?

The nature of the organic group in a silane coupling agent is a key consideration when choosing a silane coupling agent. Any silane coupling agent with three alkoxy groups on silicon should bond equally well to an inorganic substrate,

Table 29.6 Adhesion enhancer−crosslinker $(MeO)_3SiCH_2CH_2Si(OMe)_3$ adhesion of epoxy film on glass

	Curing Agent Type Hours to Lose Adhesion		
Primer on Glass	**Polyamide**	**DMP − 30**	**DEH − 24**
None	<1	<1	<1
Diaminosilane alone	1	1	1
Blend 9:1::Diaminosilane:Enhancer	C	C	C
Epoxysilane	C	8	C
Blend 9:1::Epoxysilane:Enhancer	C	36	C
Blend 8:2::Epoxysilane:Enhancer	C	C	C

C = No failure after 1 week in 70 ° C water but matching of the organofunctional group on silicon with the polymer type of the resin to be bonded will dictate which silane coupling agent should be used in a particular application.

Several silanes may be recommended for one polymer type. For example, epoxy resin recommendations can include chloropropyl, epoxy, vinylbenzylamino, and either primary amino or ethylenediamino functional silanes. Often the cure system, e.g., for an epoxy resin, amine vs. anhydride, high temperature vs. low temperature cure, aliphatic vs. aromatic amine, can affect the performance of the silane coupling agent.

A list of silane coupling agents and recommendations for use in various applications is shown in Table 29.7. A correlation can be seen between the chemistry and physical characteristics of the silane coupling agent and chemistry and physical characteristics of the polymer or the effect that is desired on the inorganic substrate.

29.6 General Applications of Silane Coupling Agents

Besides the applications in glass fiber and mineral-filled composites that have been discussed, other major applications of silane coupling agents are laminates for printed circuit boards; insulation fiberglass; silica-filled rubber tires; rubber insulation for wire and cable; and as adhesion promoters in paints, inks, coatings, and adhesives (PICA). Various applications of silane coupling agents are listed in Table 29.8.

The same principles used in selecting a silane for reinforced plastics can be used to select a silane for other applications. The nature of the organic material that is used in the application is the major criterion that governs the effectiveness of a particular silane coupling agent as an adhesion promoter in any application.

In any application, the silane should wet the inorganic substrate and stay in a permeable state until it interpenetrates

Table 29.7 Organosilane applications

Chemical Type	Chemical Name	Coupling Agent for PolymerType/Application
Amine	Aminopropyltriethoxysilane	Acrylic, Nylon, Epoxy, Phenolics, Melamines, PVC, Urethanes, Nitrile Rubber
Diamine	Diaminopropyltrimethoxysilane	Acrylic, Nylon, Epoxy, Phenolics, Melamines, PVC, Urethanes, Nitrile Rubber
Methacrylate	3-Methacryloxypropyltrimethoxysilane	Unsaturated Polyesters, Acrylics, EVA, Polyolefin
Epoxy	3-Glycidoxypropyltrimethoxysilane	Epoxy, PBT, Urethanes, Acrylics, Polysulfides
Methyl	Methyltrimethoxysilane	Hydrophobing agent for mineral surfaces
Isobutyl	Isobutyltrimethoxysilane	Hydrophobing agent for mineral surfaces Masonry water repellent
Phenyl	Phenyltrimethoxysilane	Hydrophobing, dispersing aid for minerals Blends with silanes/thermal stability
Octyl	Octyltriethoxysilane	Hydrophobing/dispersion of minerals in polyolefins; Masonry water repellent
Vinyl	Vinyltrimethoxysilane	Graft to polyethylene for moisture crosslinking EPDM Rubber, SBR, Polyolefin
Chloroalkyl	3-Chloropropyltrimethoxysilane	Urethanes, Epoxy, Nylon, Phenolics, Polyolefins
Chloroalkyl	3-Chloropropyltriethoxysilane	Urethanes, Epoxy, Nylon, Phenolics, Polyolefins
Vinylbenzy lamino	Vinylbenzylaminotrimethoxysilane	Epoxies for PCB's, polyolefins, all polymer types

Table 29.8 Silane applications

Examples
▪ Fiberglass cloth, mat, chopped glass (surface treatment) for *adhesion* in reinforced plastics (PCBs, auto, boats, tanks, etc.).
▪ Mineral (surface treatment) for *adhesion and/or dispersion* in reinforced plastics (auto, W&C, electronics, rubber/tires, etc.).
▪ Paints, inks, coatings, adhesives (primer or additive) to give *moisture resistant* adhesion to surfaces.
▪ Moisture *crosslinking* of polyethylene (Sioplas) coatings.

with the polymer. A silane is usually applied to a substrate, e.g. glass fiber, mineral, or to a flat or contoured surface and then dried before the polymer comes in contact with the surface. Drying at too high a temperature, above 125 °C, will give poor adhesion because the condensed silane becomes too highly crosslinked and impermeable to allow IPN formation. The ability of the silane to relieve stresses at the interface is also beneficial. As mentioned earlier, a complex vinylbenzylamino coupling agent with its multifunctionality is a better coupling agent for some epoxy resins than an epoxysilane and better for some polyester resins than a methacrylate silane probably because of the complex, stress relieving nature of the more complex silane.

A silane coupling agent is usually applied in a "pretreatment" step to give better adhesion at the interface between polymer and reinforcement. Chopped glass fiber is always pretreated with a silane coupling agent. Mineral fillers, such as silica, talc, mica, wollastonite, and others, are often pretreated, but the silane is sometimes added to the filler/polymer mix during compounding (often referred to as in situ addition or integral blending). Even if the reinforcement is pretreated, a compounder can later add additional silane coupling agent to enhance adhesion or provide processing benefits. A debate has existed between pretreated fillers and in situ addition of silane coupling agents, but pretreatment is usually preferable [13].

Other noncoupling benefits of silane coupling agents in composites are very important. These include change in rheology of a filled system during processing, with as much as a 90% reduction in viscosity of a silica—polyester mix; elimination of inhibition of cure caused by the reinforcement; better wet-out of the fiber or filler; improved surface smoothness; increased clarity of a composite; and healing of flaws in glass fibers. Usually a very small amount in a formulation, sometimes less than one-tenth of a percent, can make a dramatic difference in the performance of the end product making the use of silane coupling agents very cost-effective.

29.7 Industry and Utility

29.7.1 Surface Treatment of Fiberglass

Glass fiber is a very hydrophilic material and requires a protective coating to eliminate the degradative effects of moisture in a variety of applications, especially if used as a reinforcement in polymeric composites. The coating also protects and pacifies the brittleness and the abrasive nature of the glass fiber. The natural chemistry of silane coupling agents is similar to the silicon chemistry of the glass, and the favorable equilibrium of bonding silanes to glass surfaces makes them ideal for treatment of glass surfaces. Virtually all glass fiber for most applications requires a silane coupling agent to make it a viable material for intended applications. The fiberglass may be in the form of random glass matt, chopped strand, woven roving, continuous filament, or woven glass cloth, but regardless of the form of the glass fiber, it must be treated with a silane coupling agent to make it useful as a reinforcement for polymers. The nature of the final application determines which type of silane coupling agent should be used and how the silane is to be applied in the process.

29.7.1.1 General Fiberglass for Reinforced Plastics

All glass fiber that is used in reinforced plastics has a coupling agent on the surface. Fiberglass manufacturers apply silane coupling agents to the glass fiber as the filaments are gathered into strands during the glass forming process. A water-based "size" is applied to the glass. The formulation contains several ingredients including a film forming polymer, a glass lubricant, an antistatic agent, and perhaps other ingredients, but importantly 0.1—0.5% silane coupling agent. The bath is formulated as a water-based size (an important requirement by the fiberglass industry), so therefore any silane that is used must be dissolvable in water. Experimentally, application of silanes under anhydrous (vapor) conditions or from organic solvents has been successfully applied to glass fiber, but, commercially, the aqueous application is the only way that a silane is applied. The addition of a silane to water will generally give a precipitated gel via hydrolysis and formation of insoluble hydrophobic siloxane structures. But if the water is acidified to a pH of 4, a silane coupling agent will hydrolyze and dissolve in water without gelling, especially at low concentrations of less than 5%. The low pH stabilizes the silanol species against condensation, thereby maintaining a hydrophilic silanol structure, to allow the silane to dissolve and stay soluble. Usually a weak organic acid, acetic acid or sometimes formic acid, is used to adjust the pH of water to make silane solutions. An acid-sensitive silane, such as an epoxysilane, will react with acidic media at pH 4, so a higher pH of 5—6 is used. Hydrophilic silanes such as aminosilanes will form aqueous solutions at all pHs, but pH 4 is preferred for glass treatment to give correct orientation on the glass surface [3].

The magnitude of the effect of silane coupling agents on improvement of strength properties of composites is usually significant (see Figure 29.6). A fiberglass-reinforced phenolic composite with and without 0.2% diaminopropyltrimethoxysilane on the glass surface was tested as prepared (dry) and also after immersion for 2 hours in boiling water (wet). Under dry conditions, the flexural strength was 448 MPa without a silane and 620 MPa with the silane; after wet aging, the flexural strength was 296 MPa without a silane and 545 MPa with the silane. The wet strength properties are more closely related to actual use conditions than dry strength since it represents an accelerated aging test comparable to long-term conditions in the environment.

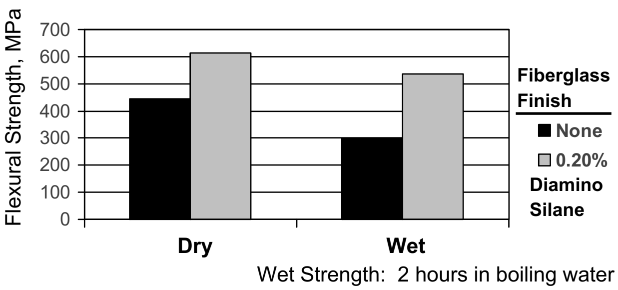


Figure 29.6 Fiberglass-reinforced phenolic laminate.

Table 29.9 Coupling agent and organic group effect on strength—epoxy/glass laminate

	Flex Strength, Mpa	
Silane Coupling Agent Type	**Dry Strength**	**Wet, Water Boil 72 hrs**
None	394	221
Epoxy/Trimethoxy	605	476
Vinylbenzylamino	670	518

The effect of the type of organic group in the silane coupling agent is shown in Table 29.9. An epoxysilane and the complex vinylbenzylaminosilane were used in fiberglass-reinforced epoxy composite formulations. Under dry conditions, the epoxysilane increased the flexural strength by 54% from 394 MPa to 605 MPa, while the vinylbenzylaminosilane increased the flexural strength by 70% to 670 MPa. Under wet conditions, after 72 hours in boiling water, the composite without a coupling agent decreased in flexural strength to 221 MPa, with the epoxysilane coupling agent to 476 MPa, and with the vinylbenzylamino coupling agent to 518 MPa. A possible explanation for the greater retention of flexural strength with the vinylbenzylamino coupling agent is because the silane has a complex silane structure with cationic character that can coat the glass fiber more efficiently, can form an IPN with the thermoset polymer more completely, has more hydrophobic character than the epoxysilane, and has a very reactive amine functionality to participate in the curing process.

29.7.1.2 Printed Circuit Board Applications

The printed circuit board industry is based largely on high-quality fiberglass-reinforced epoxy laminates that are made from layers of electronic-grade woven glass cloth on which a silane size is the critical chemical component between the glass and the resin. The requirement for better bonding of the epoxy resin to the glass surface has increased as the density of holes that are drilled in a laminate for conductive sites has increased. There is a critical requirement to eliminate failure along the glass fiber in the laminate.

The fiberglass that goes into printed circuit boards is processed a different way than conventional fiberglass for reinforced plastics. The fiberglass is first woven into a glass fabric with a starch size/lubricant on the surface. The starch is burned off and the silane is applied to the heat-cleaned woven glass fabric as, usually, the only ingredient in the bath, and therefore is the only ingredient on the glass cloth. Silane coupling agent is applied from an acidified treating bath, again at a pH of 4, at a treatment level of 0.1—0.5%. The silane-treated woven glass cloth is dried, carefully inspected for flaws, and then supplied to laminators in the printed circuit board industry where lamination and fabrication of printed circuit boards are carried out.

The resins that are used in the printed circuit board laminates determine the silanes that are used in printed circuit boards. Since high performance epoxy resins are the most used resins, then an epoxy compatible silane is required. The complex vinylbenzylaminosilane has become the state of the art for this application. Low ionic content (low chloride levels), ease of solubility in treatment baths, and minimization of agglomerates on the electronic glass surface are all important parameters in choice of a silane coupling agent.

For resin systems other than epoxy, or for other epoxy requirements, the glass weavers sometimes apply aminosilanes, epoxysilanes, and chloropropylsilanes.

29.7.1.3 Miscellaneous Fiberglass Applications

Other applications of fiberglass include insulation for construction applications, roofing shingles, and automotive insulation applications. These are not always composite applications in the strictest sense but still require a silane coupling agent for the resinous coating is applied to the glass surface.

Insulation fiberglass for construction applications uses a phenolic binder to help retain the insulation value. An aminosilane, either a monoaminosilane or diaminosilane coupling agent, is mixed into an aqueous phenolic binder solution to bind the phenolic resin to the glass fiber surface. Without the silane present, the phenolic would debond during aging in the environment to cause the glass fiber to relax and reduce the insulation value. Blown-in chopped-glass insulation also requires surface treatment. An organic binder is sometimes used, but a silicone polymer, often a silicone emulsion, rather than a coupling agent is used on the surface to give moisture resistance.

Fiberglass-based roofing shingles are similar to reinforced plastic applications and require durable organic polymers to resist the sun and other degradative effects. Special coupling agents such as the high performance vinylbenzylaminosilane coupling agent are used in the formulation to allow the products to meet the requirements of building codes and construction standards.

29.7.2 Surface Treatment of Minerals in Plastics

29.7.2.1 Nature of Bonding to Minerals

Surface modification of fillers as reinforcements in plastics have generally been directed toward improving mechanical strength and chemical resistance of composites by improving adhesion across the interface. Usually other benefits are realized, such as improved dispersion of the mineral into liquid or polymeric media; lower viscosity of the mix; greater compatibility with the polymer; change of the surface from hydrophilic to hydrophobic; improved electrical properties in a mineral-filled polymer system; prevention cure inhibition of the polymer; and other factors. Some of these benefits are listed in Table 29.10.

The interphase region between polymer and filler involves the interplay of physical and chemical factors related to composite performance. The interaction of the polymer with filler and the tremendous mechanical stress of differential shrinkage during cure will affect the physical properties of a composite. Under ideal conditions a treated filler will wet-out and disperse readily in the plastic with Newtonian flow. The treatment protects the filler against abrasion and cleavage during mixing and in the final composite. The treatment promotes optimum alignment of polymer segments at the interface and gives adhesion and an interfacial structure to give desired improved properties to the mineral-filled composite.

Mineral fillers usually contain silicon, aluminum, and other metallic elements in the chemical structure such that metal hydroxyl groups on the surface are very hydrophilic in nature. Some of the more commonly used mineral fillers include silica, wollastonite, talc, mica, glass beads, and kaolin clay (see Table 29.11). The reactive sites on the filler surface can function in a manner similar to the silanol groups on fiberglass reinforcement to be chemically treated in a similar way (see Figure 29.7). Treatment of the filler can change the surface into either a chemically reactive surface via an organofunctional silane, or become hydrophobic, organophilic, or hydrophilic depending on the silane that is used. Some types of organosilanes and the characteristics of the organic group are shown in Table 29.12. Beyond these general characteristics, a list of various silane types and polymer applications is shown in Table 29.7.

Table 29.10 Surface treatment benefits

- Mineral/Filler – 0.1% to 10% on filler (particle size = 0.1–50 micron)
  - — Plastics/Rubber reinforcement
  - — Better filler wet-out and dispersion
  - — Lower viscosity of filled liquid resins
  - — Improve moisture resistance of composite
  - — Reduce cure inhibition of filler
  - — Improve electrical properties of filled polymer

Table 29.11 Mineral/filler applications

Fillers	Comments
Kaolin Clay	Reinforced nylon, wire and cable (EPDM)
Talc	Stiffness, abrasion-polypropylene (auto)
Mica	Stiffness, polypropylene (auto)
Silica	Reinforced rubber, epoxy PCB's
Wollastonite	Reinforced plastics, coatings
Glass Fiber/Beads	Reinforced plastics
Aluminum Trihydrate	Flame retardance
Magnesium Hydroxide	Flame retardance
Crystobalite	Abrasion resistance/plastics
Titanium dioxide	Plastics, colorant, filler

29.7.2.2 Methods of Applying Silanes to Minerals

Particulate fillers may be pretreated with a silane by dry blending at room temperature or at elevated temperature. The filler surface contains residual moisture to hydrolyze the silane. Neutral trialkoxysilanes, i.e., silanes without amine groups, disperse readily over the filler surface by spraying directly onto the filler in a high intensity mixer, such as a Henschel or Littleford Mixer, or with mild agitation in a laboratory mixer. The treatment process may benefit from the addition of a trace of amine or alkyltitanate to catalyze the reaction with the filler surface. Aminofunctional silanes are self catalytic and may react too fast with the filler surface and

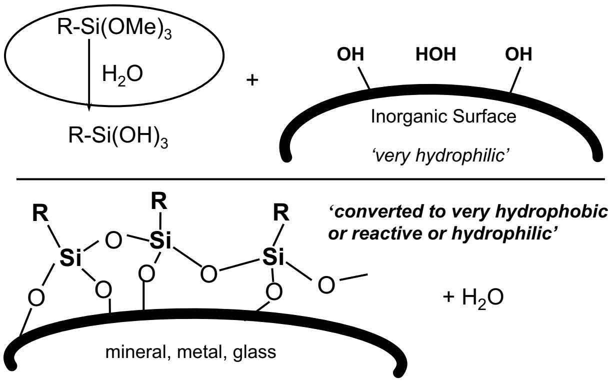


Figure 29.7 Silane bonding to inorganic surfaces.

Table 29.12 Organosilane ($RSi(OMe)_3$) characteristics

R	Characteristics of "R"
• Me	Hydrophobic, Organophilic
• Ph	Hydrophobic, Organophilic
• i-Bu	Hydrophobic, Organophilic
• Octyl	Hydrophobic, Organophilic
• $-NH(CH_2)_3NH_2$	Hydrophilic, Organoreactive
• Epoxy	Hydrophilic, Organoreactive
• Methacryl	Hydrophobic, Organoreactive

often benefit from dilution with an alcohol or ether—glycol solvent to 10% active silane in the treating solution to aid dispersion of the silane over the large surface area of a typical filter. The addition of low levels of water is often used. After thorough blending the filler can be dried at a temperature no greater than 125 °C before being used in a composite application.

At least a monolayer of silane is needed on the filler surface. The surface area of the filler and the surface coverage (square meters per gram, m^2/g) provided by the silane will determine the amount of silane that is necessary. Generally, the coverage of the silane can be estimated to be in the range of 200—400 m^2/g. For filler with a 1 micron particle size, approximately 0.2% silane is required for a monolayer coverage, but in practice about 1% silane is applied to the filler surface. Higher surface area fillers require higher levels of silane coupling agent. The amount of silane to be applied should be optimized by trial for each system. Figure 29.8 shows the effect of level of silane treatment with several different fillers on the flexural strength of a styrene—butadiene casting.

29.7.2.3 Effect of Silanes on Properties of Mineral-Filled Composites

A silane coupling agent will not only increase the flexural strength of a filler—resin composite, but also significantly lower the viscosity of the uncured resin mix to allow greater filler loadings and easier processing. The effect of the silane on the viscosity of an uncured polymer/filler blend and on the flexural strength of the cured composite is shown in Figure 29.9. With 50% silica in the liquid polyester resin, the uncured viscosity, without silane, was 24,500 Pa.s; with 0.3% methacrylate silane, there was little effect on the viscosity, 22,000 Pa.s; but with 0.3% vinylbenzylaminosilane, the viscosity decreased significantly to 8,700 Pa.s. So the nature of the organic group in the silane significantly affects the viscosity. The flexural strength of the cured resin sample shows the expected good properties with either silane after 2 hours in boiling water.

Silane treatment on fillers can also help with the cure of thermoset resins. The surface of a mineral filler can interfere with the curing chemistry to inhibit the cure. However, once the filler is treated with silane, the filler surface is changed chemically so that the inhibition of cure can be minimized. Figure 29.10 shows the effect of various silane treatments on glass filler and the effect of various silane treatments on the exotherm of peroxide-cured polyester and amine-cured epoxy resin systems where reduction of exotherm indicates inhibition of cure.

Electrical properties of filled resin systems can also be improved with silane treatment. Filler particles are naturally hydrophilic via their metal hydroxide surfaces and the particles want to agglomerate with each other when dispersed in a resin. Treatment with silane coupling agent will change the chemistry of the filler surface and impart improved electrical properties such as reduced dielectric constant and reduced dissipation factor in the composite. Table 29.13

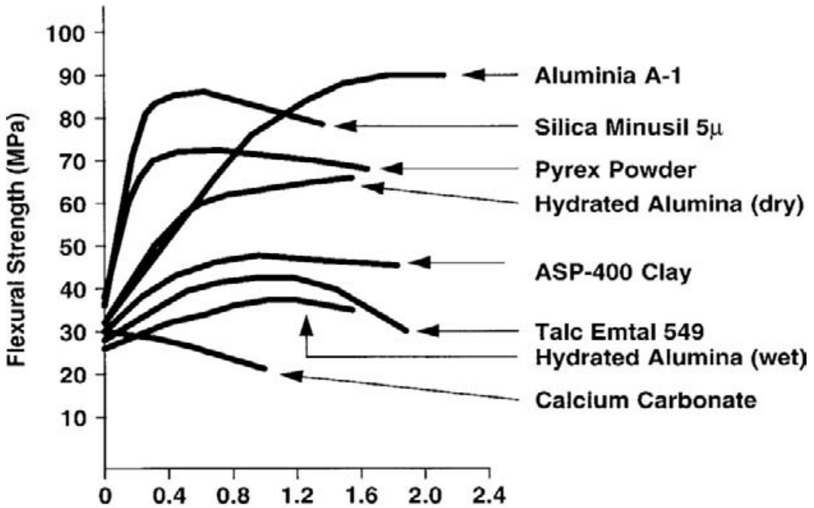


Figure 29.8 Effect of level of silane coupling agent treatment with various fillers in a styrene—butadiene casting.

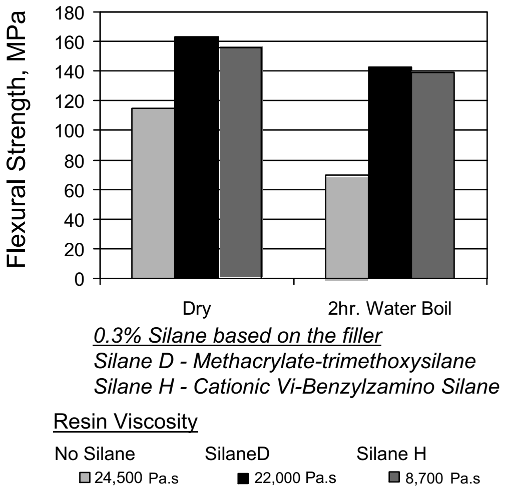
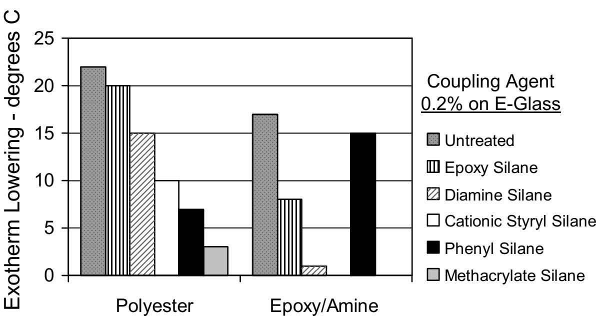


Figure 29.9 Viscosity and Coupling Effect—polyester castings with 50% silica.



Cure @ 115°C (epoxy) or 90°C (unsaturated polyester); 5g E-glass in 30 g resin

Figure 29.10 Resin exotherm lowering with silane-treated glass filler.

shows the improved electrical properties of a quartz-filled epoxy resin system (40% quartz) with 0.3% silane admixed into the formulation. Silica-filled epoxy molding compounds use an epoxysilane for this reason. In some cases a special epoxysilane is used which has low chloride and low ionic content to further minimize negative effects on electrical properties.

Other filled resin systems that require a silane coupling agent include highly filled sand cores with furan, urea–formaldehyde and urethane resins in the foundry industry, and highly filled polymer concrete where polyester and epoxy binders are used to bond aggregate into a strong and fast curing construction material.

Polypropylene and polyethylene are used in large volumes in many applications that require a filler in the polymer to improve properties such as stiffness, impact strength, physical strength, or scratch and mar resistance. The low reactivity of polyolefins makes chemical bonding to the polymer very difficult to achieve by normal coupling agents. One approach is to blend the polymer with a carboxy-functional polyethylene or polypropylene to make the blend reactive with an organofunctional silane coupling agent. The carboxy groups in the modified polymer will readily react with the aminosilane on the filler surface to give good adhesion between the treated filler and the resin [14]. Also, the filler can be treated with an octylsilane or phenylsilane to make the filler more compatible with the polymer. Titanium dioxide, talc, mica, and kaolin clay are fillers that are commonly used in polyolefin systems.

29.7.3 Mineral Fillers in Rubber Reinforcement

29.7.3.1 Rubber Tire Applications

Mineral fillers, such as silica and kaolin clay, can be treated with silanes, such as a mercaptosilane and polysulfidosilane, to function adequately as a replacement for carbon black in sulfur-cured rubber applications [15]. Since carbon black reinforced rubber is a huge industry, this has become a new large application for silane coupling agents.

Organic rubber normally used carbon filler, a natural reinforcing agent, and does not require a coupling agent. Kaolin clay and silica fillers require a coupling agent that will enter into the sulfur-base curing mechanism. The first silane applications in rubber tires used mercaptosilane to modify silica and clay fillers. Commercial applications were limited to specialty areas, such as white sidewall components, some tread stocks, and in some off-road tires, but processing and

Table 29.13 Epoxy resin/quartz filler electrical properties vs. that of silane

Silane Added	Dielectric Constant		Dissipation Factor	
	Initial	H_2O Boil	Initial	H_2O Boil
Unfilled Resin	3.44	3.43	0.007	0.005
Quartz, No Silane	3.39	14.60	0.017	0.305
Quartz/Epoxysilane	3.40	3.44	0.01	0.024
Quartz/Aminosilane	3.46	3.47	0.013	0.023

Epoxysilane = Z-6040; Aminosilane = Z-6011; 72 hr Water Boil physical property deficiencies limited commercial applications. In the late 1970s, Degussa Corporation, which has been a filler manufacturer and supplier of silica for a variety of applications, developed a tetrasulfidodisilane, named Si-69, which eventually led to the largest single application for a silane coupling agent [16]. In the 1990s, the new silane, and a new rubber admixture process, allowed the new silica-reinforced rubber technology to become commercially successful. It was also fortuitous that silica-filled tires had several important benefits compared to traditional carbon black tires: reduced rolling resistance; as much as 10% improvement in fuel economy; longer tire life via reduced wear and abrasion resistance; improved grip and skid resistance on wet surfaces; less heat buildup which led to increased life of the tire; and was more economical than the earlier silane-modified mineral filler systems. As a result a huge new market for silane coupling agents has developed. In the year 2000, it was estimated that 75 million pounds of polysulfidosilanes were sold in the world for silica-filled tires.

The predominantly used silane is the tetrasulfido silane Si-69, $(CH_3CH_2O)_3Si(CH_2)_3{-}S_x{-}CH_2)_3Si(OCH_2CH_3)_3$, where $x = 4$, but is really a mixture of $x = 2$, 3, 4, 5, and 6. Other silane variations for rubber tires have been developed (see Table 29.14). Newer technology uses similar sulfidosilanes but are predominantly based on a disulfide mixture, $x = 2$. Other new molecules are being developed, such as some disulfide monosilanes, e.g., $(CH_3CH_2O)_3Si(CH_2)_3{-}S{-}R$ and mixtures of silanes with alkyl and aryl silanes.

29.7.3.2 Wire and Cable Applications

New mineral-filled rubber formulations were developed in the 1960s for wire and cable applications where exceptional resistance was needed to prevent electrical breakdown under high, humid stress conditions. Carbon black is a conductive filler so it is difficult to meet certain insulation resistance properties of rubber made with carbon black. Silane-based mineral-reinforced rubber insulation materials meet the stricter electrical property standards not attainable with a carbon black rubber formulation. Kaolin clay and silica filler are the most used "white" fillers and amino-, vinyl-, and mercaptosilane coupling agents give good properties. Silane-treated kaolin clay has become the predominant filler for wire and cable with most applications using filler pretreated with either a vinyl silane or a vinyl siloxane polymeric material.

Table 29.14 Ethoxy silane additives for the rubber industry

$(EtO)_3Si(CH_2)_3$-SS-(CH_2) $3Si(OEt)_3$	Disulfidosilane (1)
Silane(1) blend 50% on Carbon Black	
$(EtO)_3Si(CH_2)_3$-SSSS-$(CH_2)_3Si$ $(OEt)_3$	Tetrasulfidosilane (2)
Silane (2) blend 50% on Carbon Black	
$(EtO)_3Si(CH_2)_3{-}SH$	Mercaptosilane

Note: Sulfidosilanes (1) and (2) are polysulfide mixtures

Vinyl silane oligomers, such a partially hydrolyzed vinyltrimethoxysilane and vinyltrimethoxysilane including, sometimes, some dimethylsiloxy species in the structure, have been developed as premium treating liquids for kaolin clay reinforcements. While the fillers are pretreated, additional vinyl silane, such as vinyltriethoxysilane or vinyl(tris-methoxyethoxy)silane, is added to enhance properties [17].

29.7.4 Adhesion Promoters for Paints, Inks, Coatings, and Adhesives

Organofunctional silane coupling agents function as adhesion promoters for PICA in a manner similar to the way they function as coupling agents for fiberglass and mineral-filled composites. In most cases the general conditions are similar, i.e., an organic polymer is to be bonded to an inorganic substrate. Bond failure mechanisms in PICA adhesion systems are similar to bond failure mechanisms in other silane adhesion promoter application. Moisture attack in the bonded interface region is a leading cause of loss of adhesion. A silane coupling agent with its dual functionality will operate at the interface to give improved adhesion when the bond is initially formed and then "protect" the bonded system from moisture-induced debonding and increase the useful life of the bonded systems.

Choice of the right coupling agent system for a PICA application requires similar thinking as was discussed for reinforced plastics. If chemical reactivity is present in the polymeric component in the material to be bonded, then matching the reactivity of the silane coupling agent with the reactivity in the polymer is very important. Choice of a silane system to maximize interpenetration of the coating into the silane network is also important. Silane recommendations for various polymers, as shown in Table 29.7, are useful for PICA applications as well. Blends of silanes, to give increased hydrophobicity, increased crosslinking of the silane structure and, to give increased thermal stability, can be used to improve the performance of the silane adhesion promoter system.

Silane adhesion promoters are applied to a PICA system in two possible ways—either as a primer on the substrate before the coating is applied or by addition directly to the coating system. When used as a primer, the silane is diluted in a solvent and sprayed, dipped, or wiped onto the inorganic substrate. Various solvents can be used: methanol, ethanol, isopropanol, an ether glycol, or sometimes a mixture of solvents. Ethanol is preferred over methanol for toxicity reasons. Water, at levels of 1–5%, is sometimes added to an alcohol solvent to promote hydrolysis of the silane during attachment to the surface. Usually there is enough residual moisture on the surface of an inorganic substrate to give

Table 29.15 Effect of surface primer application on adhesion

Paint	Bond Strength Paint to Aluminum Silane	Surface Preparation	Accelerated Weathering Adhesion
Urethane	None	Degreased	20
	None	Sandblasted	95
	Diamino(A)	Degreased	100
Epoxy	None	Degreased	70
	None	Sandblasted	100
	Epoxy(D)	Degreased	100
	Diamino(A)	Degreased	100

A - N-(2-Aminoethyl)-3-Aminopropyltrimethoxysilane
D - 3-Glycidoxypropyltrimethoxysilane

hydrolysis and bonding of the silane to the substrate. Water can also be used as the solvent if the silane coupling agent is an aminosilane, since aminosilanes are soluble in water.

The concentration of silane in the solvent during application as a primer controls the thickness of the silane coating on the surface. Poor adhesion is obtained if the silane coating is too thick. A thick, crosslinked silane oligomer is a weak layer and the bond would fail in the silane layer. Poor adhesion is also obtained if the silane coating is too thin because not enough silane is present to give improved bond strength and water resistance. A concentration of 0.5% up to 10% silane in solvent can be used in a primer, but usually levels of 2–5% are used. Various concentrations are tested for optimum performance. Once the silane primer solution is applied, the solvent can be allowed to evaporate at room temperature or the coated substrate can be heated to drive off solvent more rapidly. Any application of heat should keep the temperature of the surface below 125 °C to prevent excessive crosslinking of the silane on the surface, which reduces interpenetration of the coating into the silane primer interphase region.

Silane primers are applied as a much thicker coating on a surface than are comparable silane treatments on fiberglass or mineral surfaces for reinforcement applications. While adjusting the concentration of silane in the carrier solvent can control the silane primer thickness, other organic additives can be mixed with the silane to give a primer. A blend of 10% epoxysilane with a hexamethoxy-melamine resin [9] and a blend of 5% aminosilane with a styrene–butadiene latex are particularly useful silane-organic primer systems.

In an alternative method of application for a silane adhesion promoter, the silane can be mixed directly into the PICA system to be bonded to give “unprimed” adhesion. Silane levels of 0.5–5%, usually about 2%, are added to a coating system. Some techniques that are used to enhance the performance of the silane are partially prehydrolyzing the silane with water before adding it to the coating system so the crosslinked silane will be less soluble in the coating; modifying the cure system of the coating to allow the silane to migrate efficiently to the substrate; or choosing the functionality of the silane coupling agent to minimize interaction of the silane with the polymer system.

An example of silane benefits when used as a primer is shown in Table 29.15 where urethane and epoxy paints were applied to aluminum surfaces using epoxysilane and aminosilane adhesion promoters to improve adhesion. The effect of degreasing and sandblasting the surface was evaluated to enhance adhesion [18]. Plueddemann [19] has compared the effectiveness of a series of silanes as primers and additives in bonding thermoplastic and thermoset polymers to glass.

29.8 Other Types of Adhesion Promoters

Adhesion promoter chemistries, other than silanes, have been extensively promoted for many years. Organotitanates and organozirconates, promoted by Kenrich Petrochemicals and Manchem/FedChem, have shown promise as adhesion promoters but have not achieved the broad success of silane coupling agents. In metals, the highly metallic nature of zircoaluminates makes them uniquely reactive with metal surfaces. Similarly, organotitanates via their nature as excellent wetting agents and the ability to design molecules with dual, organic and inorganic, functionality can function as adhesion promoters. The reader is encouraged to consider these materials in their applications.

29.9 Sources of Silanes

Silanes are manufactured globally. They have traditionally been manufactured in the US, Europe, and Japan, but new manufacturing facilities in China are beginning to supplement the global supply. The emergence of large volume applications for silanes, especially in silica-filled rubber tires, has substantially increased the manufacturing volume and manufacturing capability with a concomitant reduction in price of silanes.

Many of the products discussed within this chapter are supplied by Dow Corning Corporation. However, similar products, as well as additional products, are available globally from other silane manufacturers, such as Degussa (now Evonik Degussa); OSi Specialties (now Momentive Performance Materials); Japanese suppliers including Chisso Corporation and Shin Etsu Chemical; and several Chinese suppliers. All suppliers have websites in which product lines, data sheet, material safety data sheets, and technical information are available. The reader is encouraged to contact these suppliers when searching for a particular product type or application information.

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30 Chemical Mechanical Polishing: Role of Polymeric Additives and Composite Particles in Slurries

Cecil A. Coutinho and Vinay K. Gupta
Department of Chemical & Biomedical Engineering, University of South Florida, Tampa, FL 33620, USA

30.1 Introduction

During the past few decades, semiconductor technology has advanced at a tremendous rate in terms of both productivity and performance. A major contributing factor for this advance has been the ability to reduce the dimensions of transistors and to increase the packing density within a single chip for faster processors that can carry out complex functions. A striking illustration of this transformation in semiconductor technology is seen in Figure 30.1. It is clear that number of transistors per chip has undergone a rapid growth over the past 50 years [1−3].

A fact that is not readily obvious from the data in Figure 30.1 is that increased density of transistors has to be complemented by the capacity to form a device network among the transistors once they are fabricated on a silicon substrate. Currently, silicon chips contain over a billion transistors within a confined area of a few square centimeters and all of these transistors must be electrically connected to realize advanced functionality, reliability, and speed in a microprocessor [4−7]. Connection of such an extremely dense array of transistors requires a complex metal wiring design that is typically achieved through a multilevel metallization structure. Present generation of logic devices used in many computers require deposition of eight or more metal layers and this multilayer fabrication is impossible without chemical mechanical polishing/planarization (CMP).

To successfully manufacture a multilevel metallization structure such as that shown in Figure 30.2a [8], the topmost layer of the previous metallization level has to be optically flat with minimal surface roughness. Any residual roughness from the previous layer gets compounded as the layers of metallization increase. After a couple of layers, the roughness will be significantly high such that further lithography (patterning) is inhibited due to issues with the depth of focus. This is evident in Figure 30.2b that shows an SEM image of an interconnect structure without a planarization step after each metallization step [8]. It is clear that it is not possible to proceed with different layers due to issues such as depth of focus during photolithography and challenges such as voids within interconnect layers due to compounded roughness. To prevent this from happening and to achieve local and global planarization across the wafer surface, CMP is the method of choice among other planarization techniques [9,10]. In CMP,

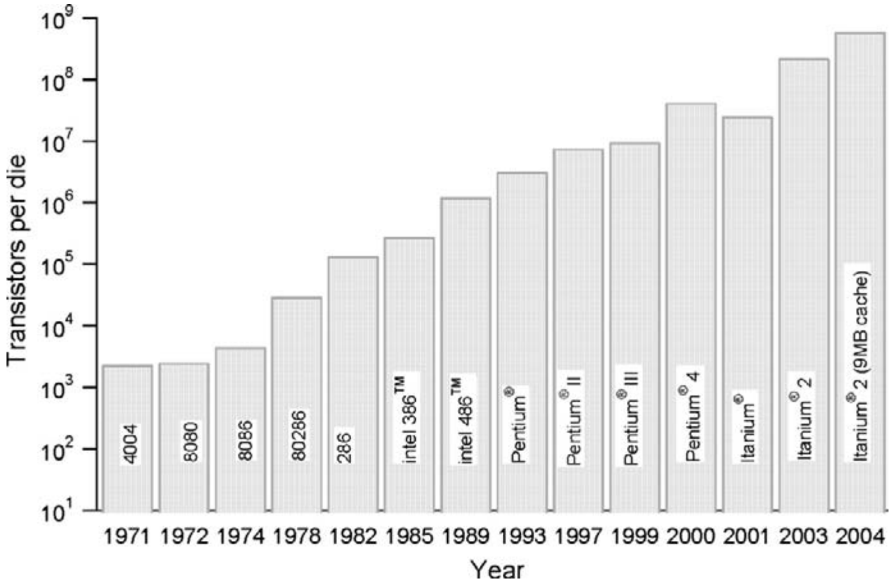

Figure 30.1 The number of transistors per die for Intel™ processors with year of introduction. Plot created using data from Intel Press room [1,2].

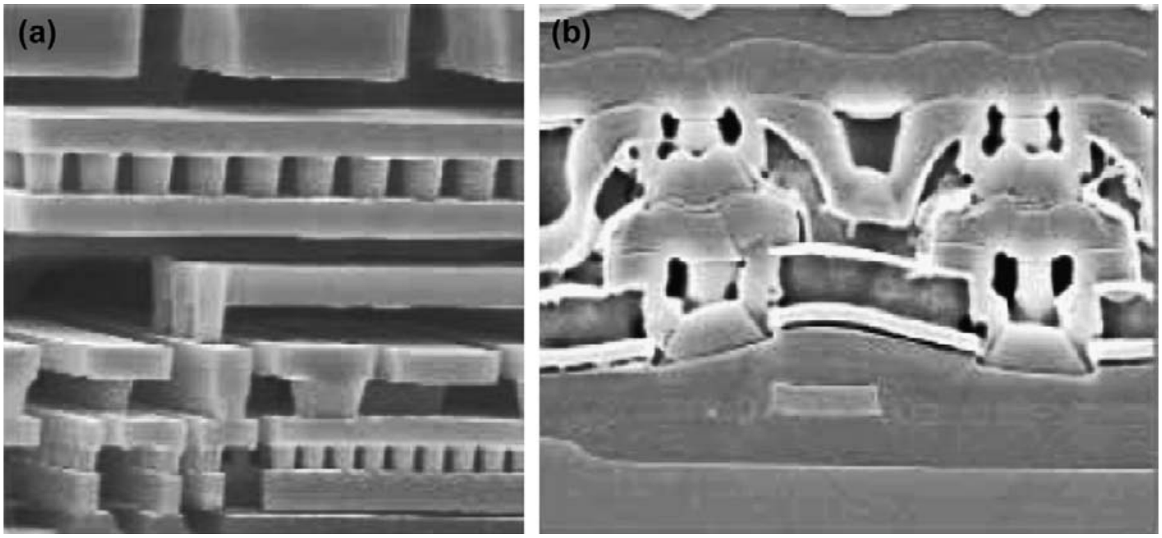

Figure 30.2 SEM images of (a) multilevel metallization structure and (b) layers of metallization without CMP (Reproduced with permission from Rhoades [8]; Copyright Mark Media, Inc. 2008).

the planarization is achieved by a synergistic combination of chemical and mechanical forces using slurries containing different chemical reagents and abrasives [11–16]. The CMP process remains a crucial step in device fabrication in order to achieve successful integration of multilevel metallization structures.

Recently, successful multilevel stacking within nodes that approach nanometer dimensions for future devices has become necessary, which in turn has made the planarity requirements for each wiring level to become exceedingly demanding and stringent since the uniformity of the planarization process has to be maintained over many levels of stacking [17–23]. At present, CMP is the only processing technique that can effectively remove these layers from the unwanted regions and also planarize the surface for subsequent lithography. To meet the stringent requirements of the next generation of devices without sacrificing throughput, innovations in the CMP process are essential, which in turn requires careful consideration of every aspect of the CMP technique.

As illustrated in Figure 30.3, the CMP process has three main components: (1) the wafer surface onto which the microelectronic devices are fabricated, (2) the polymeric polishing pad, and (3) the polishing slurry containing submicron-size particles and reactive chemical agents [24–27]. Polishing involves contact between the wafer with patterned films of silicon dioxide, copper, or tungsten, and a soft porous polyurethane polishing pad. The two surfaces are then rotated against each other and the removal of excess metal or dielectric material occurs by combined action of chemical and mechanical forces. An integral part of the CMP process is the measurement of in situ parameters such as coefficient of friction to monitor the process and the use of end-point determination techniques (e.g., four-point electrical test or

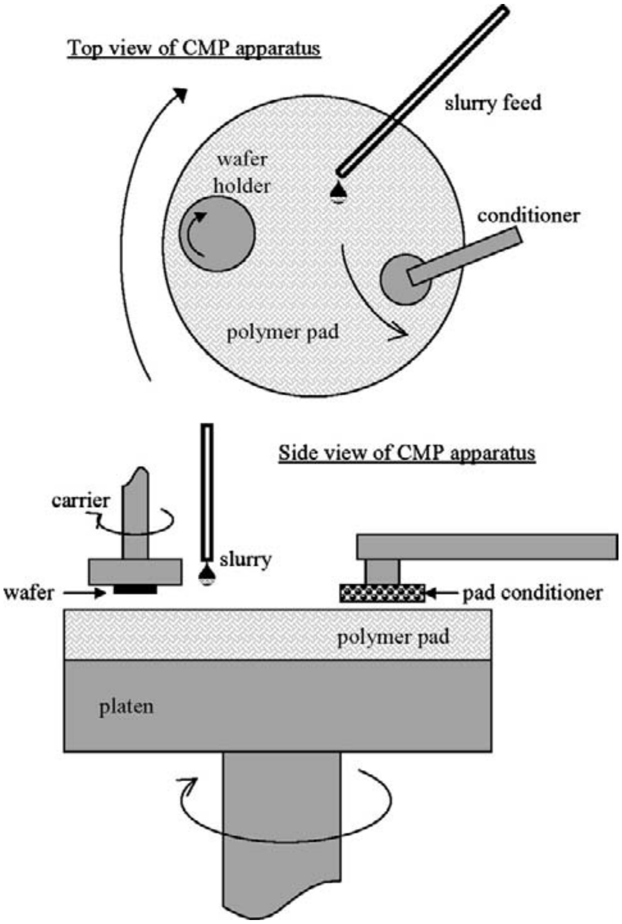

Figure 30.3 Schematic illustration of the CMP apparatus used typically for planarization.

spectroscopic ellipsometery) to measure the amount of film removal [28–30]. After the wafer is removed from the polishing tool, it is then cleaned to ensure removal of any abrasive particles, polishing debris, and chemicals from the slurry or the pad. Depending on the number of levels of metallization, repetition of the planarization and cleaning steps is then performed.

The success of the planarization process depends on two aspects. One is the planarity across the entire polished wafer surface and the other is the reduction in defects such as dishing, erosion, scratches, pits, voids, metal line, and oxide recesses [8]. A large number of operational parameters come into play such as the polishing apparatus configuration, applied pressure, rotational speed, and polishing pad conditioning [31]. Concurrently, properties of the consumables used during CMP such as the physical properties of the polishing pad, the types of slurry additives, and the physicochemical characteristics of the abrasive particles are also critical and strongly influence the polishing process in terms of both removal rates and defects caused [24,25,31–35]. In spite of recent advances in abrasive-free planarization, electrochemical polishing (ECP), and electrochemical–mechanical planarization (ECMP), the use of abrasive containing slurries still occupies a dominant position in the industry. With increased device densities and diminishing feature dimensions, it is imperative to understand the interactions between the polymer pad, wafer surface, and abrasive particles as manipulation and control of these interactions is essential for optimum planarization.

In this context, the choice of the abrasives and the additives in the colloidal slurry has a significant impact on the outcome of the planarization and the number of defects present in the final polished surface. The primary intent of this chapter is to highlight the role of polymeric additives in the slurry and the use of novel composite abrasive particles incorporating polymers as promising alternatives to traditional inorganic oxide nanoparticles. Polymeric additives are of fundamental importance to the planarization process as they can control the aggregation, dispersion, surface hardness, and stability of the inorganic oxide nanoparticles. Abrasive composites range from simple inorganic particles surface decorated with organic moieties to compressible polymeric microspheres that incorporate inorganic oxide nanoparticles. This brief review shows that innovative incorporation of polymeric components can form the basis of next generation of CMP slurries.

30.2 Inorganic Abrasive Particles

Typically, slurries used in CMP consist of a liquid solvent and a solid dispersant even though some abrasive-free slurries have been recently proposed [36–38]. The liquid phase is generally deionized water with additives like oxidizers (e.g., hydrogen peroxide), complexing agents (e.g., glycine), inhibitors (e.g., hydrazine), and surfactants (discussed below) [39–43]. The solid phase consists of abrasives, which are typically metal oxides such as alumina (Al_2O_3), silica (SiO_2), and ceria (CeO_2). While silica and alumina particles are commonly used for polishing copper and tungsten, silica and ceria are used to polish SiO_2, poly-Si, and silicon nitride (Si_3N_4) [44–49]. Silica and ceria are also used to polish lower dielectric constant organic material (e.g., methyl silsesquioxane) that are potentially advantageous as they help reduce interconnect delays, charge leakage, and simultaneously increase device speed [50–56]. Recent advances in abrasive development have involved the development of slurries containing mixed abrasive particles and abrasive composite particles [57–62], both of which are discussed below.

One of the research challenges in chemical mechanical polishing is that typically large volumes of slurries with high weight fraction of abrasive particles are necessary. Consequently, even though recipes for synthesizing particles of a wide range of composition, sizes, and shapes are available in literature [63–66], the restrictive synthetic conditions make it difficult for scale-up and adoption by the industry. This fact is also partly responsible for the numerous studies involving the planarization of metals and dielectrics with slurries containing silica particles due to the facile synthesis of spherical particles with narrow size distribution. Different synthetic routes are now available based on the early works of Iler and coworkers [64,67] that utilized an ion-exchange method with sodium silicate (Na_2SiO_3) as well as the more popular alkoxide hydrolysis of tetraethyl orthosilicate (TEOS) pioneered by Kolbe [68] and later extended by Stöber [69]. Although many other metal oxide nanoparticles such as titanium dioxide (TiO_2), Al_2O_3, or zirconium oxide (ZrO_2) have been prepared via the hydrolysis of the corresponding metal alkoxides, there is no existing literature that suggests their widespread use in CMP [70–72]. Stable dispersions of ceria nanoparticles have been prepared by precipitation in aqueous solutions [73,74] and nanosized ceria particles are well known for achieving significant removal rate during oxide CMP. Moreover, they have been shown to enhance the selectivity of the slurry and thereby, avoiding dishing during shallow trench isolation (STI) CMP [75–78].

Despite the widespread use of single abrasive slurries at all levels of metallization, major challenges still remain. Recently, it was recognized that some improvements in the planarization process, such as higher polish rate and better selectivity in film removal or reduction in defects, may be achieved by using slurries of mixed composition, i.e., those that consist of a mixture of two or more types of abrasive particles chosen from Al_2O_3, SiO_2, CeO_2, ZrO_2, TiO_2, or manganese oxide (MnO_2) [79–82]. Babu and coworkers [59] used mixtures of alumina and silica particles to polish copper and tantalum wafer surfaces. As shown in Figure 30.4, the data that Babu and coworkers have reported shows that removal rates of copper and tantalum could be manipulated and the selectivity managed by simply

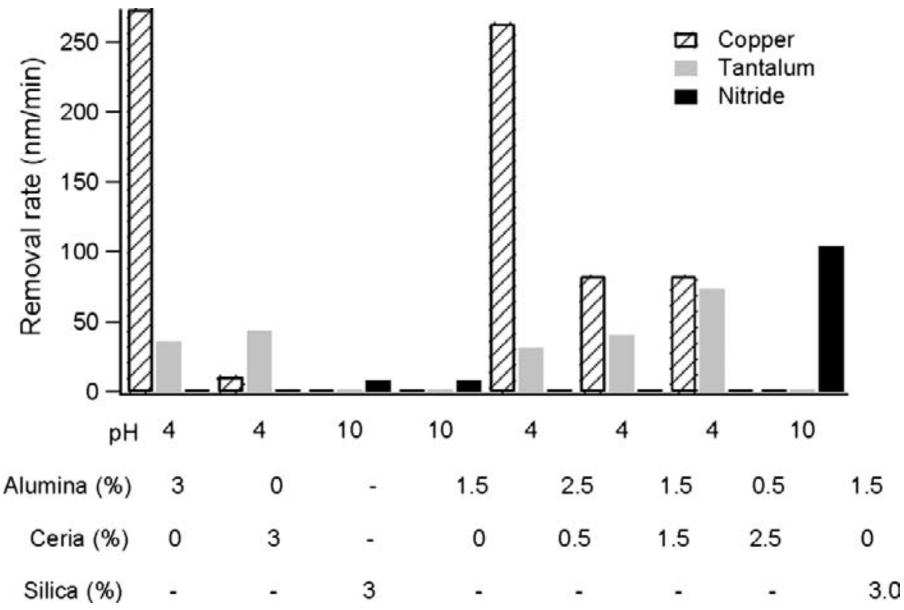

Figure 30.4 Plot illustrating material removal rates of different metallic and dielectric films using slurries containing single or mixed abrasives of silica, ceria, and alumina. The data has been taken from published studies by Jindal and coworkers [14,59] and combined in the plot.

controlling the ratios of alumina and silica particles in the slurry. In a different study [14], mixtures of alumina and ceria were employed to polish silicon nitride films and Figure 30.4 details the enhanced removal and reduced roughness on the silicon nitride surface that was achieved using mixtures of ceria and alumina as compared to the individual components. Figure 30.4 highlights the variations in material removal rate that can occur depending on the hardness of the film that is being removed, the weight fraction of abrasive particles used, and the pH conditions in the slurry. Lu and coworkers [61] have examined the polishing of oxide films using nanosized alumina, silica, or ceria alone and dispersed within mixtures. The results of their study clearly demonstrated the enhanced removal rates when mixed abrasives were employed. Other researchers have focused on using mixed abrasive slurries consisting of ZnO_2, MnO_2, and SiO_2 with lower solids content to produce inexpensive slurries that produce similar removal rates and planarity as the commercially available slurries that contain high silica weight fractions [83].

30.3 Organic Additives

The stability of the abrasive particles is an important criterion for CMP as particle sedimentation or aggregation often leads to the formation of scratches on the wafer surface after polishing [13,84–86]. Although filtration devices can remove some of the larger particles before it reaches the polishing pad, some *in situ* aggregation often occurs during the CMP process. To circumvent these drawbacks, many researchers have focused on organic additives (surfactants and polymers) to stabilize the inorganic abrasive particles via electrostatic repulsion, steric hindrance, or both [87,88].

The addition of oxidizers, inhibitors, and complexing agents to slurries for metal CMP creates a high ionic strength solution that typically results in the sedimentation of colloidal particles by electrostatic shielding. To avoid this, a variety of surfactants have been examined as additives to impart colloidal stability in slurries where electrostatic stabilization and other dispersion techniques do not perform adequately [89–92]. In principle, most ionic surfactants tend to form a bilayer around colloidal particles via hydrophobic chain interactions. Many common ionic surfactants that have no distinct polymeric component tend to stabilize the slurries by adsorbing onto the particle surface and subsequently increasing its surface charge causing electrostatic repulsion. For example, the cationic surfactant C_{12}TAB (dodecyl trimethyl ammonium bromide) has been used to prevent agglomeration in silica suspensions [93,94]. However, CMP slurries with a high ionic strength create conditions where the surface charge induced by the adsorbed surfactant is shielded by the ions in the slurry and the abrasives eventually sediment.

Conversely, nonionic surfactants tend to be polymeric in nature and stabilize slurries by adsorbing onto the particle surface resulting in steric repulsion. However, most nonionic surfactants do not significantly adsorb onto colloidal surfaces, preventing its use in current form [95–97]. In this context, mixtures of nonionic and ionic surfactants have been proven to be useful as surfactant synergism often leads to enhanced effects such as slurry stabilization. Palla and coworkers have experimentally demonstrated this using sedimentation tests [86] for slurries containing 0.1 M ferric nitrate ($Fe[NO_3]_3$) (oxidizing agent) and some of their data are shown in Figure 30.5. In their report, the settling behavior is defined as the ratio of the volume of dispersed slurry at any given time to the initial volume of slurry and the ratio ranges from 1.0 for stable slurries with completely dispersed

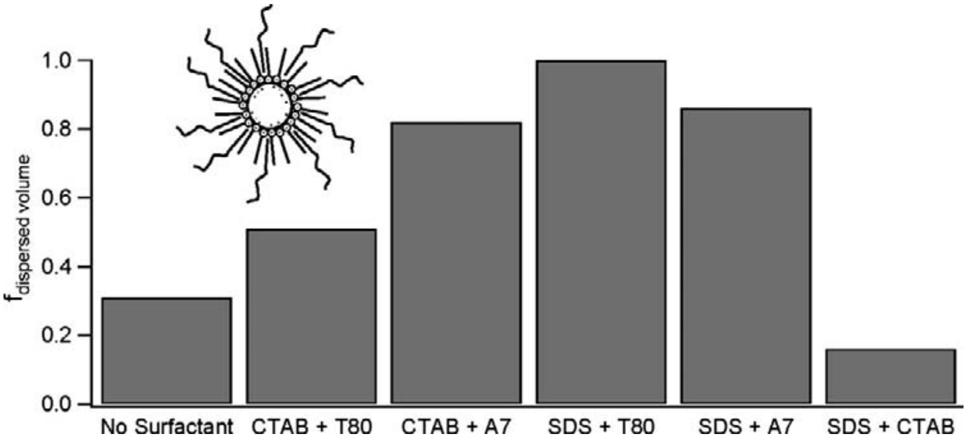

Figure 30.5 Plot illustrating the stability of slurries of colloidal alumina slurries when anionic, cationinc, and nonionic surfactants are added. The data has been selected from published study by Palla and coworkers [86]. *Inset*: A schematic of colloidal alumina with adsorbed anionic and nonionic surfactants to illustrate the long-chain nature of the nonionic additive (Adapted from the study by Palla and coworkers [86]).

particles to nearly 0.1 for unstable slurries. The data reported by Palla et al. shows that slurries with no added surfactant-stabilizing agents settle after 3 hours with a fractional dispersion volume of only 0.3. The combination of cationic surfactant such as cetyl tri-methyl ammonium bromide (CTAB) and Tween™80 (T80), which is a polysorbate nonionic surfactant, gives some stabilization. Changing the nonionic surfactant to Synperonic A7, which is an alcohol ethoxylate of lower molecular weight than T80 increases stability, but best results are seen with combinations of anionic and nonionic surfactants. In particular, the synergistic combination of an anionic surfactant such as sodium dodecyl sulfate (SDS) and Tween™80 results in fully stabilized slurry. Interestingly, the use of A7 with SDS worsens stability and a mixture of cationic and anionic surfactants results in the destabilization of the slurries with a fractional volume of dispersion less than that of the original slurry without a surfactant [86]. The schematic inset details the morphology of an alumina particle that has adsorbed ionic and chain-like, nonionic surfactants for enhanced slurry stability in ionic media.

It is evident from the data reported by Palla and coworkers shown in Figure 30.5 that a slurry with no added surfactant is unstable in an ionic media. Even though some enhanced stability of the colloidal particles is brought about by the ionic surfactants, the maximum stability is observed with a mixture of ionic and polymeric nonionic surfactants. Several other researchers have also reported the synergistic effects of mixed surfactant systems as stabilizing agents [98−101]. For example, Xu and coworkers [102] detail the adsorption of mixtures of ionic and poly(ethylene oxide) (PEO)-type nonionic surfactant onto kaolinite. They have shown that the adsorption of the polymeric nonionic surfactant is improved due to hydrocarbon chain interactions between the ionic and nonionic surfactant molecules.

The effectiveness of the polish using slurries modified with surfactants is worth mentioning. Although the surface quality of wafers polished with surfactant-modified abrasive particles is optimal with minimal surface roughness and deformation, the removal rates have been found to be low and typically, unacceptable [103−105]. At first it was speculated [103] that the micellar aggregates in the slurry inhibited particle−wafer interaction as shown in Figure 30.6. However, later studies have shown that the force per particle experienced during polishing was a few orders of magnitude greater than the force required to desorb the micellar structures [104]. Moudgil and coworkers [104] have attributed the reduction in the removal rate to a boundary layer lubrication effect, which is caused by the electrostatic interaction between the negatively charged (oxide) wafer surface and positively charged surfactant head group. The interaction has been thought to result in a lowering of the friction between the particles and the wafer surface, subsequently reducing the material removal rate. Addition of salt has been found to lead to competitive adsorption of the salt molecules to the surfactants causing desorption of the surfactant layers resulting in more appreciable removal rates [106,107].

Many polymeric dispersants have been used to impart stability in colloidal systems by promoting the adsorption of the polymers onto the surface of the abrasive particles and imparting steric hindrance [108−111]. Although there is a loss in both the translational and configuration entropy upon adsorption of the polymer chains, the overall free energy of the system is lower due to favorable chain−surface interactions. It has been shown that higher-molecular-weight polymers typically adsorb more strongly as dispersants than nonionic surfactants or lower-molecular-weight polymers. Moudgil and coworkers [103] have examined these effects by preparing slurries containing PEO with molecular weights of 8×10^3 Da and studying their adsorption onto the sol−gel

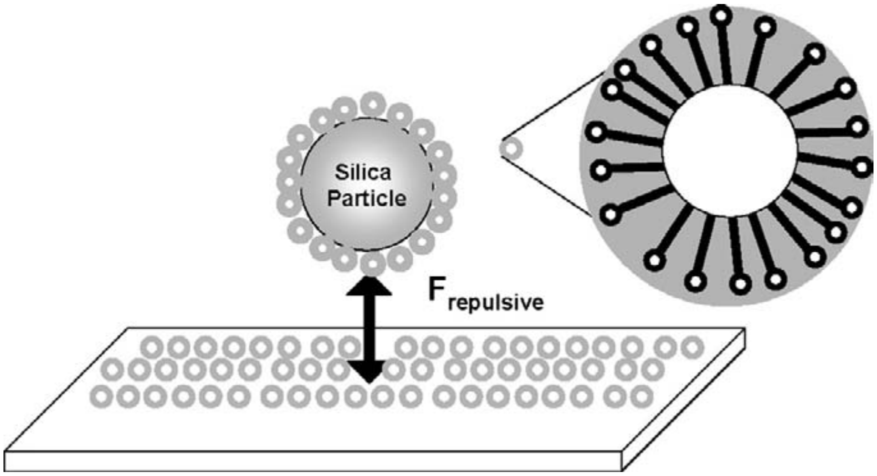

Figure 30.6 Schematic representation of the particle−substrate interactions in the presence of self-assembled surfactant aggregates on the surface of silica colloids (Based on literature report by Basim et al. [103]).

silica surface at a pH value of 9.5. The dosage of PEO used in their experiments was sufficient to fully coat the silica surface in pre-CMP studies. Although the adsorbed polymer resulted in smooth post-CMP wafer surfaces with approximately 10% decrease in surface roughness, a significant drop in the removal rates was also observed [103]. This result has been attributed to the lubrication of the particle and substrate surfaces by the adsorbed polymer layer and the occurrence of a physical scenario similar to that seen with the lower-molecular-weight surfactants.

Atomic force microscopy (AFM) friction coefficient measurement data has been obtained by Moudgil and coworkers [103] in the absence and presence of PEO at a single-particle substrate interaction level. The investigators measured the frictional force between an abrasive particle attached to an AFM tip and the silica wafer surface as a function of the normal force applied to the tip, which was then used to calculate the friction coefficient using Amonton's law. The results indicated a significant decrease of nearly 50% in the friction coefficient (i.e., from 0.25 to 0.12) in the presence of PEO, which was interpreted as polymer addition resulting in surface lubrication [103]. Boundary layer lubrication studies [112] using an AFM have shown that polymeric lubricants such as Z15 and ZDOL perfluoropolyethers lead to similar results on silica samples.

Moudgil and coworkers [103] also examined the effect of the PEO dispersant on CMP performance in the presence of salt (NaCl) to study the complementary effects of salt addition and the polymer. They found that in the presence of PEO the material removal rates increased with the addition of salt and the surface roughness values remained low (~8 Å) in spite of the increase in slurry ionic strengths due to addition of salt. By interpreting AFM force measurements, Moudgil et al. concluded that, on one hand, polymer mediation enhances surface quality through surface lubrication; on the other hand, this also results in a decreased material removal rate.

30.4 Composite Abrasives

Composite materials or composites for short are broadly classified as those materials that consist of two or more constituent materials with different physical and chemical characteristics [113]. Generally, these characteristics remain separate and distinct within the resulting composite structure, yielding enhanced properties when compared with the individual components. The study of these new materials has generated intense interdisciplinary efforts in engineering and the physical sciences because applications of these composite materials range from sensing [114] and drug delivery [115] to wastewater remediation [116−118]. Composites can be synthetic or natural. For example, wood is a well-known (natural) composite of cellulose fibers that are bound together by lignin [119]. Concrete is another

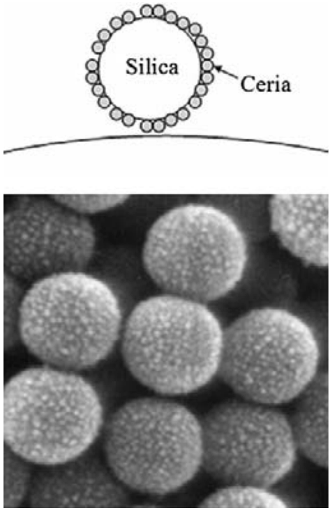

Figure 30.7 SEM image of silica particles coated with nanosize ceria (Reproduced with permission from Babu and coworkers [4]; Copyright Elsevier 2008).

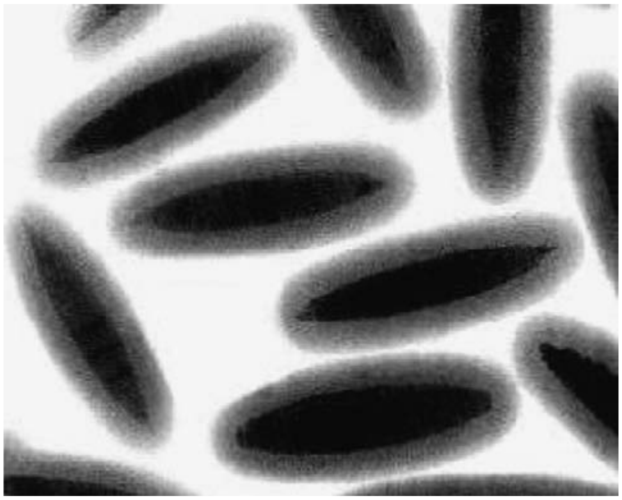

Figure 30.8 TEM image of elliptical hematite cores coated with silica (Reproduced with permission from Ohmori and coworkers [62]; Copyright Elsevier 1993).

well-known (synthetic) composite material that consists of aggregates (limestone or gravel) bound together via a cement matrix that forms chemical bonds with itself and aggregates upon hydration [120]. Composite materials can also be quite useful for tailoring the abrasive action of the particles in CMP to influence the etch rate of the oxide surface and reduce the local roughness creating a smoother wafer. At present, only a few studies exist in this arena and are discussed below.

Ohmori and Matijevic [4] have used an approach wherein ceria nanoparticles can be attached to larger silica particles to make purely inorganic composites (Figure 30.7). While Ohmori et al. rely on pH adjustments to form a bond between the acidic silica and basic ceria for a permanently attached surface layer of the latter, other approaches have also been investigated and have achieved the same result [121,122]. Another approach that has been pursued for making composite particles is the core-shell approach. This strategy allows one to tailor the characteristics of the core such as surface charge, reactive sites, and hardness, independently from the shell. The shell can be employed to manipulate the physical and chemical nature of the surface. Figure 30.8 shows TEM images of colloidal hematite (iron oxide) as cores with uniform silica layers formed by the hydrolysis of TEOS [62]. These particles have the same surface characteristics as spherical silica, and can be used to evaluate the effects of different shapes of chemically the same abrasives in polishing wafers or films.

In addition to above studies, recent investigations into organic—inorganic composites have been pursued and significant potential for the preparation of abrasive particles with controllable texture and surface hardness has been demonstrated. One example is the use of hybrid polymer particles. The incorporation of inorganic—organic groups into polymer networks to form new hybrid materials represents a powerful route to novel materials [123—127]. Coutinho and coworkers [13,105,116] have pursued the synthesis of organic—inorganic hybrid particles (Figure 30.9a) by the co-polymeriziation of *N*-isopropylacrylamide (NIPAM) with 3-(trimethoxysilyl)propyl methacrylate (MPS). The co-monomer MPS provides the polymeric particles with siloxane content and hybrid particles with different inorganic content can be obtained by changing the mass ratio of MPS to NIPAM. PNIPAM-based materials have been of tremendous interest because they are thermally responsive due to a delicate hydrophilic—hydrophobic balance that exists between the amide and isopropyl side chains [128—130]. Figure 30.10 shows the change in hydrodynamic diameter with temperature of the hybrid particles produced from MPS and NIPAM. The decrease in the particle size with increasing temperature is due to the well-known volume phase transition [131]. As shown in Figure 30.10, particles prepared using a high MPS to NIPAM ratio of 40% are not temperature responsive. However, the hybrid particle remains temperature responsive when the MPS to NIPAM ratio is 25% in the reaction mixture

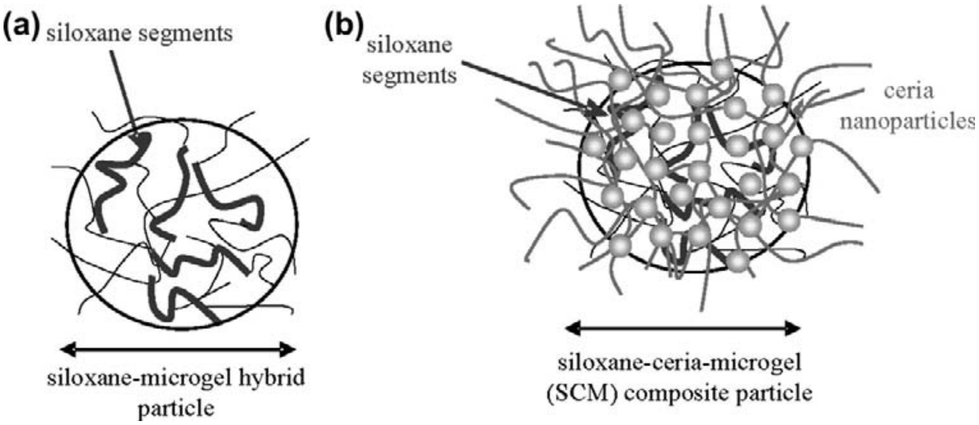

Figure 30.9 Schematic of (a) hybrid particle containing PNIPAM microgels with inorganic siloxane segments and (b) polymer-ceria composite particle consisting of ceria nanoparticles encased within an interpenetrating polymer microgel.

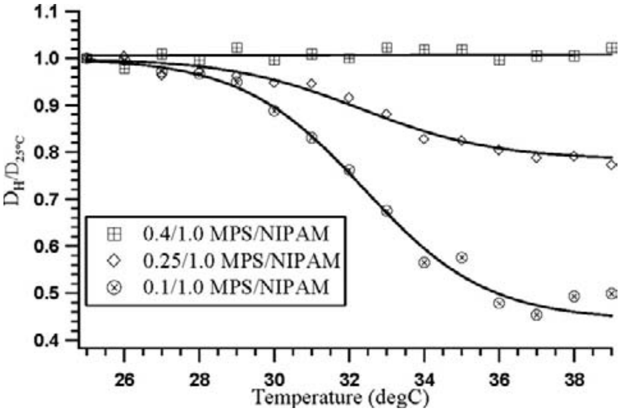

Figure 30.10 Temperature-dependent behavior [116] for the hydrodynamic diameter of the siloxane-microgel hybrid particles with different MPS/NIPAM ratio.

but the swelling ratio decreases when compared with the particles containing less MPS. Figure 30.11 shows the TEM images of two of the hybrid particles in comparison with the pure organic and the pure inorganic particle. The hybrid particles have been used for CMP studies as they are both compressible and abrasive. Although the hybrid particles produced a superior surface finish resulting in very planar surfaces compared to commercial inorganic slurries [13,105,116], the removal rates of oxide from the wafer surface have been found to be typically lower than 15 nm/min, which represents a major drawback for any commercial CMP applications and requires further developmental work.

While slurries containing nanoparticles of ceria are well known for their selectivity and removal of oxide from a wafer surface, prior studies have shown that they can also produce major and minor scratches [132−135]. To circumvent this, composite polymeric-ceria particles (Figure 30.9b) formed using the same platform of PNIPAM-based polymeric particles have also been investigated recently [13,116,136]. The average amount of ceria within the composite particles can be easily controlled as shown by the TEM images of one of a composite containing approximately 10% ceria (Figure 30.12a) and the other 50% ceria (Figure 30.12b). In both images, the white spots correspond to the ceria nanoparticles that have an average size of approximately 20 nm. The TEM images also demonstrate that the ceria is well dispersed and the composite is suitable for CMP.

Planarization studies using slurries containing the composites [13,116,136] with an average ceria content per particle of 50 wt% have revealed removal rates of

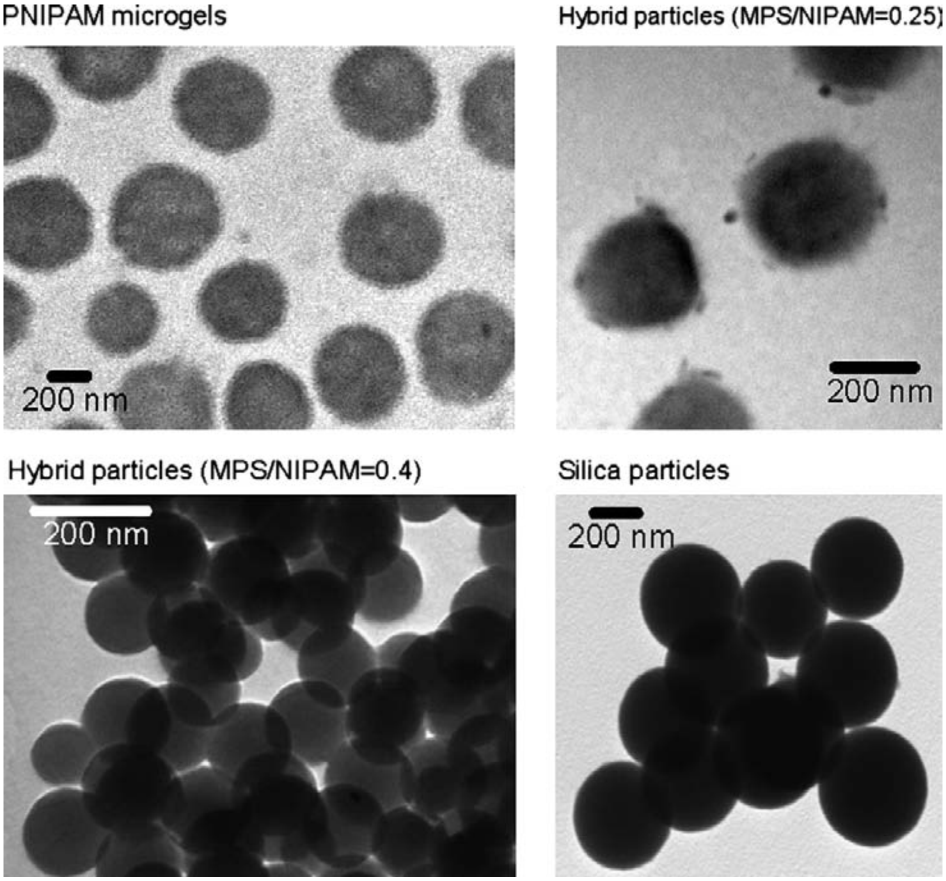

Figure 30.11 TEM images [116] of (a) PNIPAM microgels, (b) and (c) hybrid microparticles consisting of PNIPAM and siloxane segments, and (d) silica microparticles.

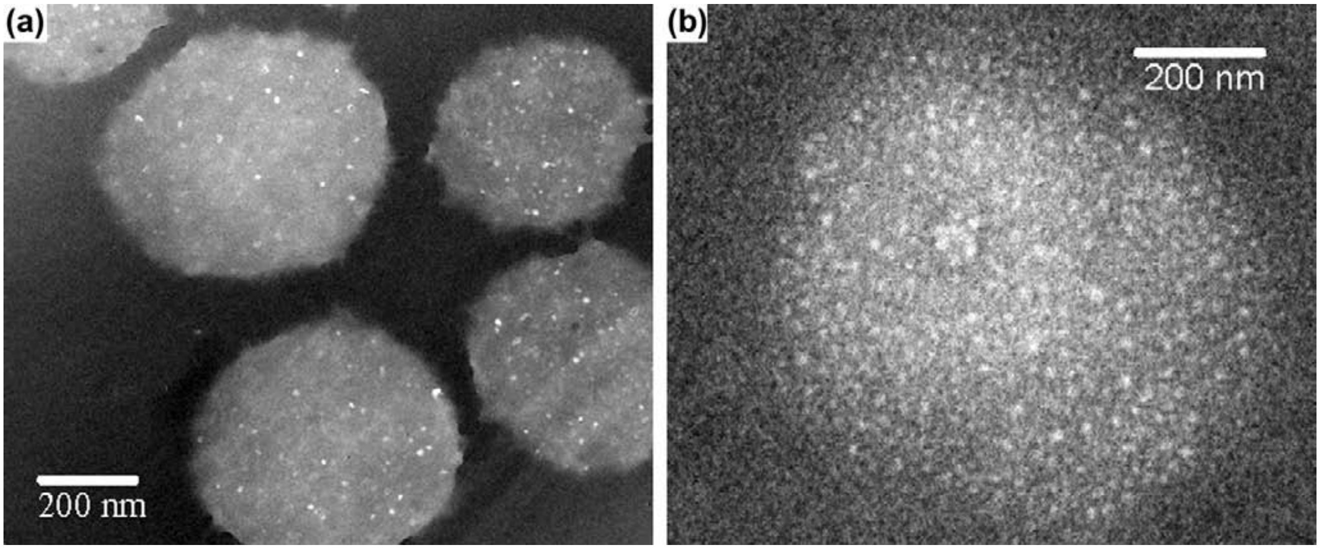

Figure 30.12 TEM images [116] of polymer-ceria composite with (a) 10 wt% ceria and (b) 50 wt% ceria. The contrast in the image has been digitally inverted to show ceria nanoparticles as white against a dark background for clarity.

~ 100 nm/min of the oxide (Figure 30.13), which was similar to the removal seen with a slurry containing only ceria at the same weight fraction. More importantly, surfaces polished with composite particle slurry showed lower topographical variations and surface roughness than when polished by slurries of only ceria nanoparticles. Interestingly, a lower coefficient of friction was measured for the polymer-ceria particles during polishing indicating reduced friction at the polishing interface, which supports the expectation that the polymeric component of the composite results in a milder abrasive interaction with the surface and also parallels results shown by other researchers that have used adsorbed polymers on particles [103].

Another type of organic—inorganic composite particle has been reported by Armini and coworkers that involves use of silica shell and a polymer core [79,137,138]. This composite was synthesized by either creating chemical bonds via silane-coupling agents or tuning the pH of the solution to form electrostatic attractive interactions between the core and the shell. Overall, fewer and shallower scratches were detected using either composite for oxide CMP versus the colloidal silica nanoparticles alone. However, the number of scratches using the composites created by electrostatic attraction was found to be lower than the composite with a silica shell formed by hydrolysis of TEOS. The investigators have attributed this finding to the irregular shape of the composite made by TEOS hydrolysis and the compressibility of the

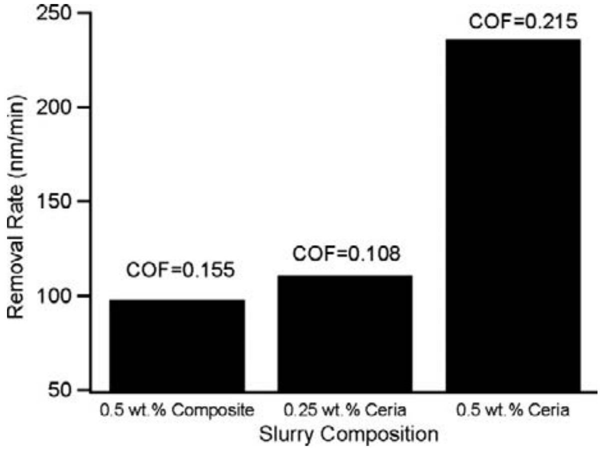

Figure 30.13 Removal rate and COF analysis when using slurries comprising of only ceria nanoparticles or composite particles to polish oxide films (Data from study by Coutinho [116]).

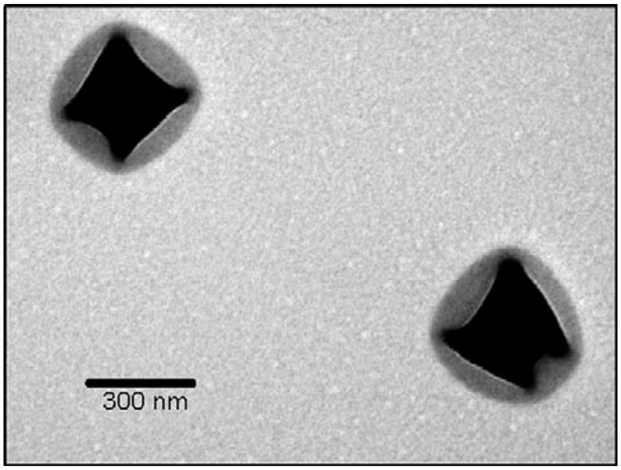

Figure 30.14 TEM images [116] of core (silica)-shell (polymer) particles.

other composites that do not have a complete silica shell but instead islands of silica on the polymeric core.

An inverted morphology based on a core of silica with a surrounding shell of polymer has been investigated [116]. These particles contained a core of silica and a shell of PNIPAM and as the polymer is temperature responsive, the thickness of the shell can be manipulated by changing the temperature of the slurry solution. Figure 30.14 shows a TEM image of these core-shell particles. However, oxide CMP studies conducted with slurries containing 0.5wt% of these particles did not produce satisfactory removal rates. Clearly, further investigation is required into optimizing these abrasives.

30.5 Conclusions

CMP is a critical step in semiconductor manufacturing. The transformation in electronic devices that has occurred in the past few decades has relied greatly on the efficiency and effectiveness of planarization using slurry polishing. The CMP process draws upon a broad base of knowledge from the fields of science and engineering, which range across colloidal science, surface and interfacial phenomena, polymer physics and chemistry, tribology, fluid mechanics and dynamics, and surface metrology. This review has focused on several aspects that are important in understanding the challenges of CMP and highlighted the potentially promising role that polymeric additives and polymeric composites can play in slurry formulation for achieving improvements in the CMP technology. While the focus in this discussion has been largely on literature studies of abrasive particles and the surface-active slurry additives, it is important to emphasize that the polishing pad used in CMP provides yet another area where polymers and composites can have a significant impact.

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Part V: Design and Applications

31 Design of Plastic Parts

David Kazmer
Plastics Engineering, University of Massachusetts Lowell, Lowell, MA 01854, USA

31.1 Introduction

Plastics provide many unique advantages when used in product design. From a cost perspective, plastics offer not only a low cost per unit volume of material, but also low manufacturing and assembly costs due to their ability to be easily formed into net shape products containing assembly features [1]. Their light weight and ease of recyclability also often result in the lowest possible life cycle costs compared to product designs based on other types of materials [2]. Concurrent with their cost advantages, plastics offer an extremely wide range of color, chemical, electrical, mechanical, thermal, wear, and other properties. Given the potential cost benefits, thermoplastics can be well utilized for many components in a complex product design. The primary challenge in their use is the optimal decomposition of the overall system into a set of components that best utilize the capabilities of the constitutive materials. Primary design considerations in engineering design often include structural performance, end-use temperature, electrical and thermal conductivity, manufacturability, assembly time, material costs, and others [3].

Once the decision to design a plastic part has been made, the product development team typically follows a structured methodology with tollgates as shown in Figure 31.1 [4]. In the first development stage—product definition—the team performs concept development, sales forecasting, and budgeting concurrently to determine the product layout. Estimates of production quantities are required to determine the manufacturing process for procuring the product's components. Lower production quantities will tend to drive the design to processes such as milling or thermoforming that have a lower initial tooling cost but higher marginal cost [1]. Higher production quantities tend to justify higher tooling costs that can yield more complex and economical designs, higher production rates, and lower costs.

All components in the product should be fully (or near fully) detailed during the product design stage. Perhaps the most important set of decisions involves the specification of the material and manufacturing process for each component. Given this information, the design team lays out the assembly, often determining the shape of the product by industrial design and the detailed dimensions by engineering analysis or manufacturability concerns. Fits and tolerances are driven by assembly guidelines and are verified with functional prototypes. Afterward, the detailed designs may undergo further development with the creation and commissioning of the hard tooling. Product launch usually occurs after one or more rounds of pilot production and beta testing, in which the product design and tooling may undergo revisions.

There is a substantial literature related to product design and plastic product design in particular. Among the most cited books on general product design are those written by Ulrich and Eppinger [5] as well as Boothroyd and Dewhurst [6]. Texts specific to plastic product design include those by Malloy [7], Erhard [8], and Campo [9]. Given this broad body of work, this chapter aims to provide new and generally helpful information for plastic part design. A first objective of this chapter is to provide the rationale for the use of plastics rather than other materials. Once the use of plastic is assumed, the chapter provides support for the determination of which of the four major plastics manufacturing processes should be used. Some general guidance is then provided about the design of plastic parts for stiffness and strength. Finally, the chapter considers part consolidation strategies according to the design for manufacturing and the assembly guidelines to minimize the total life cycle cost.

31.1.1 Material Selection

The decision to use plastic rather than wood, aluminum, or steel will have consequential ramifications on the shape, manufacture, cost, and end-use of the product. As such, product designers should consider what properties are truly required in a given application when developing plastic parts. Selection of an appropriate plastic material is vital in product development since the properties of the plastic are closely tied not only to the product design but also to the mold designs and process optimization. Inappropriate material selection may incur severe costs and delays late in the product development cycle (Figure 31.1) related to trying different materials and product redesigns.

31.1.2 Mechanical Properties

Figure 31.2 provides a comparison of different plastics and metals with respect to yield stress and elastic modulus.

Applied Plastics Engineering Handbook

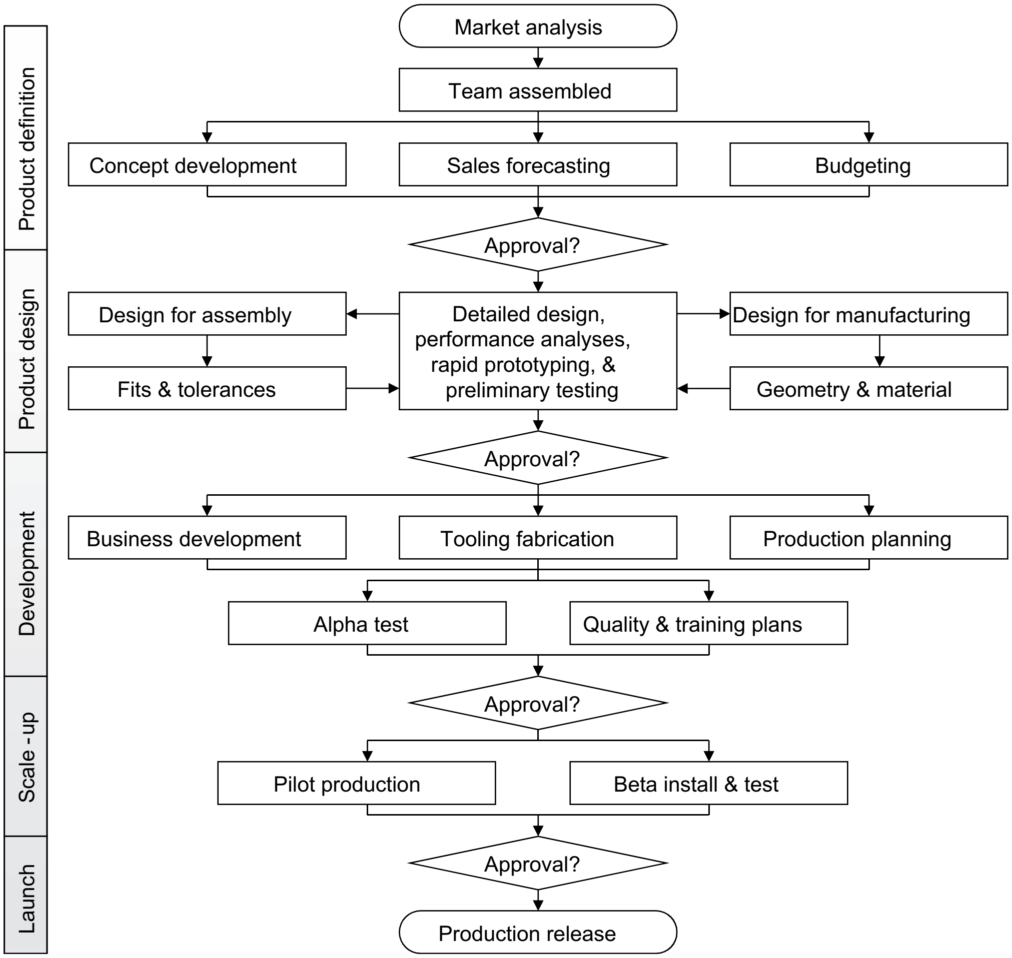


Figure 31.1 Methodology for design of plastic parts.

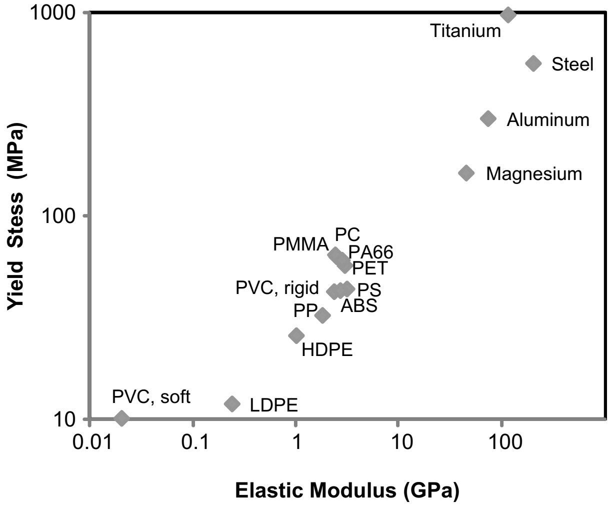


Figure 31.2 Comparison of yield stress and elastic modulus.

The plotted values for the various types of plastic are median values of hundreds of grades while the plotted values for the metals correspond to Aluminum 6061-O, Titanium 6-4, tempered AISI 1045 steel, and Magnesium M1A. In most applications, designers wish materials that will not deflect or break so materials in the upper right quadrant of Figure 31.2 would be preferred. It is important to note the use of log scales in the plot, such that the properties of the plastic materials are one or more orders of magnitude less than those of the metals. At first glance, it may seem impossible for plastics to compete on any measure but cost!

While plastics have low elastic modulus and yield strength compared to steel, aluminum, titanium, magnesium, and other alternative materials, their use in structural applications can be justified due to their low density and high strain to failure. For example, a designer may believe that the limiting constraint on a design may be strength to failure, when in fact the performance in end-use is more often driven by stiffness or impact strength. If stiffness is important, the designer may wish to consider the stiffness, *S*, per unit weight, *W*, rather than the modulus. Since the product weight is proportional to the density, the wall thickness, *H*, of plastic parts can be substantially thicker than those metal parts with no increase in cost or weight. The stiffness is proportional to the moment of inertia, which in turn is a function of the thickness of the cube.

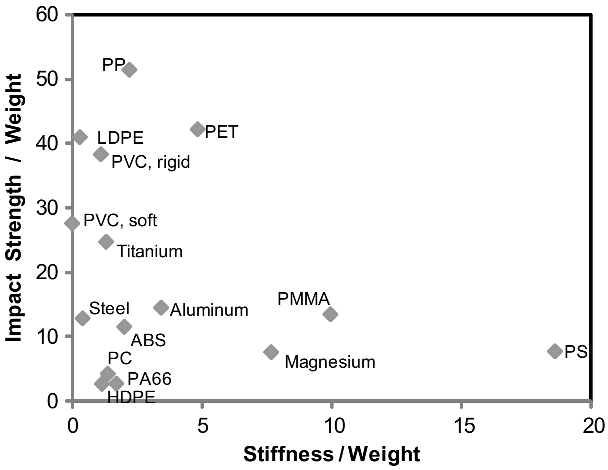


Figure 31.3 Comparison of impact strength and stiffness per unit weight.

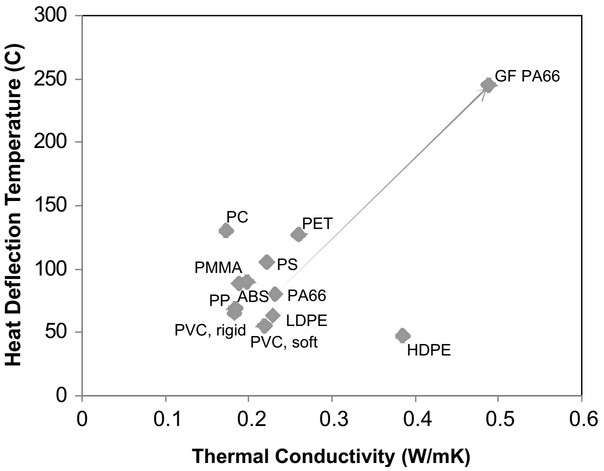


Figure 31.4 Thermal properties of plastic materials.

The stiffness per unit weight can then be evaluated as a function of the elastic modulus, E, and the density, ρ, as:

$$\frac{S}{W} \propto \frac{E}{\rho^3} \tag{31.1}$$

Similarly, the designer may wish to consider the impact strength, I, per unit weight rather than the yield strength if failure avoidance is important. The impact strength per unit weight is approximately equal to the modulus times the elongation at failure, $\varepsilon_{\max}$, divided by the density:

$$\frac{I}{W} \propto \frac{E \bullet \varepsilon_{\max}}{\rho} \tag{31.2}$$

Figure 31.2 indicates that the designer should clearly prefer titanium, steel, and other metals to all plastics if higher modulus and yield stress are solely desired. For comparison, Figure 31.3 plots the stiffness and impact strength per unit weight for the same. When the lower density and higher elongation to break are considered in actual application, plastics can outperform the metals by offering higher stiffness and/or impact strength per unit weight. Indeed, plastics can be specifically selected to provide high stiffness per unit weight (such as polystyrene) or high impact strength per unit weight (such as low density polyethylene or polypropylene) or different combinations of impact strength and stiffness.

31.1.3 Electrical and Thermal Properties

Polymers are typically considered insulating materials in electrical and thermal applications. With respect to electrical properties, plastics have very high electrical resistivity, on the order of 10^{15} Ωcm, with polypropyelene and polyvinyl chloride providing even greater resistivity of 10^{17} Ωcm. Dielectric strengths for plastics range from 20 to 120 KV/mm. For comparison, aluminum alloys have an electrical resistivity on the order of 10^{-5} Ωcm and no dielectric strength. These electrically insulating properties make plastic materials excellent candidates for enclosures, chassis, and other housings that contain or interact with electrical components.

Thermal properties are of critical importance in many applications in which the plastic parts must withstand an end-use of environment above room temperatures or otherwise permit the conduction of heat. The heat deflection temperature (HDT) is a commonly used method to determine the temperature at which a plastic beam deflects under a given load. Median values for HDT of various materials are plotted against thermal conductivity in Figure 31.4. The data indicate that unfilled plastic materials have heat deflection temperatures between 50 and 120 °C at applied pressures 1.8 MPa. Thermal conductivities vary between 0.2 and 0.4 W/mK. For comparison, aluminum has a solidus temperature of 582 °C and a thermal conductivity of 180 W/mK. Still, neat plastics can be used in most commodity applications without difficulty. Plastics can also be used in many engineering applications requiring high heat resistance through the use of fillers. For example, the use of 40% glass fiber (GF) to nylon 66 raises the heat deflection temperature to 250 °C and the thermal conductivity to 0.5 W/mK, thereby permitting the use of this material in automotive under hood applications.

31.1.4 Processing Properties

From a processing perspective, plastics manufacturers prefer materials that are easy and quick to process. The ease with which a material can be processed is often related to the viscosity of the polymer melt since the viscosity is an intrinsic measure of the material's resistance to flow given an applied pressure. A plastic melt with a higher viscosity will

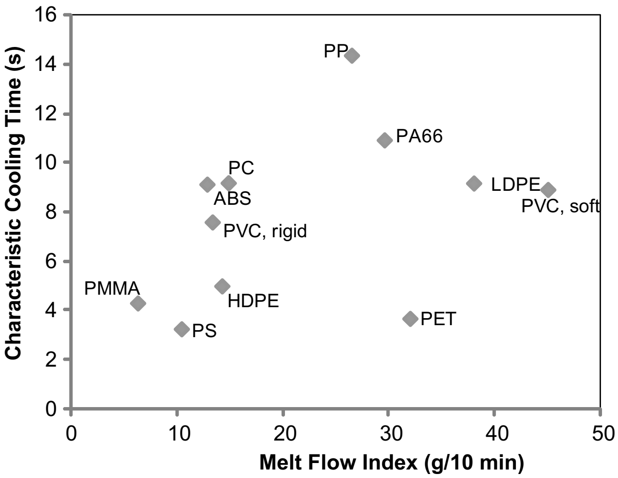


Figure 31.5 Processing properties of plastic materials.

require more pressure, more time, or elevated processing temperatures during the forming of the plastic part than another plastic melt with a lower viscosity.

The rate at which a material is processed is often determined by the time required to (1) heat the plastic from the solid to melt state and (2) cool the melt back to a solidified state at which the formed part may be handled. The heating times will vary greatly depending on the heating mechanism used by the process. Extrusion, injection, and blow molding provide rapid melting of plastic pellets through the combined heat conduction and internal viscous generation along the screw. By comparison, thermoforming more slowly heats the plastic sheet by mixed radiation/conduction. In all processes, however, the cooling time relies on internal conduction to remove heat from the formed part to the surrounding media. The characteristic cooling time can be estimated as a function of the part's wall thickness, H, thermal properties, and processing temperatures:

$$t_c = \frac{H^2}{\pi^2}\frac{\rho \bullet c_p}{k}\ln\left(\frac{4}{\pi}\frac{T_{\text{heating}} - T_{\text{cooling}}}{T_{\text{eject}} - T_{\text{cooling}}}\right) \tag{31.3}$$

Figure 31.5 provides a comparison of the melt flow index and the characteristic cooling time for different types of materials assuming a wall thickness of 2 mm. In general, a higher melt flow index and a lower characteristic cooling time are preferred. The data indicate that polyethylene will likely have a longer processing time than polyester for a part with the same wall thickness. Also, the data suggest that PMMA will be the most difficult to force through a die or into a mold. Plastics parts and their corresponding molds/dies should be designed such that the desired processing times and conditions are achievable. Changes in wall thickness and material type/grade can have significant impact on the quality of the plastic parts and the productivity of the plastics manufacturing process.

31.1.5 Summary

The preceding sections provided comparisons of different types of plastics. Yet, the properties of different plastic grades vary greatly through the purposeful control of morphology, additives, and fillers as described elsewhere in this book. In designing plastic parts, the part designer must select a material with mechanical, thermal, and processing properties that reasonably match the needs of the application. In optimizing the design, the single most important decision is often the specification of wall thickness. The reason is that the wall thickness affects so many properties including the part weight, stiffness, strength, impact resistance, heat transfer, processing cost, and others. The interaction between multiple performance attributes complicates the selection of the type and grade of plastic for a specific application. It is sometimes unclear if a thinner wall thickness used with a more expensive engineering thermoplastic, such as a PC/ABS blend, is preferable to a thicker wall thickness used with a commodity plastic, such as PP. To clarify the decision, the part designer should rank the importance of the part specifications, analyze alternative designs composed of different materials, and select the design and material having the most preferable trade-off.

31.2 Process Selection

Once the determination has been made regarding the use of plastic for a part design, the next most important decision is likely the selection of the manufacturing process. While there are many types of plastics manufacturing systems [10], four of the most common are extrusion, injection molding, blow molding, and thermoforming. Together with rotomolding, these five plastics conversion processes accounted for sales in the United States of over 94 billion dollars in 2007 [11]; global sales of plastics products is several multiples higher [12]. Sales by extrusion represents 36% of the dollar sales and a majority of the resin consumption since this process provides high volumes of pipe, profile, film, tubing, and sheet products. Injection and blow molding each provide roughly 25% of the industry sales, though with lesser volumes of resin consumption. Thermoforming and rotomolding combined provide roughly 10% of the plastics product sales. While blow molding, extrusion, injection molding, and thermoforming are respectively discussed elsewhere, a brief review from a plastic part design perspective is provided in the next section.

31.2.1 Extrusion

Plastics extrusion [13] is a continuous process used to form a linear product having a constant cross-section. A single screw extruder is depicted in Figure 31.6, and is comprised of a heated barrel surrounding one or more rotating screws driven by a motor. During operation, the solid

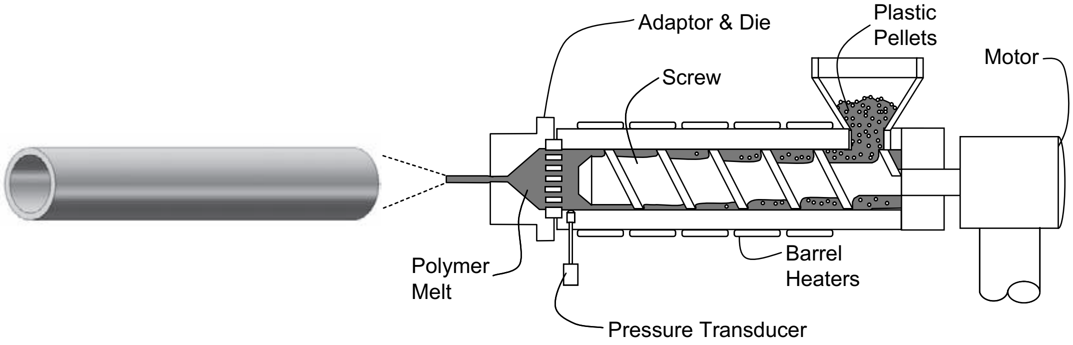


Figure 31.6 Plastics extrusion.

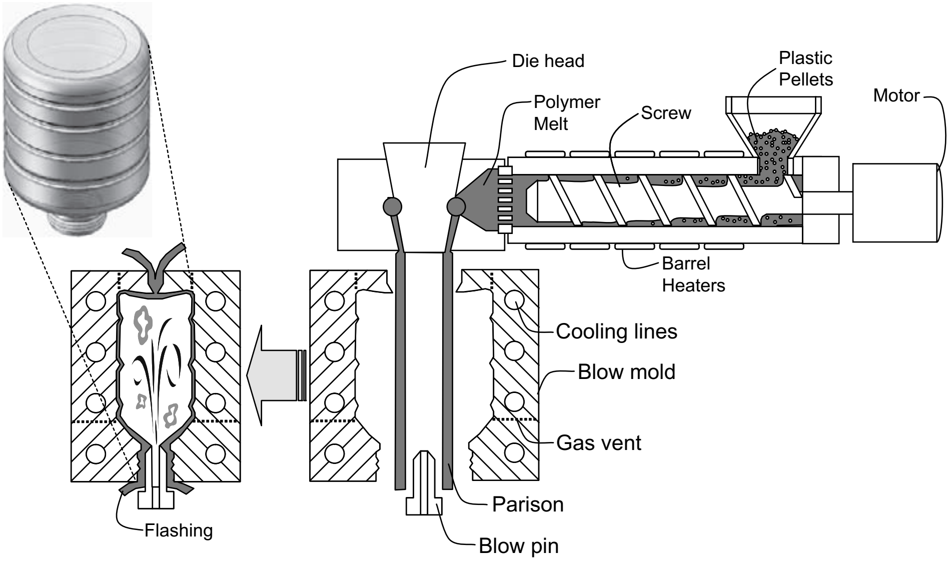
plastic pellets are fed to the screw. The screw is carefully designed to auger the material forward toward the die with continued rotation. As the material is conveyed forward, the plastic is compressed and converted to a molten state by a combination of heat conduction from the warmer barrel and internal shear heating caused by the flow of the plastic within the screw. By the time the plastic reaches the extruder outlet, a homogenous polymer melt should be formed with a desired melt temperature.

A breaker plate, screen pack, and die are located at the extruder outlet. These components serve to seal the interface between die and the extruder, filter any contaminants, increase the flow resistance and plastication pressure, and ultimately form the polymer melt into a desired shape. As the plastic leaves the die, it may swell due to the change in pressure at the die lip and subsequent polymer relaxation. Afterward, the extrudate may pass through calibrator dies or calendar rolls to control the solidification and dimensions. If dimensional control is not critical, the extrudate may simply be pulled through a water bath or just air cooled prior to spooling, cutoff, or other post-processing. In terms of sheer volume of plastic parts, the most common applications of extrusion are pipe, tubing, film, sheet, and custom profiles. Altogether, extruded products represent approximately 35% of the plastics industry output.

31.2.2 Blow Molding

Blow molding [14] is a common process for production of hollow containers, ranging from commodity products such as soda or water bottles to highly engineered products such as gas tanks and electrical enclosures. The two most common types of blow molding are extrusion blow molding and injection blow molding with many variants related to handling of the parison and molds. Figure 31.7 depicts an extrusion blow molding process, in which a cylinder of semi-molten plastic, called a parison, is extruded downward between two open mold halves. Once a parison of sufficient length is extruded, the mold is closed and a blow pin pressurizes the inside of the parison. The air pressure forces the parison to inflate until it contacts the entire surface of the mold cavity. The heat from the formed plastic is then transferred through the mold to the cooling lines. Once the plastic

Figure 31.7 Plastics blow molding.



is sufficiently rigid, the mold is opened, the product is removed, and any flashing is trimmed.

Because of the mold's irregular interior geometry, blow-molded products will tend to have a non-uniform thickness with weak and strong sections. To optimize the wall thickness, the die head in many blow molding machines can be programmed to adjust the parison's thickness down the length and across the diameter of the parison. While this level of control is often sufficient for commodity products, better distribution of the material may be provided with injection blow molding, in which a pre-form is injection molded and later inflated in a blow mold, or injection stretch blow molding, in which the pre-form is stretched prior to inflation. Furthermore, many blow molding processes use multiple extruders and complex die heads to provide a multilayer parison or pre-form. These multilayer systems can provide improved structural and barrier properties while minimizing the processing and materials costs [15].

31.2.3 Injection Molding

Injection molding [16] is a cyclic process used to make extremely complex parts to tight tolerances. An injection molding machine is depicted in Figure 31.8. While there are many different variants of the injection molding process, most injection molding processes generally include plastication, injection, packing, cooling, and mold resetting stages. During the plastication stage, the polymer melt is plasticized from solid granules or pellets through the combination of heat conduction from the heated barrel and the internal viscous heating caused by molecular deformation with the rotation of the screw. During the filling stage, the polymer melt is forced from the barrel of the molding machine and into the mold. The molten resin travels down a feed system, through the gate(s), and throughout one or more mold cavities where it will form the desired product(s). Since the polymer melt flows inside a thin-walled cavity, the melt pressures in injection molding are typically much higher than those in extrusion or blow molding.

After the mold cavity is filled with the polymer melt, the packing stage provides additional material into the mold cavity as the molten plastic melt cools and contracts. The plastic's volumetric shrinkage varies with the material properties and application requirements, but the molding machine typically forces 1−10% additional melt into the mold cavity during the packing stage. After the polymer melt ceases to flow, the cooling stage provides additional time for the resin in the cavity to solidify and become sufficiently rigid for ejection. Then, the molding machine actuates the necessary cores, slides, and pins to open the mold and remove the molded part(s) during the mold resetting stage. Compared to the other processes described here, injection molding tends to provide not only the fastest cycle times because the mold cools the plastic from two sides but also the best dimensional consistency since the mold also acts as a fixture during cooling.

31.2.4 Thermoforming

Thermoforming is a cyclic process for making large or small plastic products that typically have one large open face, such as refrigerator liners, bath tubs, or drinking cups. There are many different types of thermoforming processes including vacuum forming, pressure forming, plug assist forming, and others. Figure 31.9 depicts a vacuum forming

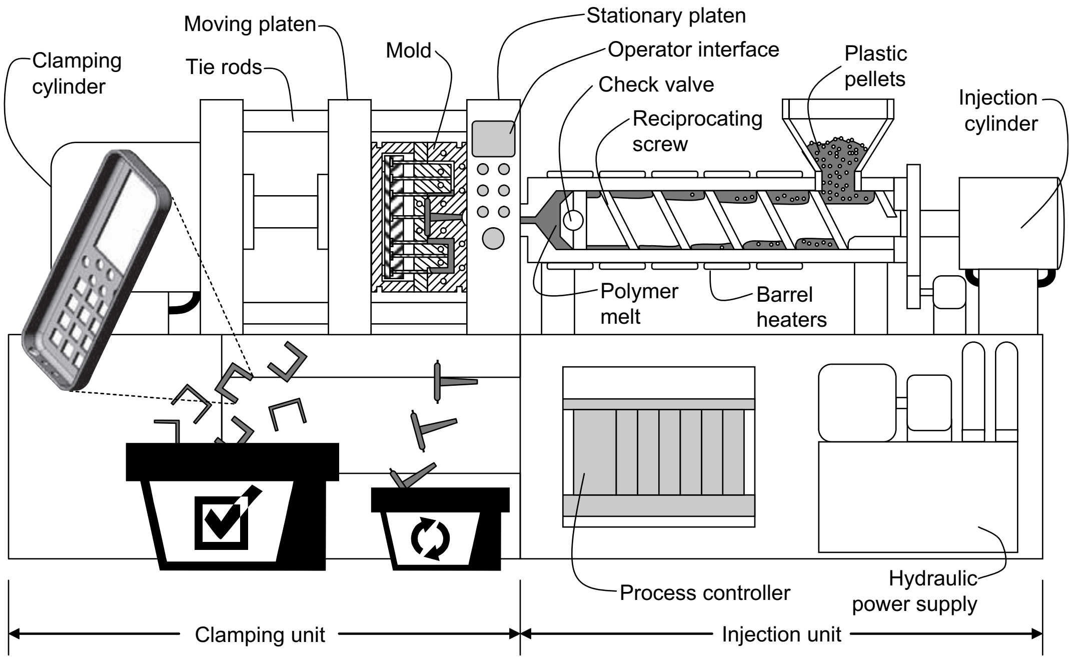


Figure 31.8 Plastics injection molding.

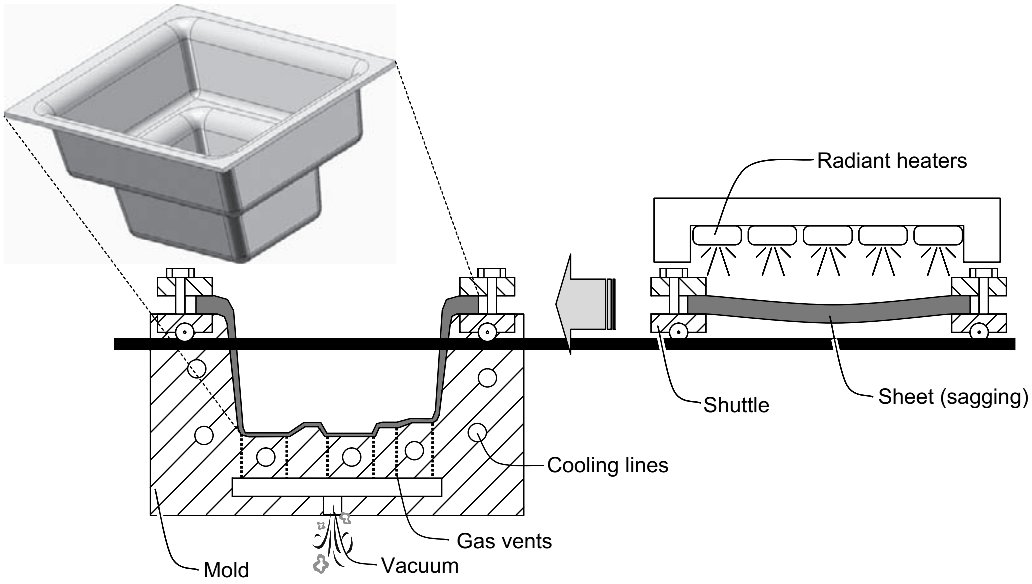


Figure 31.9 Plastics thermoforming.

process, which is the simplest of these processes. In this setup, the thermoplastic sheet or film is heated in an oven by radiant heaters. Once the sheet is sufficiently compliant, the sheet is shuttled to the mold where a vacuum is applied to remove the air between the sheet and the mold cavity surfaces. The sheet is held against the mold surface until sufficiently cooled and rigid. The sheet with the formed part is then removed from the mold and trimmed. As with blow molding, the inflation of the sheet into a deep, non-uniform mold cavity can result in broad variations in the wall thickness of the thermoformed part.

Compared to the previous processes, thermoforming may be the simplest process with the lowest investment in tooling but also the lowest production rates. Additional investment can improve the economics and capability of thermoforming processes. For example, the two-station setup of Figure 31.9 may have almost twice the production output of a single-station thermoformer since one sheet may be heated while a previously heated sheet may be loaded, formed, cooled, and unloaded. As another example, pressure forming uses larger positive pressures than vacuum forming to more rapidly deform the sheet with larger forces, thereby forming more complex and thinner sheets to higher levels of detail. As yet another example, moving plugs may be used to deform the heated sheet during the former process and thereby assist the distribution of the plastic throughout the thermoformed part.

31.2.5 Discussion

The design of a plastic part and the selection of the plastics manufacturing process are extremely inter-dependent; it is critical to match the plastic part design to the capabilities of the plastics manufacturing process. For example, a plastic part designed for injection molding will not be interchangeable with a part designed for blow molding so the part designer should select the process early in the product development cycle (Figure 31.1).

Each of the four major plastics manufacturing processes has unique characteristics that determine advantages and disadvantages as listed in Table 31.1. For example, the continuous nature of the extrusion process directly determines the low design complexity of the plastic extrudate. Still, the extrusion process' relatively simple die design provides affordable tooling while the two-sided cooling and continuous nature provide high production output rates. With machining, bending, and other secondary processes, extrusion can produce more sophisticated designs than conventionally considered.

Thermoforming and blow molding, as low pressure processes, allow the use of non-ferrous molds that are lower cost to produce. Since the forming mechanism relies on inflation, these processes also allow the molding of much larger parts than would be economically feasible with extrusion or injection molding. However, the low pressure inflation also inhibits the formation of small, detailed features such as ribs and bosses. Another related issue is the local thinning due to the drawdown of the sheet or parison as it is being formed. A third drawback is that the heat transfer during cooling is predominantly through one side of the formed part into the sheet, which greatly increases the cycle time compared to similarly thick products made by extrusion or injection molding. For these reasons, the thermoforming and blow molding processes are extensively used to produce thin, commodity products though there has been recent growth in thicker and more complex plastic parts [17].

Of these four processes, injection molding is the most able to produce complex geometry to tight tolerances. The reason is that the fully enclosed mold cavity supports the

Table 31.1 Process comparison

	Extrusion	Injection Molding	Thermoforming	Blow Molding
Type of process	Continuous	Cyclic	Cyclic	Cyclic
Type of product	Extruded profile	Complex but not hollow	Open faced	Hollow
Design complexity	Low	High	Medium	Medium
Forming mechanism	Viscous flow	Viscous flow	Inflation	Inflation
Forming pressure	Medium	High	Low	Low
Cooling mechanism	Two-sided convection or conduction	Two-sided conduction	One-sided conduction	One-sided conduction
Cooling rate	Medium	High	Low	Low
Dimensional variation	Medium	Low	High	High
Tooling cost	Low	High	Low	Medium

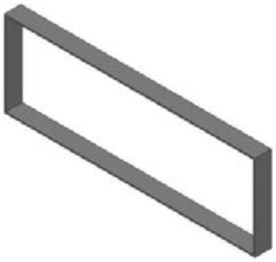
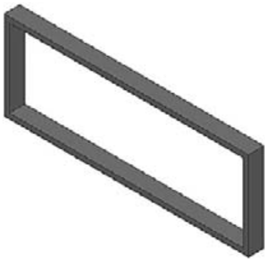
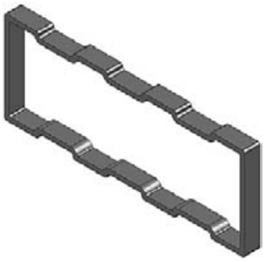
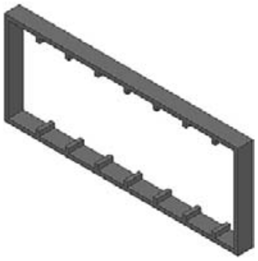
plastic as it flows at high pressure around arbitrarily complex surfaces. These same surfaces constrain the plastic as it cools while the process compensates for volumetric shrinkage by conveying additional polymer during the packing/holding phases. The injection molding process also provides for high production rates since the plastic can cool quickly with heat transfer to both sides of the mold cavity. Yet, these capabilities come at the cost of more expensive molds and machinery. As such, the plastic part designer must consider what attributes are vital in their application, choose an appropriate process, and then seek to optimize the design to best utilize that process' capabilities.

31.3 Structural Design

31.3.1 Design for Stiffness

Compared with steel and aluminum, plastic parts receive their stiffness through the use of thicker wall sections and non-planar geometry. Some alternative cross-section designs are shown in Table 31.2, all providing an internal cross-section area of 150 mm by 50 mm. It should be understood that these sections are intended for use in a larger system, such as an enclosure, and may be split into multiple parts and assembled to provide a finished product. Still, the comparison of these fundamental designs provides

Table 31.2 Section designs for stiffness

Steel Box	ABS Box	Corrugated ABS Box	Ribbed ABS Box
			
Thickness: 0.5 mm	Thickness: 3.4 mm	Thickness: 3.1 mm	Thickness: 2.8 mm
Stiffness: 8560 g/mm^2	Stiffness: 8610 g/mm^2	Stiffness: 8640 g/mm^2	Stiffness: 9520 g/mm^2
Mass: 15.9 g/cm	Mass: 14.3 g/cm	Mass: 13.9 g/cm	Mass: 13.2 g/cm
S/M: 5380 mm^{-1}	S/M: 6020 mm^{-1}	S/M: 6220 mm^{-1}	S/M: 7210 mm^{-1}

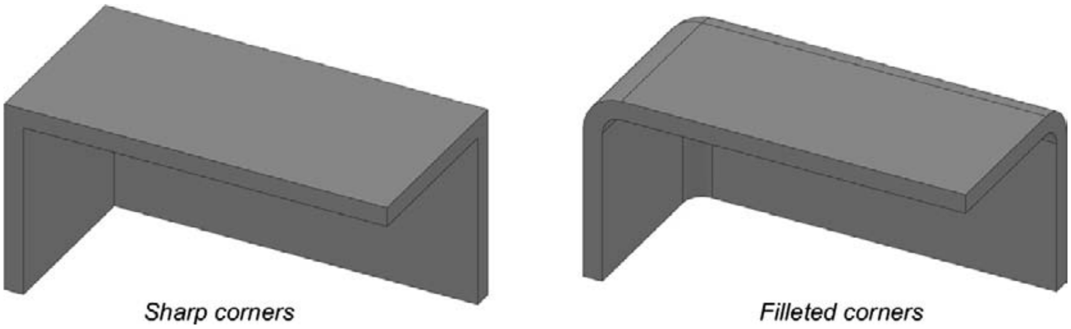


Figure 31.10 Avoid stress concentrations.

significant guidance toward the optimal design of plastic parts.

Consider first the design of a steel box beam section provided on the left side. This structure is typical of products incorporating bent sheet metal components. With a gauge thickness of 0.5 mm and an elastic modulus of 205 GPa, the stiffness is governed by the moment of inertia on the horizontal axis with a value of 8,560 g/mm^2. The mass of the steel section is 15.9 g/cm of length. If a similar design is implemented with an ABS plastic, having an elastic modulus of 2 GPA, then the wall thickness must be increased to 3.4 mm. The stiffness now exceeds that of the steel design while a 10% weight savings is achieved, which is consistent with the material properties plotted in Figure 31.3.

While the low density of the ABS provides a high stiffness—weight ratio that exceeds that of steel—the plastic part design can be further improved by using the geometric flexibility afforded by the plastics processing. Two common strategies for increasing the stiffness of plastic parts are also shown in Table 31.2. The use of a corrugated structure provides for vertical connecting walls between the upper and lower surfaces of the corrugation. As a result, the nominal wall thickness can be decreased while further increasing the part stiffness. For this reason, corrugation is often used to stiffen blow-molded and thermoformed products that would otherwise have extremely low stiffness. Injection molding also provides the ability to add vertical ribs to directly stiffen the product, though care must be taken to ensure that the ribs do not reduce the internal functionality or otherwise impair the manufacturability of the product. In such a manner, the ribbed ABS design provides a stiffness:weight ratio 34% greater than the steel design while also allowing incorporation f many other features into the design at negligible cost.

31.3.2 Design for Strength

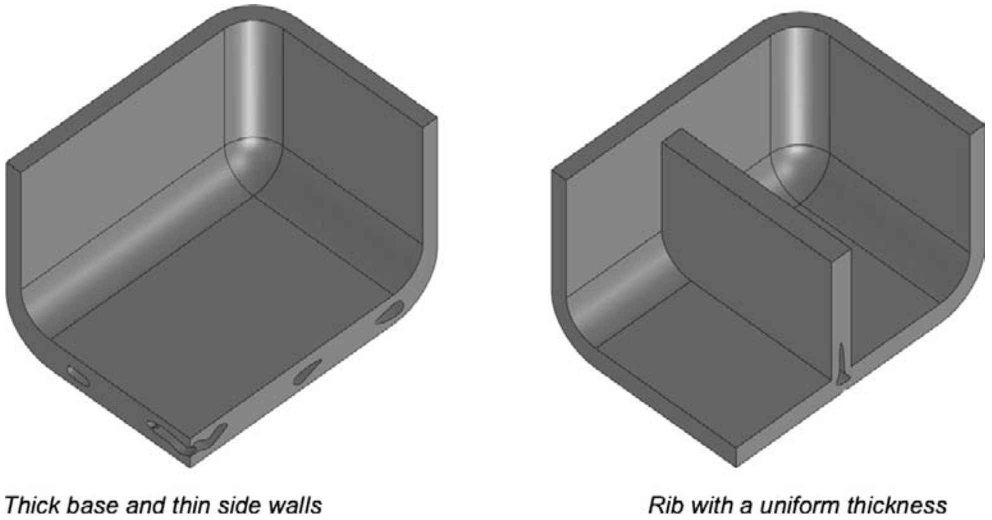
Structural plastic part failures occur for a variety of reasons including ductile failure, brittle failure, fatigue, and others. Ductile failure sometimes results in catastrophic failure of the plastic part in end-use, but more often the ductile failure causes excessive deformation that may be rectified by increasing the stiffness as discussed in the preceding section. Perhaps the most undesired failure mode is unexpected brittle failure, which can occur in plastic products due to stress concentrations, buckling of ribs, inadequate processing, highly loaded knit lines, and poor joining [18].

One common issue is the lack of filleted corners as demonstrated in Figure 31.10. While filleting the corners is a recurring rule in plastic product design, it is often avoided for aesthetic or cost reasons or simply overlooked. The importance of avoiding sharp corners stems from the avoidance of stress concentrations, K, which are a function of the corner radius, ρ:

$$K = C\sqrt{\frac{1}{\rho}} \tag{31.4}$$

where the coefficient C is a factor of the geometry and material properties [18]. Plastic parts composed of brittle materials such as acrylic, nylon, styrene, and phenolic tend to be brittle and will exhibit fewer failures with an internal fillet greater than the nominal wall thickness. Filleting the corners also provides other benefits including more uniform heat transfer during processing, less geometric warpage, improved part ejection, and longer mold life as well.

In optimizing the product design, designers are often tempted to specify non-uniform thicknesses throughout the product, with thicker wall sections in areas under higher load and thin wall sections elsewhere. However, the use of a uniform thickness throughout the plastic part design provides several benefits related to strength and other product quality attributes. From a processing viewpoint, the use of non-uniform thicknesses can result in varying levels of residual stress as well as non-uniform ejection temperatures. These conditions can induce geometric warpage and a poorly fitted assembly that contributes to a structural failure. In response, plastics manufacturers will tend to extend cycle times to use the mold as a fixture and eject the polymer at a more uniform temperature. While this strategy does improve the tolerances of the plastic parts, it can exacerbate



Thick base and thin side walls

Rib with a uniform thickness

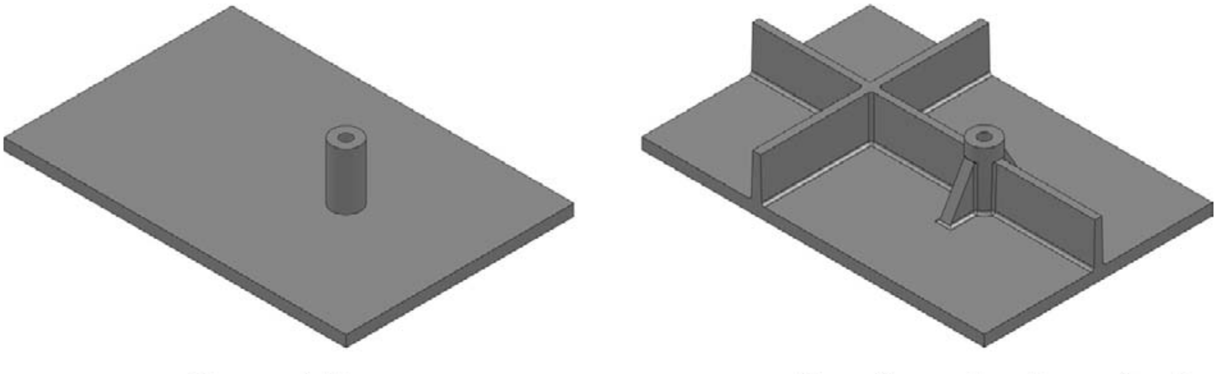
Figure 31.11 Carefully manage thickness.

the residual stresses and does not necessarily lessen structural issues due to aging and end-use.

Two common plastic part design issues related to nonuniform thicknesses are shown in Figure 31.11. At left is the design of a base that has a wall thickness substantially greater than the side walls. When processed by extrusion or injection molding, the thick base can exhibit significantly higher volumetric shrinkage such that voids are induced internal to the part. Such voids are not always readily observable by the plastics manufacturer and can significantly reduce the structural performance of the product. At right is a design in which a rib has been used with the same nominal wall thickness as the base of the part. Since the rib is relatively tall, polymer can be drawn from the base to compensate for volumetric shrinkage in the rib. The result is an internal void and/or a deflection in the outer wall of the base opposite the rib. Again, the structural performance of the product can be compromised. To avoid issues related to thickness, thicknesses in plastic parts should be maintained within 30% of a nominal value. Ribs, bosses, gussets, and other protruding features should have a slightly reduced wall thickness. The optimal percentage reduction for these feature's wall thickness will vary with the amount of volumetric shrinkage exhibited by the polymer.

Another issue that can result in brittle failure is the lack of lateral support on structural components such as bosses and ribs. On the left of Figure 31.12 is an unsupported boss, which is likely to fracture due to lateral or torsional loads. To increase the strength of the boss, gussets and/or ribs should attach the outer surface of the boss to the base. In this design, the boss and the attached supports have a base thickness equal to 75% of the nominal wall thickness. A draft of 1.5° is provided to assist with ejection—higher draft angles are needed with materials exhibiting very low shrinkage. A fillet of 0.5 mm is also provided at the base and intersection of all features to avoid stress concentrations.

Much of the foregoing examples have been implicitly directed to injection molded parts. Yet, many of the same principles apply to parts made by extrusion, blow molding, and thermoforming. For example, extruded parts should



Unsupported boss

Boss with gussets and supporting ribs

Figure 31.12 Provide structural supports.

utilize a uniform thickness with slightly thinner ribs to increase stiffness. Thermoformed and blow-molded parts do not provide for the use of ribs, bosses, or gussets. However, careful mold and process design is needed, often with corrugated designs as shown in Table 31.2, to achieve products with desirable thickness profiles, stiffness, and strength.

31.3.3 Design for Manufacturing and Assembly

There have been significant increases in plastic part complexity due to the development and widespread implementation of design for manufacturing and assembly (DFMA) guidelines that leverage the capability of the injection molding process. One common DFMA guideline calls for the consolidation of multiple parts whenever possible, which leads to fewer but more complex components. The following cases are exemplary [19]:

- NCR used DFMA to redesign a sophisticated electronic cash register so that its 15 parts (down from 75) can be assembled by an unskilled, blindfolded worker in less than 2 minutes.
- IBM redesigned its Proprinter so that it had 79% fewer parts and no fasteners in the final assembly. Assembly time was reduced from 16 minutes to 3. Since labor costs associated with the assembly process were dramatically reduced, IBM brought its Proprinter manufacturing operation back to the United States.

Given the potential functionality arising from plastic parts, it is not uncommon for a molded part, such as an inkjet cartridge, to specify more than 30 critical dimensions with tight tolerances. The optimal decomposition of more complex products into multiple components formed of polymeric and other materials is next discussed with respect to design for assembly, tolerances, fastening, and risk mitigation.

31.3.4 Design for Assembly

Design for manufacturing and assembly guidelines (DFMA) have been developed to minimize total life cycle cost while maximizing quality, robustness, and end-use performance [6,20]. One significant benefit of DFMA is the considerable savings in assembly cost from fewer parts that need to be assembled. The general intent of DFMA is to consolidate as many discrete parts into fewer (but potentially more complex) parts requiring less assembly as demonstrated in the NCR and IBM case studies. The optimal configuration for a given product depends significantly on the application characteristics such as form, complexity, tolerance, profit margin, assembly cost, production volume, and life cycle.

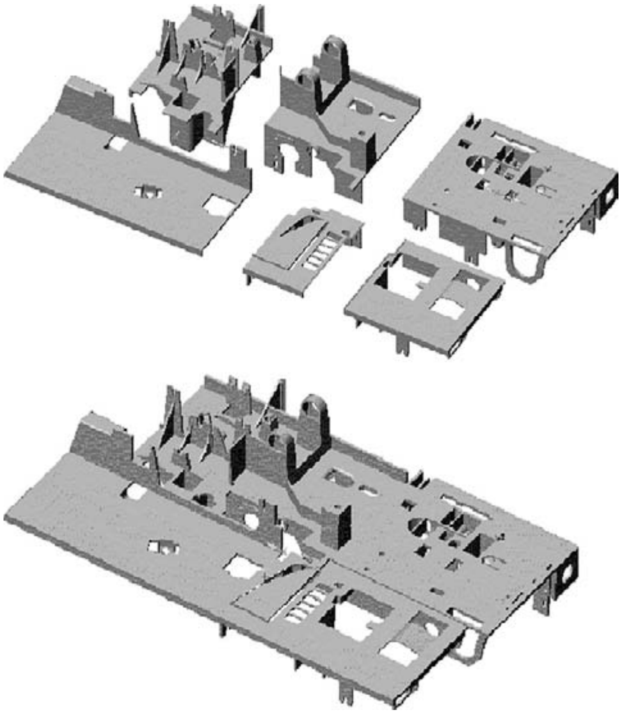


Figure 31.13 Assembly designs for an internal chassis.

Still, DFMA guidelines suggest that discrete components should always be combined except when:

- the components move relative to each other,
- the components need to be of different materials, or
- the components need to be separable for disassembly or maintenance.

For example, consider the potential for component consolidation in a complex application, such as the internal chassis of an office automation product shown in Figure 31.13. In this design, the assembly design includes approximately 1,000 features and 20 critical dimensions. The component can be made as a single-integrated components, decomposed into six discrete components, or reconstituted by 42 component variants with 80 alternative assembly designs. In determining the level of components consolidation, the plastics part designer must consider the obvious trade-offs to be made between savings in assembly—increased complexity in mold tooling—and potential for quality issues during processing. Delays in product development should also not be overlooked, since a high tech product that reaches the market 6 months late, even on budget, will earn 33% less profit over 5 years while finishing on time but 50% over budget will reduce a company's profit by only 4% [21]. Accordingly, discrete components should not be combined if the consolidation does not reduce the number of tools, the components have vastly different quality requirements, and the design and manufacturing processes are not certain of delivering the more complex plastic parts on time [22].

Once parts are optimally consolidated within an assembly, there are additional DFMA guidelines that should be considered to reduce assembly times and costs. Perhaps most importantly is the use of top down assembly in which parts are assembled from above in straight-down motions; this strategy also supports fully automated assembly in applications with high production volumes. The motivation for the top-down approach is that it allows for the fixturing of a base part on an assembly line without need for subsequent re-orientation for access to the reverse side of the base. An operator can then rapidly insert other parts in the assembly given visual access to the assembly. With both hands free, the operator can use one hand to insert the part and their second hand to use a tool if necessary. Plastic parts should be designed (and fasteners specified) to be identical or clearly differentiated by size, color, or obvious asymmetry. In this manner, the number of components in the assembly's bill of materials is further reduced while minimizing the assembly times and potential for operator error.

31.3.5 Fastening

The four most common types of fastening in assemblies with plastic parts include (1) welding, (2) adhesives, (3) mechanical fasteners, and (4) snap fits. Welding is a technique that relies on the softening of the polymer(s) to encourage molecular diffusion between two or more parts, such that the parts are permanently secured when the polymers solidify. Adhesives rely on either mechanical or chemical interaction with the plastic parts, such that the parts are secured on the setting of the adhesive. These two fastening mechanisms are not further discussed in this chapter since they are presented in more detail elsewhere in this book. Still, some guidelines for the use of mechanical fasteners and snap fits are provided next.

Mechanical fasteners for securing parts in an assembly commonly include screws, bolts, rivets, and nuts. The self-threading screw [23] is among the most popular of mechanical fasteners since it allows rapid, secure, and reversible assembly using relatively simple plastic parts designs. Still, the use of self-threading screws can induce failure modes in assembly or end-use so a proper detailed design is necessary. A cross-section of a recommended self-threading design is provided in Figure 31.14.

As shown, a screw with outer thread diameter, *D*, should be inserted into a boss having an outer diameter of 2−2.4 times *D*. The boss' inner diameter, *d*, is typically equal to 88% of the screw thread diameter, *D*. This means that the wall thickness of the boss is nominally equal to 0.7 times *D*. Given that the boss should be thinner than the nominal thickness as previously discussed, the nominal thickness of the part is approximately equal to *D*. Conversely, these design guidelines imply that an appropriate diameter of a self-threading screw can be directly determined by the nominal thickness of the part. For example, a plastic part having a wall thickness of 3 mm should use self-threading screws having a diameter of around 3 mm with bosses having inner and outer diameters of 2.6 and 6.6 mm, respectively.

Nuts, bolts, and washers are also commonly used in assembly of plastic parts. In general, the strength of metal fasteners is much higher than the attached plastic material, so nuts and bolts with small diameters are typically used with washers having a larger outer diameter to reduce the shear stresses in the plastic and to avoid failure. Figure 31.15

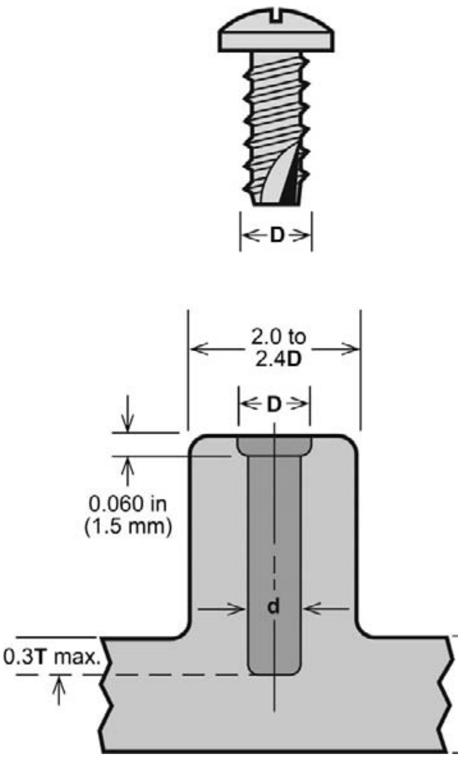


Figure 31.14 Recommended self-threading screw application.

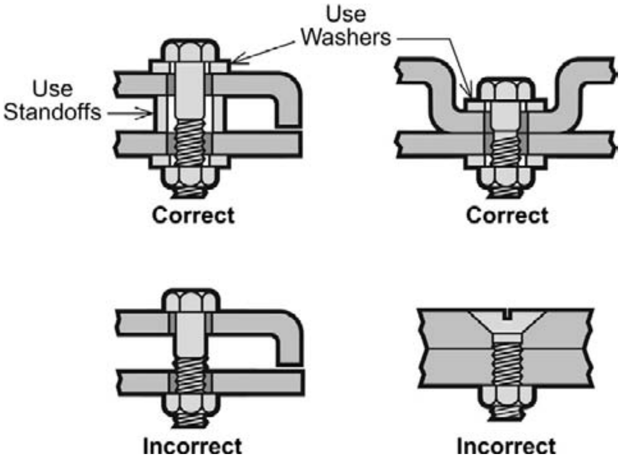


Figure 31.15 Correct and incorrect fastening applications.

provides some common designs as well as some common issues. At top right is a correct use of fasteners in which a washer and the head of the bolt has been recessed within a well of the plastic part. The second part directly abuts the first part with a second washer and the nut located on the other side. Alternatively, the function of the washer and nut could have been integrated directly in the second piece in the form of molded plastic threads or alternatively a metal insert molded into the part. If the two plastic parts are to be separated by a set distance, then a standoff should be used as shown at upper left of Figure 31.15. The use of the standoff allows for uniform compressive stresses throughout the plastic parts and standoff so that the washer and nut can be securely tightened.

Two incorrect assembly designs are shown at the bottom of Figure 31.15. At lower left is a potentially poor design for mating two plastic parts. The absence of a standoff allows the parts to flex when the nut is tightened, thereby causing uncontrolled deflection elsewhere in the parts. Furthermore, the absence of a large mating surface (previously provided by the washers) increases the likelihood of failure. While this approach is not necessarily a bad design, careful engineering would be required to ensure that the assembled system behaves as desired—given potential variations in assembly and end-use. The design at lower right of Figure 31.15 uses a flat head screw which is typically motivated to provide a more compact design or use fewer components or provide self-locating assembly. Still, this design often leads to failure given that the tightening of the nut causes hoop stresses around the bolt's tapered head. For this reason, machine screws and flat head bolts are commonly used.

Rivets are common in sheet metal assemblies, and are also often used with plastic parts when the disassembly is not required. Some common types of rivets are shown in Figure 31.16. Rivets typically rely on permanent deformation of the rivet itself to form a geometric interference with the mating plastic parts. Two key advantages of rivets over other fasteners are (1) their rapid installation and (2) their ability for installation from one side of the assembly without access to the reverse side of the mating plastic part. Plastic rivets typically have a head diameter around three times the hole diameter. For maximum strength, they should be of a similar material as the plastic parts in the assembly. Rivets are often sized such that the hole diameter approximately matches the combined thickness of the plastic parts being assembled. In such a design, the assembly will typically fail due to the shear stress across the axis of the rivet or due to shear stresses in the head or tail of the rivet. For these reasons, rivets are more often used in lightly loaded assemblies and other fastening means should be considered if higher loads are required in end-use.

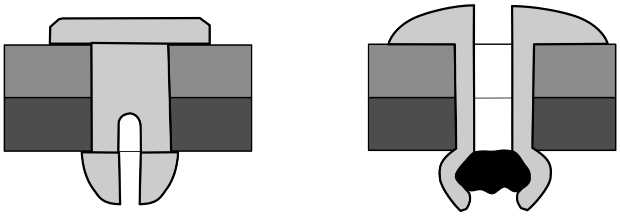


Figure 31.16 (a) Push-in and (b) expansion rivets.

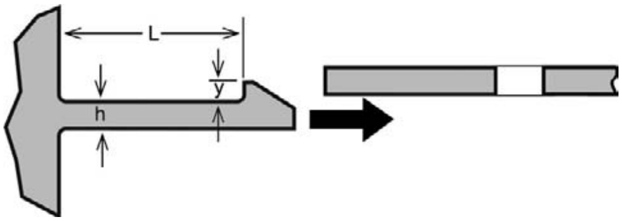


Figure 31.17 Snap fit concepts.

Just as rivets rely on elastic or inelastic deformation to form a mating between parts in an assembly, snap-fitting features can be similarly integrated with plastic part designs [24,25]. A cantilever type snap arm (also referred to as a hook or finger) is shown in Figure 31.17. The cantilever bends upon the plastic part insertion until it mates with a corresponding catch, returning to its undeformed shape to lock the assembled parts in place. There are many variations to the snap fit concept including annular snaps, ball and socket, and others. Messler et al. have provided a methodology for designing integral snap features into plastic parts for assembly [24]. The unifying concept between snap fit designs is the elastic deformation of a plastic part feature during assembly, such that the feature returns to a desired shape and prevents subsequent separation of the assembly.

In the developing of the detailed plastic part design, the designer should understand the relationships between the design parameters and the assembly's performance. Some critical variables include the angles of the retention and insertion faces, the width and thickness and length of the snap feature, and amount of interference between the insertion face and catch surface. Analytical formula and finite element simulations can allow the designer to model and optimize the design. For example, the strain in the cantilever beam of Figure 31.17 is:

$$\varepsilon = \frac{3h}{2L^2} y \tag{31.5}$$

where h is the thickness of the beam, L is the free length of the beam, and y is the amount of interference. The strain in the beam largely dictates the insert and removal forces. Accordingly, the designer can control the insertion, removal, and failure loads by careful selection of the design parameters.

Plastics provide significant value by their ability to be formed into complex products. Designers should seek to leverage this capability by designing assemblies that have fewer components and integrated assembly features that facilitate rapid and secure assembly. Plastic part designers have historically focused almost exclusively on detailed design of individual locking features such as cantilever hooks, bayonet-fingers, compressive hooks, and matching traps [24]. However, the use of these topologies assumes a geometry that is unlikely to be optimal in many applications. Accordingly, the designer is encouraged to consider the requirements in their application and the geometric constraints within the assembly to derive the best possible design.

31.3.6 Tolerances

Plastics parts can pose significant issues in applications requiring tight tolerances. The reason is that the part dimensions are not governed solely by the geometry of the mold/die but also by the material properties and manufacturing process conditions as well. Specifically, the varying temperature and pressure distribution during plastics processing will tend to imbue residual stresses in the plastic, which will cause the part dimensions to shrink and vary from the mold/die geometry [26]. By comparison, the tolerances of metal components are typically governed solely by the accuracy of the machining/stamping process and can be precisely specified and ensured.

Plastic part designers, who are aware of tolerance issues with plastic parts, may tend to tightly specify many dimensions on a plastic part. This approach may appear technically sound but is often not helpful in practice. The reason is that the specification of many critical dimensions does not actually assist the plastics manufacturer in delivering quality product. Ideally, every specified dimension on every manufactured product would be inspected. However, this approach is infeasible given the expense of fixturing and metrology together with time delays required for the manufactured products to equilibrate [27]. As such, this ideal approach is typically compromised to infrequent sampling of a few critical dimensions to determine the acceptance of a batch of products. Alternatively and more commonly, the dimensional properties of molded products are estimated using weight [28]. In this approach, the products are weighed as they are manufactured, with dimensional consistency assumed if the weight is within prescribed limits.

To improve manufacturing yields, the designer should specify the vast majority of dimensions with standard tolerances—tight tolerances and adjustment mechanisms should be used in the design only when necessary. A significant issue in plastic part design, however, is the precise definition of "standard" and "tight" tolerances. The process dynamics and material properties that determine variations from the mold/die geometry vary greatly across plastics applications. The achievable tolerances will vary not only with the type of plastics manufacturing process, but also with the material being used by the process as well as the actual geometry of the plastic part being manufactured. In general, the achievable tolerances will improve with increasing density of the material, decreasing wall thickness of the part, increasing melt pressure during processing, and increasing time of the molded parts within the mold/die.

Table 31.3 provides some representative positional tolerances by process. Since the shrinkage rate of the polymer is applied to the entire length of the dimension, tolerances in plastics processing are typically expressed as a percentage of the nominal dimension. For example, a length of 100 mm with a tolerance of 0.4% would have an absolute specification on dimension of 100 ± 0.4 mm while a thickness of 2 mm with a 0.1% tolerance would have an absolute specification of 2 ± 0.002 mm. In the table, a "loose" tolerance indicates that which is easily achieved and should not require verification. A "standard" tolerance should be readily achieved with modern machinery but should be verified if not consistently inspected during production. A "tight" tolerance often requires careful mold/die design, process verification/optimization, and intermittent inspection. The "achievable" tolerance does not indicate the tightest tolerances possible, but what can be achieved with state of the art machinery, processing, and quality control techniques. The tolerances in Table 31.3 should be considered approximate since the final part dimensions will vary with the material properties and process dynamics as previously discussed. In general, injection molding will tend to provide the tightest tolerances and extrusion the lowest—tolerances in extrusion can be greatly improved through the use of calibration dies during the cooling of the extrudate. Thermoforming and blow molding provide an intermediate level of dimensional control.

An important concept in plastic part tolerancing and plastics manufacturing is that the ability to hold a tolerance is dependent on the type of specified dimension. Dimensions on wall thickness will generally be more challenging to control than other positional tolerances governed by in-plane shrinkage of the polymer. The reason is that the polymer is not constrained in the thickness direction during processing,

Table 31.3 Tolerances by process

	Extrusion	Injection Molding	Thermoforming	Blow Molding
Loose	5%	1%	2%	2%
Standard	2	0.5	1	1
Tight	1	0.2	0.5	0.5
Achievable	0.4	0.05	0.2	0.2

while the part length and width are often constrained by the mold/die geometry during cooling. As a result, the thickness dimension will tend to shrink more than the other part dimensions and so will be more difficult to control. It is not uncommon for plastics manufacturers to double the tolerances indicated in Table 31.3 when discussing thickness specifications. Similarly, specifications on angularity, parallelism, and runout may be significantly affected by out of plane warpage and more difficult to control such that the tolerances suggested in Table 31.3 may not be achievable in all plastics applications.

In terms of quality assurance, the plastics part designer may wish to consider what tolerances will truly dominate the success of the plastic part during end-use. In conjunction with the plastics manufacturer, a quality assurance plan should be developed, implemented, and verified. Many plastic part designs may have forty or more dimensions that are truly critical. However, the designer and manufacturer should strive to identify the two or three specifications (increasingly referred to key product characteristics or KPCs in Six Sigma methodologies [29]) that dominate all other requirements—are easily/accurately measurable—and that can be used for on-line quality control [30]. For example, if a thickness or runout specification is difficult to control in a plastics manufacturing application, then that specification should be used to determine part quality acceptance without the need to measure other easier to control dimensions.

31.3.7 Risk Mitigation

Risk is an inherent part of plastic product development, and the level of risk can actually increase as plastic part designs become more efficient. The reason is that as the plastic part designer improves the design, more constraints on the design become obvious. For example, consider the selection of wall thickness for the internal chassis depicted in Figure 31.13. A large wall thickness of 5 mm can be used to provide stiffness but will tend to increase the cost of the plastic part due to excessive material costs and processing times. The plastic part designer will likely be motivated to use a lesser wall thickness to reduce part weight, material cost, and processing cost. However, as the wall thickness decreases, the plastic part is subjected to additional constraints including insufficient stiffness, excessive injection pressures, and others. Accordingly, the plastic part designer cannot be overly aggressive with respect to the part design since bad decisions will lead to the redesign and delays in the product development cycle of Figure 31.1. Hedge strategies as indicated in Figure 31.18 are useful to mitigate risk regarding crucial design decisions.

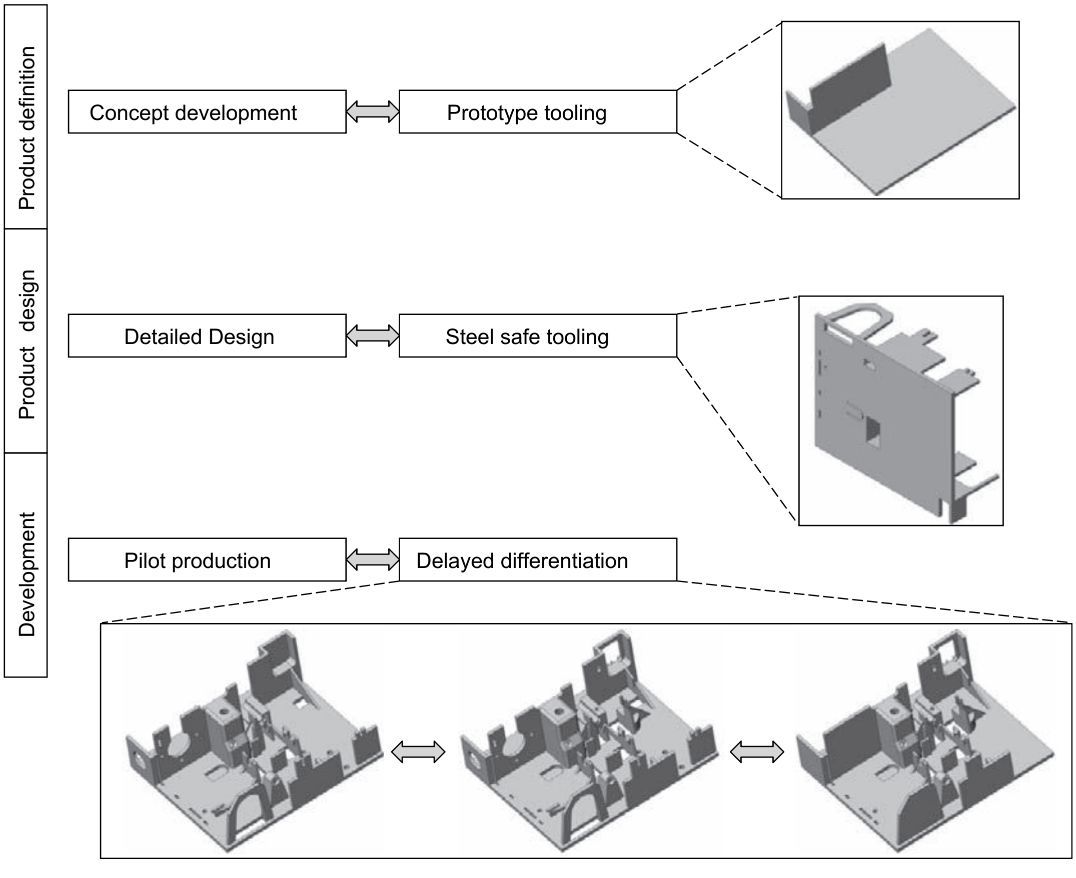


Figure 31.18 Plastic part design hedge strategies for risk mitigation.

Prototype tooling is a common strategy to verify not only the design concept but also the feasibility of the manufacturing process with respect to cycle time, dimensional tolerances, and yields. Mold tooling is often machined from soft metals such as aluminum QC7 or AISI 4130 steel that would not provide a long life in production. In addition, the complete part design is often not fully implemented in the prototype tooling. Still, many of the key benefits about polymer shrinkage and process cycle time can be gleaned by machining a simplified mold consisting of the part's overall size, wall thickness, and gating.

Often, the part and/or mold designers are faced with uncertainty regarding critical decision such as wall thickness, exact feature positioning, gating, and others. In these uncertain situations, the mold should be designed with dimensions that are "steel safe," which means that the design should call for the removal of less mold steel than may ultimately be required. For example, a part designer may be uncertain as to the precise diameter and location of a through hole used in assembly. As such, the design may initially include a larger core to provide a larger hole. Once the design is implemented and the exact needs verified, the core may be machined to a smaller size to provide the needed hole (or slot) at the correct location. Similarly, a mold designer may be uncertain as to the best diameter of a feed system. By rounding the feed system diameter down one or two standard sizes, the mold designer still has the freedom to machine the mold to increase the diameter and achieve better pressures and flows in processing.

A third strategy for design hedging is to delay product and tooling differentiation as long as possible during product development. As shown by the three design variants at the bottom of Figure 31.18, this approach allows the development team to use the same mold with various inserts to provide different products having the same overall topology, but localized feature specialization. There are two primary advantages to this approach. First, delayed differentiation supports "steel safe" practice by avoiding the implementation of critical details until after the mold is constructed and tested. By leaving features such as bosses, snap fits, and other mold cavity surfaces in a semi-finished state, the mold designer can finalize the design and implementation of these features after the shrinkage has been characterized. Second, delayed differentiation when used with modular mold tooling allows different mold inserts to be used to provide semi-custom designs to different customers without completely different molds. While delayed differentiation can extend the total product development time, the risk during mold development is reduced and the quality of the manufactured plastic parts can be increased.

Plastics manufacturers clearly wish to avoid incurring significant part design and mold tooling costs on projects that may not be commercially viable. When faced with significant uncertainty in production quantities, plastics part designers may wish to adopt a "bootstrap" strategy. In this approach, simpler plastic parts are designed to be produced by machining, rapid prototyping, or plastics manufacturing processes having lower tooling costs such as extrusion, blow molding, or thermoforming [1]. While this method will result in higher per unit costs, the total upfront investment in the project can be substantially reduced. Once demand is justified by market sales, more sophisticated and expensive mold designs can be implemented to economically provide higher volumes of complex plastic parts.

31.4 Conclusions

The versatility of plastic material properties presents unique challenges in plastics part design given the diversity of application requirements. Plastics can provide superior performance over other materials, but the actual performance will vary with the optimality of the design. A formal plastic part design methodology is useful to lead the designer from the concept to realization, from "art" to "part." Critical design decisions include the following:

- The type of material and grade of plastic
- The selection of the plastics manufacturing process, for example extrusion, injection molding, thermoforming, and blow molding
- The determination of the appropriate wall thickness
- Detailed design of features with dimensions and tolerances.

This chapter has sought to provide insight into each of the critical design decisions. Clearly, plastics have a lower modulus and ultimate strength than metals such as steel and aluminum. However, these lower properties are more than compensated by a reduced density and increased strain to failure. When these factors are analyzed, plastics will outperform metals in terms of stiffness and strength per unit weight. Plastics are even more advantageous when their low cost per unit weight and manufacturability into complex shapes are considered.

The selection of the manufacturing process is critical since the plastic part design must vary accordingly. Extrusion, injection molding, thermoforming, and blow molding each rely on different process mechanisms to shape the plastic. As such, each provides a fundamentally different part geometry. In general, the plastic part's geometric complexity and dimensional precision increases with the cost of the tooling used with the process. In addition, the process largely determines the nominal rate at which plastic parts can be produced. Plastic part designers will often assume the use of a particular process, such as injection molding, from the onset of concept development. While the initial process selection is often justified, other processes may sometimes provide unique economic and technical advantages when used creatively.

Determination of wall thickness is perhaps the single most critical detailed design decision. The wall thickness not only governs the stiffness of the part, but also largely determines the part weight, materials cost, and production rates. As such, slight changes in the nominal wall thickness can have a significant impact on the cost and quality of plastic parts. Designers should strive to reduce the wall thickness to reduce the total life cycle cost, though the minimum wall thickness is constrained by both known and unknown constraints. For this reason, part designers may wish to use hedge strategies such as prototype tooling, steel safe design, delayed differentiation, and bootstrapped processes to mitigate risk when making detailed design decisions.

Acknowledgments

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32 Plastics in Buildings and Construction

Sushant Agarwal and Rakesh K. Gupta
Department of Chemical Engineering, West Virginia University, Morgantown, WV 26506, USA

32.1 Introduction

Modern building construction, for both residential and commercial purposes, is subject to diverse constraints and objectives. Besides the basic concerns of durability, comfort, and cost-effectiveness, building designs also need to take into account energy efficiency and ecological and environmental concerns. In this quest, polymer-based building materials have not only been used as replacements for traditional materials such as brick, cement, concrete, metal, wood, and glass, but they have also been shown to work in a complementary fashion with traditional materials to enhance their performance with unique and innovative applications satisfying the demands of the modern building construction industry. One of the key advantages of plastic materials is their lightweight and their ability to be formed into complex shapes. Other features include durability, low maintenance, low cost, and availability in a range of shapes and forms, and possessing a wide spectrum of properties. From the aesthetics point of view, plastic materials are available in attractive colors and textures, and they require minimal or no painting. Another selling point of plastics is their inherent resistance to heat transfer and moisture diffusion. Being electric insulators as well, plastic materials do not suffer from problems like metallic corrosion or microbial attack.

From polyurethane foam insulation, which is a thermoset, to transparent polycarbonate glazing, which is a thermoplastic, to wood-plastic composites (WPCs) for decking and railing, polymers are used in innumerable applications in the building industry for both structural and non-structural applications. Indeed, the building construction industry accounts for about 18% of plastic consumption [1] in the United States. In the first half of this chapter, some of the major applications of polymeric materials in the building construction industry are presented and discussed in terms of material usage, important physical properties, method of production, and relative advantages and disadvantages. The second half of the chapter is devoted to the use of polymer-matrix composites in infrastructure applications.

32.2 Applications

32.2.1 Siding or Cladding

Siding or cladding forms the outermost layer of a building or a house. Consequently, it is required to satisfy two important functions. The first one is to form a protective cover around the building to shield it from the outside elements, and the second is to impart aesthetic beauty to the building. Polyvinyl chloride (PVC) sidings, also popularly known as vinyl sidings, are perhaps the most well-known plastic product used in the building construction industry. Vinyl sidings are popular because of their ease of installation, durability, low maintenance, and low cost. Plastic sidings are lightweight, and they do not require painting. Due to their inherent low-thermal conductivity and moisture resistance, plastic sidings offer good protection against weather elements such as heat, cold, rain, and snow.

Aluminum, wood, stucco, brick, and fiber cement are other materials that are popular alternatives to plastic sidings, but vinyl sidings continue to dominate the field with about 38% of market share [2]. Initially, vinyl sidings grew at the expense of aluminum, but, with new innovations, they are also successfully competing against wood and fiber cement sidings [3]. Here, plastic sidings need improved performance in the areas of appearance (wider color choices and color retention), thickness, and weather resistance properties. In general, vinyl sidings are available in light color palettes; however, the competition from paintable wood or fiber cement sidings necessitated the development of darker color palettes that retain color over the lifetime of the siding. This requires protecting the vinyl siding from weather damage that causes fading of colors. To meet this challenge, vinyl sidings are co-extruded with a capstock material that is more weather-resistant, such as PVC with a high loading of TiO_2. Another method is the use of more weather-resistant films, such as acrylic films, plasticized PVC, and polyvinylidene fluoride (PVDF) to coat the PVC siding [4]. Yet another issue is the thickness and thermal expansion of vinyl sidings. Generally, vinyl sidings are only 0.05 in. thick, and this gives them a flimsy appearance as compared to the thicker and stiffer wood or fiber cement sidings. Foamed and WPC

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sidings are being developed that are thicker and stiffer than solid-state PVC sidings in various designs, such as hollow, capstocked, and multilayer configurations [5]. A more recent innovation in siding technology is the use of insulated vinyl sidings. These consist of an expanded or foamed polymer layer at the back of a regular vinyl exterior layer. This combination provides an extra layer of insulation and imparts more stiffness and impact strength. The foamed layer can be made from extruded polypropylene (XPP) or expanded polystyrene (EPS) [5,6]. The presence of the foamed layer also reduces any problems due to the thermal expansion of vinyl sidings.

Glass-fiber-reinforced polyester (GFRP) is also used as a cladding material but for bigger structures [7]. In wall panels, it works as a decorative layer on concrete and brick structures providing various color and texture options [8]. But, GFRP claddings are expensive, and, as a result, their application is not as widespread as that of thermoplastic based claddings and sidings.

32.2.2 Insulation: Foundation Insulation, Spray Foam, and Structural Insulated panels

Insulating materials constitute a major application area for polymers in buildings. Plastics are inherently poor conductors of heat, and most of them are hydrophobic as well. This makes them very attractive starting materials for fabricating thermal and moisture barriers. In a building, insulation is applied to surrounding walls, basement, attic, and roof. It can be used in a variety of forms, including batts or rolls, loose fill, sprayed foam, and foam boards. The insulation is also applied to domestic hot and cold water supply lines and to heating/cooling systems. While the main non-plastic insulation systems are fiberglass and mineral wool, the most widespread plastic insulation is made from polyurethane (PU). Also encountered are polyisocyanurate (PIR), polystyrene (PS), and PVC. Plastic insulation has gained popularity because of the ability to form closed-cell foams that trap gases or air inside the bubbles; the result is a material with a very low-thermal conductivity and negligible convection heat transfer because the trapped gas is stagnant. Thus, foaming creates a structure that is lightweight and highly resistant to heat transfer. Figure 32.1 shows the heat resistance factor (*R*-value) for several materials that are used for insulation. Note that a material with a larger *R*-value has better heat insulation performance. It can be seen that foamed plastics have superior insulation properties.

Foamed PU, PIR, extruded polystyrene (XPS), and EPS are popular polymer foam insulations. PU and PIR are thermoset foams that are produced by the reaction between a polyol and a polyisocyanate, both of which are in liquid form. Typically, the polyol is part of an aqueous mixture of catalyst, surfactant (foam stabilizers), flame retardants, and blowing agents [9]. When this mixture is combined with the isocyanate, an exothermic reaction takes place, releasing significant quantities of energy which activates the blowing agent and expands the reaction mixture into a foamed structure as it polymerizes and solidifies.

Isocyanates can also react with each other to form a PIR in the presence of a proper catalyst. If this reaction takes place in the presence of polyols, a mixed structure composed of foams of both PU and PIR can be formed [10]. By controlling the relative amounts of catalyst, foam stabilizers, and blowing agents, foams with various morphology and properties can be obtained. PU and PIR foams are employed in several forms which include sandwich panels for walls and roofs, flexible boards, slab stocks for construction-size pieces, and spray-on foams [10]. To make a preformed rigid PU structure, the reaction mixture is introduced into box-shaped molds where the foam is synthesized and solidified. Panels of various shapes and sizes can then be cut from the stock panels. Prefabricated panels are useful when working with large flat surfaces where discontinuities and joints can be avoided. However, when complicated surfaces and structures are involved, spray-on foam is preferred. In this case, a precursor mixture is formulated with a proper catalyst to ensure fast reaction and curing. In applying such a spray polyurethane foam (SPF), the liquid reaction mixture is directly sprayed on to the surface. As it is applied, it adheres to the surface and expands. Being in liquid form it easily fills cavities, cracks, and gaps forming a better barrier against water and air infiltration as well. Closed cell SPF is also accepted as a roofing system, and it adds to structural strength as well [9].

The XPS and EPS are other popular foamed products for insulation. As the name suggests, XPS foam boards are produced by an extrusion process where the resin is fed to an extruder which melts and pressurizes it. A physical blowing agent, such as pentane or a hydrochlorofluorocarbon, is introduced into the extruder, and the result is a single-phase polymer mixture. When the molten PS exits through the die, the dissolved gas expands, creating foam. A closed-cell rigid-foam structure is obtained as the extrudate cools and solidifies. EPS is made by molding expandable PS beads that have already been saturated with a blowing agent such as pentane or butane [11]. A mold cavity is filled with EPS beads and heated. As the temperature rises, the polymer melts, and foaming occurs. Here again, a closed-cell structure is obtained, and this is preferred because it increases the structural strength of the foam and resists moisture penetration as well. Typical thermal and moisture diffusion properties of various insulation materials are listed in Table 32.1 which shows that plastic foamed materials have much superior water resistant properties as well. XPS foam, for example, absorbs only 0.3 wt% moisture [12].

Good thermal and water resistance properties, combined with good structural strength of plastic foams, have led to the development of structural panels known as insulated concrete forms (ICFs). The process of making an ICF involves pouring

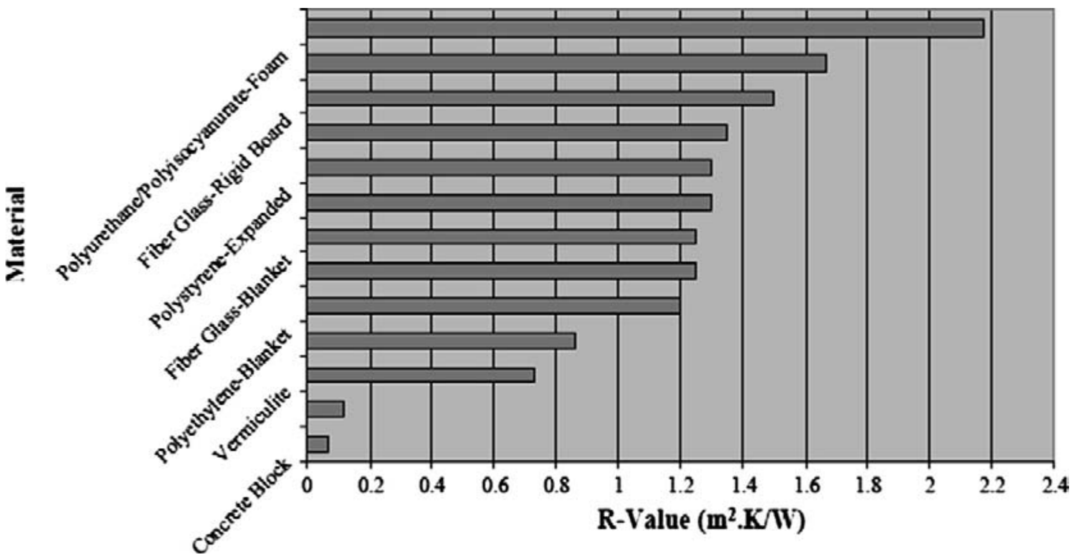

Figure 32.1 Heat resistance factor (*R*-value) for 5 cm thick insulation materials (*Adapted with permission from Ref. [46]*).

concrete in between the panels of foamed plastics, mostly XPS and EPS. The panels are tied together by metal or plastic ties. The resulting product has the strength and durability of concrete and the barrier properties of plastic foams [13]. In addition, ICFs also provide less air leakage and better acoustic protection [14]. Initially, ICFs were used in below-grade foundation wall forming systems. Now they are being used as part of interior walls, noise abatement systems, storm shelters, and structural elements [13]. Foamed plastics are also used to make structure insulated panels (SIPs) in which a sheet of foamed plastic is sandwiched between wood boards or concrete walls. XPS and XPP foam boards are used for this purpose.

32.2.3 Roofing

Roofing systems and house wraps together constitute a protective envelope which safeguards a building from weather elements, such as rain and snow. Roofing systems, as the name suggests, protect the roof while housing wraps or weather resistance barriers protect the surrounding walls. In addition to guarding against water leakage, these systems also provide insulation against heat transfer to and from a building. This section discusses the use of polymers in roofing, while housing wraps are discussed in the next section.

Roofing systems are essentially a film or a layer that retards the leakage of water to the concrete or wood roof structure. The membrane must be strong enough to withstand stresses and flexible enough to accommodate any building movement; the expected service life is in excess of 10 years. Traditionally, bitumen and coal tar have been used, and these are still the dominant roofing materials. Layers of molten bitumen are applied to the roof which is known as built-up roofing. Since the1960s, though, polymeric sheets have acquired a growing role as roofing materials. Plastic-based roof membranes were first introduced in the1960s in Europe and in the1970s in the

Table 32.1 Typical thermal and vapor barrier properties of common insulation materials

	Material				
Physical Property	**Glass Wool**	**Mineral Wool**	**XPS**	**EPS**	**PUF**
Density (kg/m^3)*	13–100	30–180	20–80	18–50	30–80
Thermal Conductivity (W/mK)*	0.03–0.045	0.033–0.045	0.025–0.035	0.029–0.041	0.020–0.027
Temperature Application Range (°C)*	−100–500	−100–750	−60–75	−80–80	−50–120
Water Vapor Permeance (Perm-inch)†	118	116	1.2	2.0–5.8	0.4–1.6

Data from Papadopolous [51].

†*Data from ASHRAE Handbook [47].*

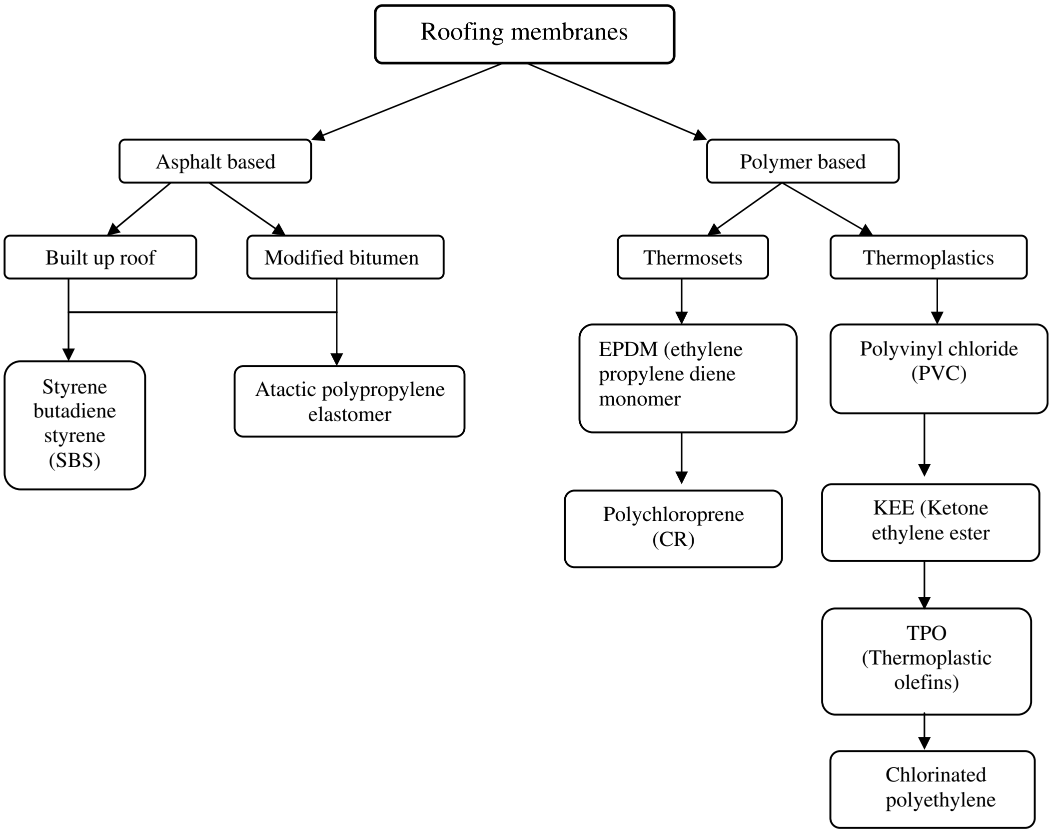

Figure 32.2 Plastics used in roofing systems (*Adapted from Ref. [16] with permission*).

United States [15]. The main component of this system is a water-proofing membrane which is applied directly to the roof structure or on the top of a layer of insulation [16]. Single-ply roofing membranes consist of reinforcing fibers or fabric sandwiched between two sheets of flexible material. The reinforcing material can be short-glass fiber mat, polyester scrim, or non-woven polyester mat [16]. Polymeric sheets can be either thermoplastic or thermoset. The latter are applied to the roof in a cured state, but it is then necessary to use an adhesive tape for joining and sealing the edges of the membranes [17]. Figure 32.2 illustrates the various polymeric materials that are being used as roofing materials, and these include bitumen, modified bitumen, PVC, polyethylene (PE), chlorinated PE (CPE), chlorosulfonated PE (CSPE), ethylene propylene diene monomer (EPDM), ketone ethylene ester (KEE), polyisoprene (PI), and polyisobutylene (PIB). Amongst all these choices, PVC sheets were the first thermoplastic to be used as roofing membranes. Flexible thermoplastic polyolefins (FPO) membranes were first introduced in the1990s in Europe and a little later in the United States where they are referred to as thermoplastic olefins (TPO) [15]. A typical TPO roofing polymer is a polypropylene (PP) copolymer which provides higher physical strength than PVC or EPDM [17]. First, one of the advantages of using polymeric sheets is that large sizes, as wide as 50 ft, can be produced which reduces the need for seams and joints. Secondly, the thermoplastic sheets can be heat welded together without the need for any connectors or adhesives. The welded joints are as strong as the sheet itself. Polymer sheets are produced by calendering, spread coating, lamination, or extrusion. The sheet thickness can vary from 40 to 100 mils.

Roofing materials are exposed to harsh conditions which cause degradation in properties over time. Deterioration occurs due to wind damage, sunlight exposure, rain, snow, hail, and temperature variations [18]. To prevent, or to at least slow down these processes, thermal and UV stabilizers, antioxidant materials, and flame retardants are added to the plastic in appropriate amounts. PVC membranes also contain plasticizers for flexibility.

Apart from serving their main function as a barrier against water leakage, the new plastic roofing systems are being required to act as good heat insulators. Energy-efficient building designs require that heat transfer through the roof is minimized. Dark color roofs absorb more radiative heat, and the surface temperature can be several degrees higher than the atmospheric temperature which adds to the cost of air-conditioning. A cool roof design seeks to minimize the heat absorption and conduction while maximizing heat reflectance and emissivity of roofing systems. Thermal insulation layers, generally in the form of foamed plastics sheets of PIR or PS, are used under the roofing membrane. To maximize the heat reflectance and emissivity, light color plastic sheets are utilized, and these are made by using light color pigments in place of dark color pigments such as carbon black. In some cases, where it is not possible to use light color pigments, as in EPDM sheets, light color paint may be used instead.

32.2.4 House Wraps, Building Envelopes, and Barrier Films

In building design, it is critical to protect the structure and interior of a house from the outside weather elements while maintaining comfortable atmosphere inside in an energy efficient manner. House wraps, building envelopes, or barrier films, collectively referred to as weather-resistive barriers (WRB), are employed to protect a building from intrusion by water and air by forming a protective envelope around it.

Heat transfer to or from a building occurs by means of heat conduction, convection, radiation, and air infiltration. While radiation usually constitutes a small part of the total heat loss, conduction and convection losses can be minimized by the use of proper insulation and design. However, it is estimated that in a typical US household, half the energy used in air-conditioning is used to heat or cool the air that enters the house by infiltration [19] or air leakage. Air infiltration occurs not only via open doors and windows but also through gaps in the joints where various structural elements of the building frame come together. The second issue is to minimize the penetration of water into the building structure. Though claddings or sidings form the first layer of protection against rain water, water may still leak through various gaps or as the result of an improper drainage system. In addition, accumulating water absorbed by wood may lead to mold formation and rotting of the structure. House wraps prevent the penetration of water and help in drainage of water away from the exterior walls.

House wraps can serve these dual functions if they possess a required set of properties. While a house wrap film should form a barrier against penetration by liquid water, it should be permeable to water vapor [20]. Similarly, while it should prevent air leakage, it must be permeable to air at the same time [21]. These characteristics are necessary so that the moisture does not build-up, and a healthy circulation of air is maintained inside the house. It is also necessary to allow the exterior walls to dry out. Figure 32.3 shows schematic diagrams of WRB installation in structures where brick wall, vinyl siding, and stucco form the external surface.

Traditionally, organic fiber felt and kraft paper saturated with asphalt have been used as house wraps. Since the1980s, however, polymeric films have seen increasing use as house wrapping material [22]. Polymeric house wraps are mostly polyolefin based, with PP and high-density polyethylene (HDPE) being the most common. Polymeric house wraps are thin sheets (only few mils in thickness) which can be classified as either woven or non-woven. Non-woven sheets are obtained by an extrusion process while woven sheets are made from few micron-thick very-fine spun fibers which are bonded together by heat and pressure.

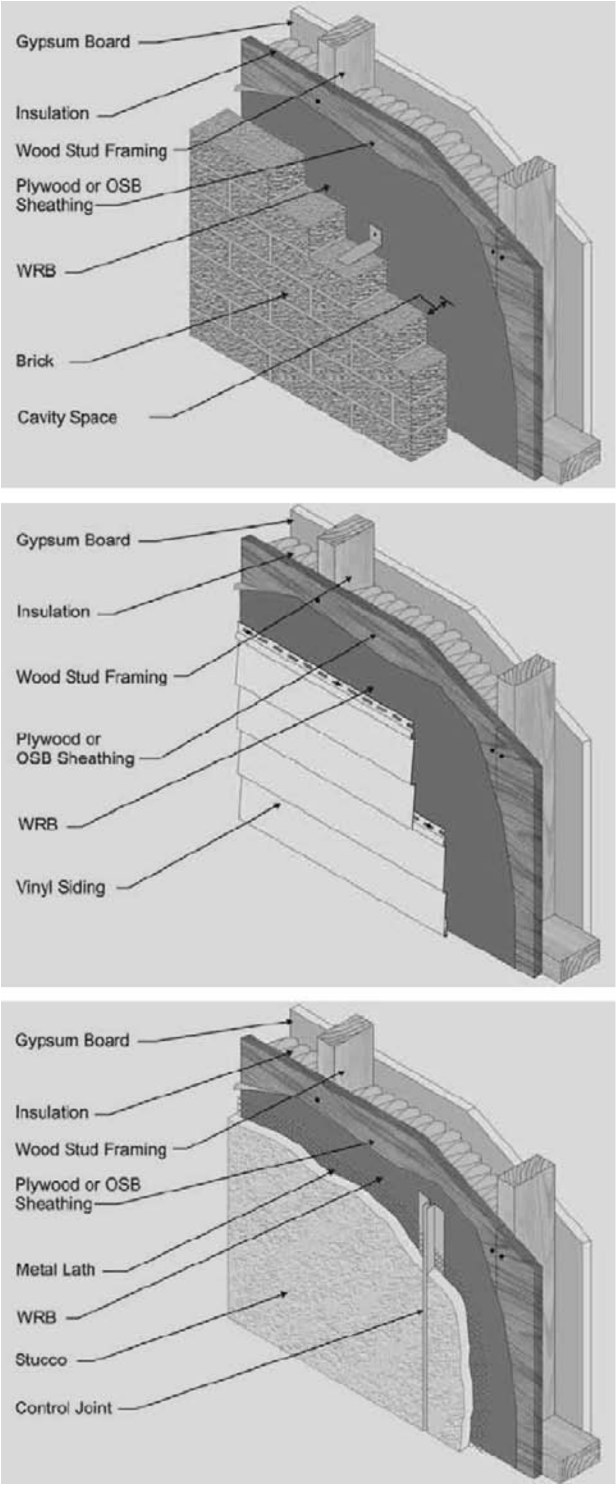

Figure 32.3 Weather resistance barrier installation in a wall structure (*Adapted from Ref. [23] with permission*).

Sometimes, in order to impart proper water permeability, microscopic holes are perforated through the films. A filler material is also used to make the films opaque, white, or translucent, as required. Polymeric films have several advantages over traditional asphalt films [22]. They are stronger and have better tear resistance. They can be manufactured in large sheet sizes, minimizing joints, and seams. They have better air and water permeability performance. On the other hand, they are relatively expensive and can have low UV stability. Various building codes and ASTM standards are employed to test the performance of house wraps. Some of these standards were formulated to evaluate traditional asphalt-based house wraps but have not been modified to accommodate polymeric house wraps [22,23]. For air leakage and porosity, TAPPI T460 and ASTM E 283 tests are performed. For water permeability and transmittance, ASTM D226, ASTM D779, ASTM E96, and AATCC127 standards are followed. ASTM D1117 is used for tear strength while ASTM D882 is used for tensile strength measurements. Flammability properties are classified according to ASTM E84 standard.

32.2.5 Electrical Wiring Insulation and Conduits

Thermoplastics and thermosets are very good insulators of electricity as their electrical resistance is in the range of 10^{12} ohms-cm or higher. As a consequence, they are widely used as insulating and sheathing materials for wiring and cables for electrical and data transmission. Besides natural polymers like rubber, phenolic resins (Bakelite) were the first synthetic polymers to be used for electrical insulation in the1920s followed by PVC in later decades [24]. Many different types of polymers are now used which include PP, low, medium and HDPE, crosslinked polyethylene (PEX), polyamides, ethylene propylene rubber (EPR), polyesters, and fluoropolymers [25]. Electrical cable and wiring are used for underground, residential, and distribution purposes, and each has to satisfy different performance criteria. Electrical properties of interest are dielectric constant, dielectric strength, and surface and volume resistivity [26]. Other distinguishing properties are strength, flexibility, fire and solvent resistance, durability, and cost. Table 32.2 lists the various plastic electrical insulation materials and their relative advantages.

Additives, such as plasticizers, fillers, colorants, stabilizers, flame retardants, smoke-suppressants, and lubricants, are added to achieve different performance criteria. In building construction, PVC is the dominant polymer used as wire insulator because of its inherent flame-resistant properties [27], strength and low cost. But due to high stiffness, plasticizers are added to make it flexible. However, toxic smoke that is generated on combustion is a major concern in its use, and various smoke reducing additives are added to minimize this phenomenon. PE is lightweight and water and solvent resistant. HDPE is preferred over LDPE because it has higher abrasion and tear resistance and higher tensile and shear strengths [28]. PEX is used because it can withstand higher operating temperatures than PE. In addition, larger amounts of fillers such as carbon black and flame retardants can be incorporated into PEX, resulting in a more fire and abrasion resistant material [28]. PVC is also the main thermoplastic used to make electrical wire conduits since it is corrosion free and water resistant. Consequently, it can be easily buried underground and in concrete structures. Other plastics used to make electrical conduits are PE, nylon, and polyester.

Table 32.2 Polymeric wire insulation materials and their advantages

Polymer	Advantages
Polyethylene	Good electrical properties; high moisture and chemical resistance; light, flexible, cheap and readily available
PVC	High outputs possible; property modification by the use of additives; cheap and readily available
Nylon	High strength; heat and abrasion resistance
Polytetrafluoro ethylene (PTFE) and blends	High toughness; very good solvent resistance; outstanding electrical properties
Polyester	High temperature resistance; improved adhesion to wires
Thermoplastic rubbers	Good environmental and heat resistance; improved aging characteristics vs. PE
Rubbers	EPR – improved heat resistance, easier processing; silicone-rubber – very high temperature resistance, very flexible

Adapted from Podolsak and Liu [50].

32.2.6 Glazing, Windows, and Doors

Glazing as window panels, building facades, skylights, or roof domes provide separation from exterior elements such as hot and cold weather, high winds, rain, and snow while letting daylight in and allowing outside visibility. Glass has been used as the traditional material for glazing applications. However, the use of plastics in this area has increased steadily over the years, and their application in flat glazing constitutes one of the largest applications for transparent plastics [7]. Acrylics such as polymethyl methacrylate (PMMA), polycarbonate, GFRP, and PVC are some of the materials that are being increasingly used to replace traditional glass glazing. A glazing material should be lightweight, inexpensive, UV protector, transparent, good

Table 32.3 Typical properties of plastic glazing materials compared with glass

Glazing Material	Specific Gravity (ASTM D792)	Coefficient of Thermal Expansion (ASTM D696) $10^{-5}/°C$	Visible Light Transmission	Tensile Strength (ASTM D638) MPa	Impact Strength (Notched Specimen) J/M (ASTM D256, Izod Test)	Flexural Modulus (ASTM D790) GPa
PMMA (acrylic)	1.19	3.1	91–93	72	21–27	2.4–3.4
Polycarbonate	1.2	3.8	82–89	62–72	640–860	2.2–2.6
GRP	1.40–1.60	3.4–4.4	76–85	76–117	430–1070	50–100
PVC	1.30–1.40	5.0–10	76–89	38–62	13–64	2.60–3.7
Sheet glass (Soda-lime glass)	2.46–2.49	0.85	88–90	–	brittle	–

Adapted from Blaga [48].

insulator, and easy to install. In addition, it should have good structural and impact strength, good fire resistance, and reduced smoke generation [29]. Plastic glazing materials have some distinct advantages over glass in the above-mentioned properties. Plastic glazings are much lighter than glass and are self-supporting, so that very large structures, such as stadium roofs, can be engineered easily. They also have much larger impact strength compared to glass. This is especially true for PC which is significantly more shatter-resistant than glass. This makes the installation of plastic glazing much easier, since they are not only much lighter but they also do not break easily. Typical properties of plastic glazing materials are provided in Table 32.3.

Another major advantage of plastic glazing materials is their superior thermal insulation properties compared to glass. In a building, window panes or facades contribute to significant heat losses. With increasing emphasis on energy-efficient building designs, plastic glazings offer a very attractive alternative to glass-based designs due to the fact that the thermal conductivity of plastics is much lower than that of glass. The thermal insulation property of glazing is usually characterized by means of a U-factor (or R-value $= 1/U$) which encompasses total heat transfer through the window. For energy efficient solutions, a window must have a low U-factor or a high R-value, indicative of high thermal resistance. A multi-pane plastic window can have a U-factor as low as 0.16 Btu/ft^2 h °F. For similar U-factor performance, a glass window would weigh much more than a plastic window [29]. Despite having some obvious advantages over glass, plastic glazing materials suffer from problems like yellowing, discoloration, crazing, cracks, and low-scratch resistance. However, new technologies and materials are being developed that overcome some of these problems. For example, glazing sheets can be coated with UV resistant or scratch-resistant coatings.

Plastic glazing sheets are generally produced by processes of extrusion, co-extrusion, or casting. These sheets can be a few millimeters in thickness and several feet in width and length. In the case of thermoplastic grades, various shapes can be obtained by thermoforming. Sometimes co-extrusion is used to apply a thin film of one polymeric material to another to enhance the UV stability of glazing materials. Fiber-containing glazing sheets are generally produced by a casting process.

Another application area of plastics is in manufacturing of window profiles and doors as a substitute for traditional materials such as wood and metal. In case of doors, the market is dominated by wood and metals, while plastic doors lag behind. In case of windows, wood and plastic compete closely, while metals still dominate the market [30]. However, plastic doors and windows are expected to show growth in the market due to the fact that they have recycling potential. Unplasticized PVC (UPVC) is the main thermoplastic used in this regard. Both unfilled and fiber composites are used to make window profiles and doors. Glass fiber and WPCs are expected to show about 37% growth rate as window materials [31]. Glass fiber reinforced windows have polyester as the matrix material, whereas for WPC, mostly PVC is used. Composite windows are strong, durable, paintable, and have low-thermal expansion. Acrylic styrene acrylonitrile (ASA) capped acrylonitrile butadiene styrene (ABS) is also used as molding material for window profiles [32]. Despite being more expensive than PVC, ABS window profiles offer better impact strength, higher heat deflection temperature, less shrinkage, and better resistance to weather damage.

32.2.7 Piping

Plastic materials have long been used to make pipes and tubing systems. These are categorized as gravity pipes meant for building and civil engineering and pressure pipes for utilities and plumbing. The gravity sector is the larger of the two. The first plastic pipes were made from PVC in the1930s, and later PE and ABS joined the family of materials for mass production of pipes and tubes. Various other polymeric materials are also used to make pipes, and these include chlorinated PVC (CPVC), CPE, PEX, polybutylene (PB), PP, PVDF [33,34], and various glass-reinforced thermosets, such as epoxy and polyesters [35]. However, PVC and various grades of PE dominate the plastic piping market. According to a report prepared by the Freedonia group on plastic and competitive pipe market, worldwide demand for plastic pipes is going to increase by 4.5% per year to 8.1 billion meters by 2012 and 4.6% per year to 18.1 million metric ton by weight, indicating increasing usage in larger diameter pipes. PVC will continue to dominate, with about two-thirds of the market, but newer materials such as molecularly oriented PVC and bimodal PE will show greater growth as well [36]. Note that a variety of additives are normally incorporated into plastics to endow them with specific desirable properties. Some essential additives used in plastics for piping applications include heat and ultraviolet stabilizers, antioxidants, lubricants, coupling agents, and colorants. Some of these additives protect pipes that are used outdoors from degradation due to weathering.

Pipes made from plastic compete with traditional materials such as metallic pipes made from copper, steel, or aluminum and also with pipes manufactured from cement and concrete. Plastic pipes offer many advantages over traditional materials. They have good hydraulics (low resistance to flow, high resistance to scale or build-up), are lightweight, low cost, and easy to manufacture. Very small to large diameters and long lengths can be extruded and transported. Plastics are flexible and they can bend easily to go around corners and tight spaces without breaking. Long lengths and flexibility minimizes the need for many joints and connectors. Since plastics are nonconductive, they do not suffer from electrochemical degradation such as corrosion or rusting. They are resistant to chemical and biological degradation also. They are durable, and easy to maintain and replace. One major advantage with plastic piping systems is the variety of joints and connectors that can be used to make leak proof and durable connections. Non-plastic piping systems require flange-type or threaded fittings to make connections which are prone to leaking and failure. By contrast, thermoplastic piping can be joined by heat welding or solvent cementing which creates joints that are almost seamless and as strong as the rest of the pipe. A variety of metallic and plastic fittings and connectors are compatible with plastic pipes. However, plastic pipes are limited to low-pressure and temperature applications due to their low strength and the tendency of the polymers to soften at elevated temperatures. This is the reason that the drainage and wastewater pipelines from sinks and toilets are made from plastics, but pressurized hot and cold water distribution systems in a household are still predominantly metal, especially copper. However, with new innovations in plastics technology, the use of plastic piping is being extended to more demanding applications such as hot-water supply, radiant floor heating, and fire sprinkler systems. In what follows, various grades of plastics used in piping systems are described.

PVC and CPVC are the most widely used plastics to make piping systems. In the United States, PVC accounts for two-thirds of water distribution systems and about three-fourths of sanitary sewer systems [37]. Rigid or UPVC is preferred, because it has the highest strength of all other plastic piping materials, as shown in Table 32.4. It also has excellent long-term strength, high stiffness, and resistance to chemicals. PVC piping is available in a wide range of sizes and wall thicknesses for both pressure and non-pressure applications. PVC piping is classified based on its tensile strength, impact strength, and stiffness. PVC is recommended for temperatures up to 60 °C [34] for non-pressure applications.

CPVC is obtained by adding extra chlorine to PVC which results in a material that is similar in strength and modulus to PVC but has a higher temperature rating. CPVC can be used at temperatures up to 93 °C for pressure and 100 °C for non-pressure applications [33], making it suitable for both hot and cold water applications. PVC materials have excellent flame-resistant properties due to the presence of halogen atoms in the polymer structure. Therefore, they are recommended for household fire sprinkler systems.

The other major material for plastic pipe manufacture is PE, a polyolefin. This is the second most common plastic material after PVC. PE is classified broadly into three types. LDPE is Type I which is soft, flexible, and has low-temperature-resistance. Type II is medium density PE (MDPE) which is stronger and more temperature resistant. Type III is HDPE which is much stronger, tougher, and more temperature resistant. HDPE is also the preferred material for piping [34]. PE is less strong as compared to PVC, but, because it has a very low glass transition temperature, it maintains flexibility even at low temperatures. It has better chemical resistance and a smoother surface which reduces friction losses. It can be easily heat welded to fittings and connectors, ensuring virtually leak-proof joints. The main applications of PE piping are in water distribution and in sewage and drain systems. Because of their better crack resistance properties, PE pipes are also used for natural gas delivery. HDPE is used for moderate water pressure supplies (6.3 MPa), LDPE is used for low-pressure water (4 MPa) whereas a blend of MDPE with HDPE is used for higher pressure requirements (8–10 MPa) [7]. Recently, ultrahigh molecular weight PE

Table 32.4 Typical physical properties of thermoplastics for piping

Property	ASTM Test Method	Approximate Values at 24 °C						
		ABS	PVC	CPVC	PE	PEX	PB	PVDF
Specific gravity	D792	1.08	1.4	1.54	0.95	0.94	0.92	1.76
Tensile strength (MPa)	D638	48.3	55.2	55.2	22.1	19.3	28.9	48.3
Tensile modulus (GPa)	D638	2.3	2.8	2.9	0.82	1.0	0.38	1.5
Izod impact strength (J/m)	D256	213.6	53.4	80.1	>534	>534	>534	202.9
Coefficient of linear expansion (m/m°C)	D696	108	54	63	162	162	130	126
Approximate operating temperature limits (°C)								
Non-pressure		80	65	100	70	100	100	150
Pressure		70	55	80	60	95	80	140

Adapted from McGrath and Mruk [33].

pipes have become available, and these have a higher resistance to stress cracking.

PEX is the most widely used thermoset in the piping industry. It is obtained by the process of crosslinking PE molecular chains after the extrusion process, as this creates a stronger molecular structure. The three methods used for crosslinking are peroxide, silane grafting, and irradiation. Compared to PE, PEX has higher heat resistance; at higher temperatures, it becomes flexible but does not melt. The recommended temperature limit for PEX usage is 93 °C. It also has better creep resistance, UV stability, and resistance against environmental stress cracking. Other thermosets encountered are mostly reinforced materials which are used more in industrial applications for more demanding situations than in building applications.

PB is also a polyolefin which is flexible but has much larger long-term strength. In addition, it retains its long-term strength at higher temperatures much better than PE. That is why it is recommended for use up to 93 °C as compared to 60 °C for PE [33], making it suitable for domestic hot-water applications. Note that antioxidants have to be added to both PEX and PB in order that these materials perform well at 93 °C. An equally important member of the polyolefin family used in piping systems is PP. It has more stiffness and strength than PE but less impact strength. It is more temperature resistant and has better chemical and solvent resistance. It is classified as Type I which is stronger but has less impact strength and Type II which is less strong but has higher toughness.

ABS is a copolymer where a rubbery polybutadiene phase is dispersed in a rigid but brittle styrene-acrylonitrile (SAN) phase. The presence of rubber particles imparts flexibility and impact strength to the material even at low temperatures. Due to its excellent strength, ABS pipes are also available where the pipe wall is made of foamed core rather than a solid wall which decreases weight without compromising physical properties. The major use of ABS pipes is in drain, waste, and vent (DWV) applications.

The demand for these different types of plastic pipes is expected to remain strong due to replacement of concrete and metal pipes by plastic and also because of the need for new water supply and sewer systems to satisfy the needs of a growing global population.

32.2.8 Decking, Fencing, and Railings

Decking, fencing, and railings are outdoor building applications, and these are generally made from wood. Deforestation and the use of hazardous chemicals such as chromated copper arsenate which is used as anti-fungi agent are the main reasons for seeking alternatives to wood in such applications. Plastic products used in these applications are known as plastic lumber (PL) which include both unfilled and fiber reinforced plastic products. Demand for PL, in addition to environmental concerns, is also driven by product variety, durability, aesthetics, and low maintenance that one expects from plastic products. However, neat thermoplastics have much less strength and stiffness compared to wood which is the cause of sagging of decking and railings. By adding wood flour and biofibers, such as cellulose, as reinforcing materials, a significant improvement in these properties can be obtained [38].

Biofibers and wood fibers start to degrade at 200 °C, and, therefore, only resins that are processable at temperatures less than 200 °C are used as matrix polymers for WPCs. Thermoplastics used in these applications are various grades of PE, PP, PS, PVC, and ABS [39,40]. About 80% of the market is dominated by polyolefins, but PVC is likely to gain an increasing market share. A significant portion of the matrix material in WPCs is post-consumer recycled plastic, such as HDPE and LDPE from recycled plastic bags and milk containers. The wood content can vary anywhere from 20 to 80% by weight, but most commercial products contain 50–60% wood by weight. This is because higher loadings are difficult to process due to a sharp increase in melt viscosity which causes problems in extrusion. WPC decking and railing are obtained by the profile extrusion process, but co-extrusion is also used to apply capstock for UV protection or to create a solid skin around a foamed core. Profile extrusion can be a single-stage or two-stage operation. In the single-stage operation, resin, additives, processing aids, and wood flour are directly fed to the extruder where melt blending takes place, and the blended product is then extruded through a profile die. In the two-stage process, the plastic resin and wood are compounded in the form of pellets in a twin-screw extruder, and then these pellets are used for profile extrusion in a single-screw extruder.

PVC and WPC as well as polyolefin-based wood composites are the main materials that are used to make fencing profiles and slats. Due to low maintenance and greater tolerance to heat and moisture degradation, the plastic fencing market has seen rapid growth in recent years, particularly WPCs which have gained wide acceptance. The plastic fencing market has also benefited from the fact that fencing is not considered to be structural. As a result, building code requirements are not stringent except in some cases, such as pool or ranch fencings or in hurricane affected areas [41]. PVC and WPC fences also have the advantage of being available in various surface and paint finishes; this is achieved by using capstock or by giving the WPCs embossed texture. Plastic fencing can have a foamed core or a solid core structure, and it is produced by a profile extrusion/co-extrusion process, similar to the one used in the WPC decking industry. Since recycled PVC, polyolefins, and recycled wood flour are used as raw materials to make plastic fencing, these products can be viewed as a part of green and sustainable building design.

32.3 Plastic Applications in Green Building Design

With rising cost of energy and concerns regarding global warming related to CO_2 emissions, much emphasis is being placed on constructing buildings utilizing materials, designs, and systems that are environmentally friendly, energy efficient, and sustainable. These improvements are sought not only for new construction but in renovation and repair of existing buildings as well. Federal, state, and local governments are encouraging the use of green technology by providing various incentives in terms of tax rebates, low-interest loans, and subsidies. In the United States, the residential and commercial building sectors, taken together, account for 40% of total energy usage. In a typical US household, as much as 45% energy use is for heating and cooling [42], and most of this is expended on energy loss due to air infiltration and leakage. The Energy Policy Act of 2005 provides for tax incentives for 50% reduction in energy and power cost over the International Energy Conservation Code (IECC) for residential buildings and American Society of Heating, Refrigerating, and Air-Conditioning Engineers (ASHRAE) codes for commercial buildings [43]. Plastic materials play a major part in achieving these goals which involves improving the performance of interior lighting, heating, cooling, ventilation, hot-water, and building envelope insulation [44]. Solid foam insulation for walls and roofs, such as SPF, light-colored plastic roofing membranes, plastic glazing, and skylights with high *R*-values, plastic piping for hot-water and radiant heating, and foam-insulated concrete panels containing XPS are some of the examples of the applications of polymer-based materials in making the building construction more eco-friendly.

The US Green Building Council (USGBC) has developed a program called Leadership in Energy and Environmental Design (LEED) to set standards and certification mechanisms for green building designs. Points are awarded based on sustainable site selection, water efficiency, energy and atmosphere, materials and resources, and indoor air quality. Based on discussions presented in previous sections, one can see that the use of polymeric materials can be very helpful in this regard. Under LEED guidelines, the use of materials that are recycled, recyclable, reusable, and renewable is encouraged; these include WPCs which are based on recycled and renewable wood and recycled and recyclable thermoplastics. Similarly, the use of plastic piping which reduces water leakage or the use of plastic WRB would help in achieving green building design certification. A recent exciting development is the use of phase change materials (PCMs) that go from solid to liquid at temperature ranges between 0 °C and 60 °C [45]. PCMs are commercially available, and they absorb energy and melt when the indoor temperature goes above the human comfort range. When the temperature falls, they solidify and release energy. When incorporated into building materials, PCMs help to reduce energy costs for heating and cooling. In the coming years, building construction based on green building design will continue to increase, and polymer-based materials and systems will constitute a significant part of the construction industry.

32.4 Conclusions

Polymeric materials, both thermoplastics and thermosets, have wide applications in the building construction industry.

They provide unique and innovative solutions at low cost. Their use is likely to grow only in the future.

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33 Infrastructure Applications of Fiber-Reinforced Polymer Composites

Hota GangaRao
Constructed Facilities Center, College of Engineering and Mineral Resources, West Virginia University,
Morgantown, WV 26506, USA

33.1 Introduction

Fiber-Reinforced Polymer (FRP) composites are promoted as the twenty-first century material with potential to replace conventional materials such as steel or concrete in infrastructure systems. The main reasons for such promotion are as follows: (1) higher specific strength and stiffness (actual value divided by specific gravity) than conventional materials; (2) greater fatigue strength and energy absorption capacity; (3) better resistance to corrosion (non-conductive), fire, attacks from microorganisms, insects, and other pests; and (4) lower installation, operation, and maintenance costs. For military infrastructure applications such as aircrafts, deckhouses in ships, turret bases, etc., appropriate designs with FRP composites offer additional benefits such as blast-, shock- and fatigue-resistance with reduced acoustic and magnetic interferences [1].

Recently, researchers have been focusing their efforts on developing advanced FRP composites for applications such as windmill blades, utility poles, highway posts, highway pavement, pipes for natural gas lines, and many other civil infrastructure systems. For example, high pressure resistant and durable FRP composite pipes are desired for natural gas transmission systems and water lines. Similarly, FRP composites have also been receiving greater attention than ever before from utility industries for distribution and transmission poles, especially up to 120 ft in height. It is anticipated that more ductile FRP poles, signposts, and guardrails will significantly improve the Nation's highway safety, because of FRP's improved dynamic response under highway accidents, wherein better vehicle—post interaction leads to a higher level of passenger safety and sheared poles penetrating into the cab is prevented. Furthermore, FRP composite planks for boardwalks in marina infrastructure will substitute traditional materials such as wood in order to overcome both the structural and material degradations under the harsh environment. It is expected that the boundaries of composite applications in infrastructure will be greatly expanded as a result of multiyear joint effort through National Science Foundation sponsored and industries supported Industry/University Collaborative Research Center, entitled "Center for Integration of Composites into Infrastructure (CICI)" [2].

The objective of this chapter is to provide an overview of current FRP composite applications in infrastructure with an emphasis on bridge and highway structures and also provide near-future trends of this twenty-first century material for poles, pipes, radar towers, and turbine blades for wind energy. In addition, a brief narration is given herein for blast- and fire-resistant FRP structures.

33.2 Products and Applications

33.2.1 Demand for Bridges and Other Highway Structural Components

Advances in FRP composite products, especially glass fiber-reinforced ones, have led to the structural systems that allow for rapid deployment of bridge decks and other highway structures using modular system development concepts. The bridge structural elements under discussion include pavement panels, bridge decks, stringers, beams, abutment panels, rebar, dowel bars, and posts. Other FRP highway structures are signposts, signboards, guardrails, sound barriers, drainage systems (pipes, culverts), etc. Each of these products represents a huge market: (1) approximately $50 billion was spent on highways and bridges in 1999 [3] including $8.1 billion for bridges in the US [4]. It is estimated that the annual market for bridge decks is about $2—3 billion; (2) 36 million highway signposts are in-service in the US with an annual replacement of about 2 million signposts due to off-the-road accidents, generating a market of $100 to 200 million [5]; (3) 2000 miles of guardrails are constructed each year on Federal-aid projects, leading to $180 million of material sales; (4) the new construction of railing uses 2 million guardrail posts and 2 million spacer blocks, resulting in another $60 million of the FRP material market.

In a comprehensive survey, JEC Composites of Paris, France (2009) forecast that the global market in 2013 will be around US $107 to $114 billion per year (approximately 22 billion pounds of FRP composites) in comparison to about $81 billion in year 2008. About one-quarter of the global

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demand for FRPs resides in the US, accounting for about 5.4 billion lbs in year 2008. The global composites industry is expanding by about 4% per year despite the current (2008–2009) economic slowdown. For example, more than 13,000 facilities are processing composites in the US, employing about 236,000 people and contributing over $24 billion to the nation's economy [47]. The major market share in the US includes about 32% in transportation, 21% in construction, 12% in corrosion-resistant equipment, 10% in marine, and 10% in electrical or electronic industries with only 0.6% being used in aircraft and aerospace industries (SPI Composites Institute, May 1999).

33.2.2 Applications of FRP Composites for Bridges

Bridges are iconic and their design, construction, and maintenance have changed a great deal in the past 100 years. It is expected that construction and maintenance techniques will change even more dramatically in the next 25 years. Advanced technologies such as design-built bridge systems have increased steadily with the use of innovative materials such as high performance steel and concrete [6]. In addition, field implementation of glass or carbon fiber-reinforced polymer (FRP) composites has been steadily gaining notoriety because of their many advantages, including high strength and stiffness to weight ratio, excellent durability, non-corrosiveness and non-conductivity. Because of lower self-weight and use of rapid deployment techniques, composites lend themselves well to prefabricated bridge construction leading to minimized traffic delays and enhanced on-site safety of construction workers.

Composites have been used as superstructural elements as well as substructural elements of bridge structures. Composites are ideally suited for use in unique bridges, such as floating or movable bridges. In addition, composite systems can be manufactured with smart materials to identify damage and lead to self-healing or even self-cleaning mechanisms [7]. Composite applications are not limited to new structures, as they can be utilized to rehabilitate or upgrade existing structures for safety or to increase load-carrying capacity. A few of these aspects are briefly described in the sections given below.

33.2.2.1 Bridge superstructures

Bridge system design and construction are intriguing because generic structural and material responses can be combined in an innovative manner to arrive at durable and economical structures. Some of the generic responses are as follows: (1) beam bending, (2) membrane action through arching which converts bending forces primarily into compressive axial effects, and (3) pretensioned cable and/or suspension systems which help efficiently transfer vertical loads to the ground while providing adequate stiffness through superstructural elements such as decks, longitudinal beams, and diaphragms. All of these structural elements provide adequate stiffness to limit displacements, vibrations, and fatigue while helping to maintain structural durability and longevity. One of the fascinating structural systems being advanced to its maximum span limits is the suspension cable system coupled with stayed cable system where steel or concrete is typically used as a superstructure material. Many of these suspension/stay cable systems vary in terms of strand configuration as well as cable arrays. These systems are even coupled with structural systems with arch sections to enhance load transfer efficiencies of a superstructure. However, the maximum clear span length is currently limited to approximately 6400 ft because self-weight-induced stresses play a design-constraining role with reference to conventional materials. For example, the Akashi-Kaikyo Bridge built in 1998 (see Figure 33.1) consumed 91% of the allowable design stresses toward dead load (self-weight) induced stresses, while only 9% was allowed for live load induced stresses. Another example of a suspension bridge is the Kanmonkyo Bridge, built in 1973 (see Figure 33.2), whose span is 2335 ft, where the dead load induced stress was about 75% of the total design stresses. These bridges have conventional decking and deck-stiffening systems ranging around 200–300 pounds per square foot. However, the use of high strength polymer composite decking and possibly even carbon composite based deck-stiffening suspension/stay cable systems not only reduce the percentage of self-weight-induced stresses, but also these advanced materials do provide absolute higher resisting stresses for design in comparison with conventional materials. Therefore, the maximum clear (single) span length of future bridges can be increased to 10,000–12,000 ft by utilizing a combination of advanced composite materials with conventional materials.

To minimize the self-weight-induced stresses, innovative deck cross-sections with high sectional (bending and shear) efficiencies coupled with innovative materials have to be invented. A few such cross-sectional shapes of FRP composite decking were successfully implemented by various State Departments of Transportation in the US. The decking systems are shown in Figure 33.3, with cost comparisons in Table 33.1.

The geometry of these decks changed from a hexagonal shape to a box shape and further modified to a 4-inch (rectangular) multi-cellular low-profile deck to optimize for structural efficiency per unit self-weight [43]. As result of design and manufacturing processes, lighter weight decks were costing around $\$40/\text{ft}^2$ in 2006.

33.2.3 Field Implementation of FRP Bridge Decks and Pavements

Since 1996, over 150 FRP composite deck bridges have been installed on US highways and most of them are still

Figure 33.1 Akashi-Kaikyo bridge. *(Photo courtesy of Wikipedia.org).*

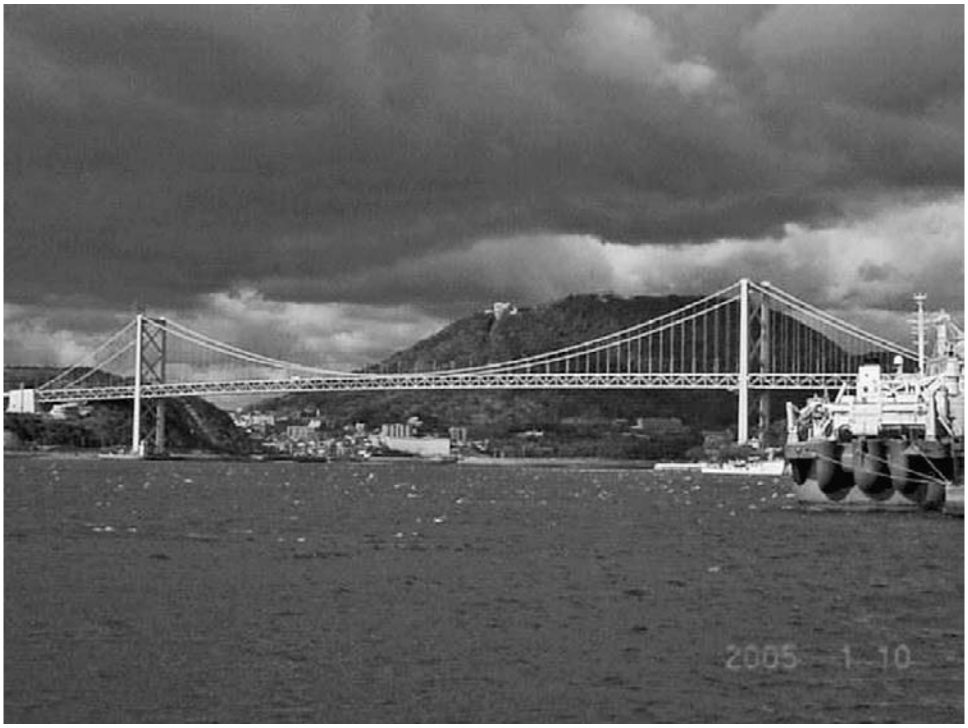

Figure 33.2 Kanmonkyo bridge. *(Photo courtesy of Wikipedia.org).*

in-service [36]. The single-span Market Street Bridge (~210 ft including approaches) is shown under construction in Figure 33.4a, and field implementation details of the Laurel Lick Bridge, an FRP deck with FRP abutments, are illustrated in Figures 33.4b–d. The FRP bridge deck panels are placed transverse to the bridge span (i.e., perpendicular to flow of traffic) and are supported by longitudinal steel/FRP stringers (Figures 33.4a,b). The deck panels are usually interconnected using adhesive bonding (Figure 33.4c). Besides bonding, the panels can also be bolted with mechanical fasteners (Figure 33.4d) for moment and force transfer from one panel to another. The adhesive is applied to

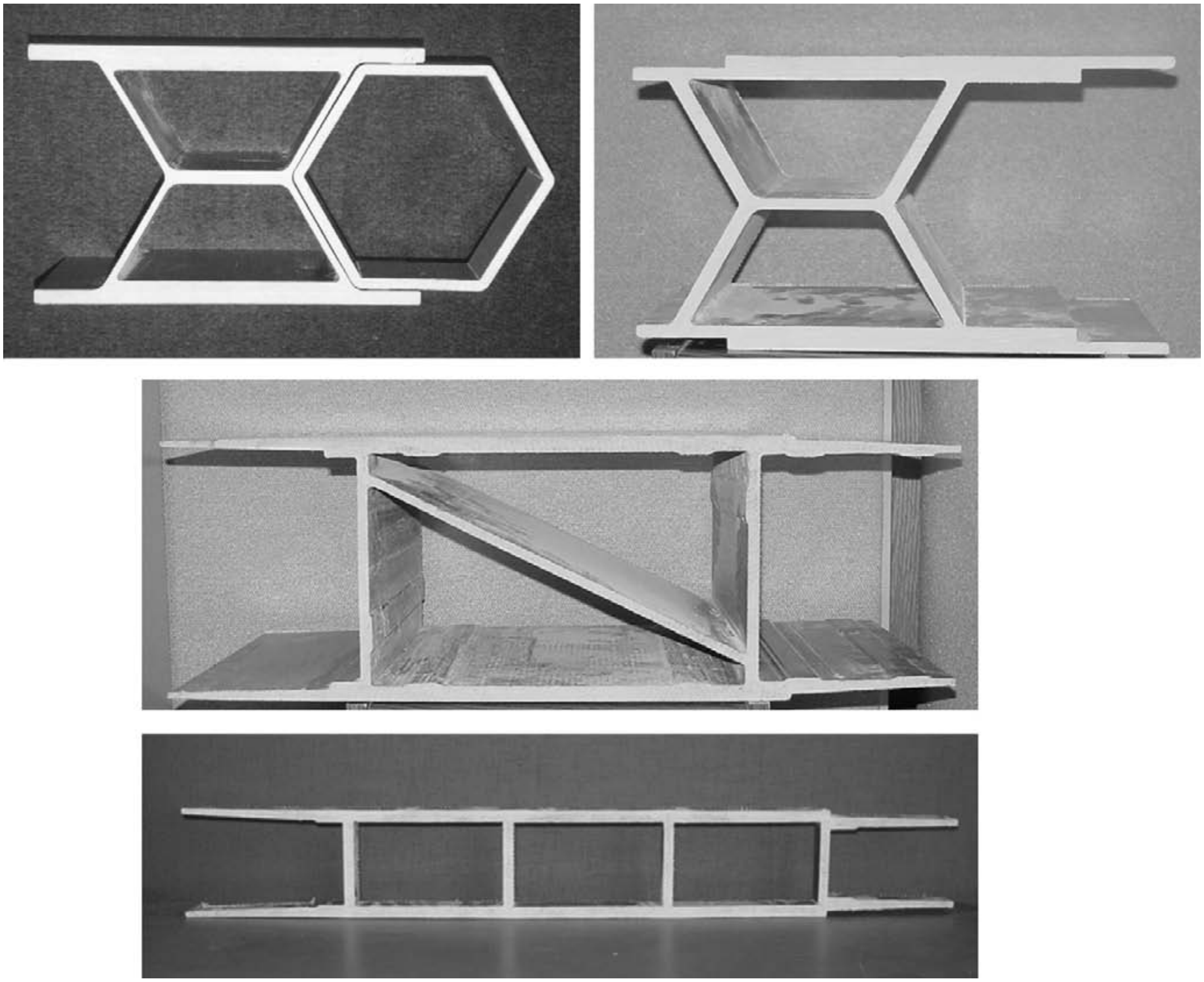

Figure 33.3 Top Left: 1. Double trapezoid and hexagonal deck; Top Right: 2. Revised trapezoidal deck; Middle: 3. Lightweight composite bridge deck; Bottom: 4. Low profile bridge deck. *(Photos courtesy of CFC-WVU).*

Table 33.1 Cost comparisons of FRP decks [43]

Deck Type	Weight per Unit Area (lbs/ft^2)	Cost per Unit Area (\$/ft^2)	Cost per Unit Weight (\$/lb)	Failure Stress (ksi)
#1: Double trapezoidal 1998	22	~80	3.64	10
#2: Revised trapezoidal 2000	19	~58	3.05	30
#3: Lightweight composite 2002	15	~34	2.27	30
#4: Low profile 2003	10	~25	2.5	35–40
Concrete	90–120	~30	0.29–0.35	4–6 compressive <1 tensile

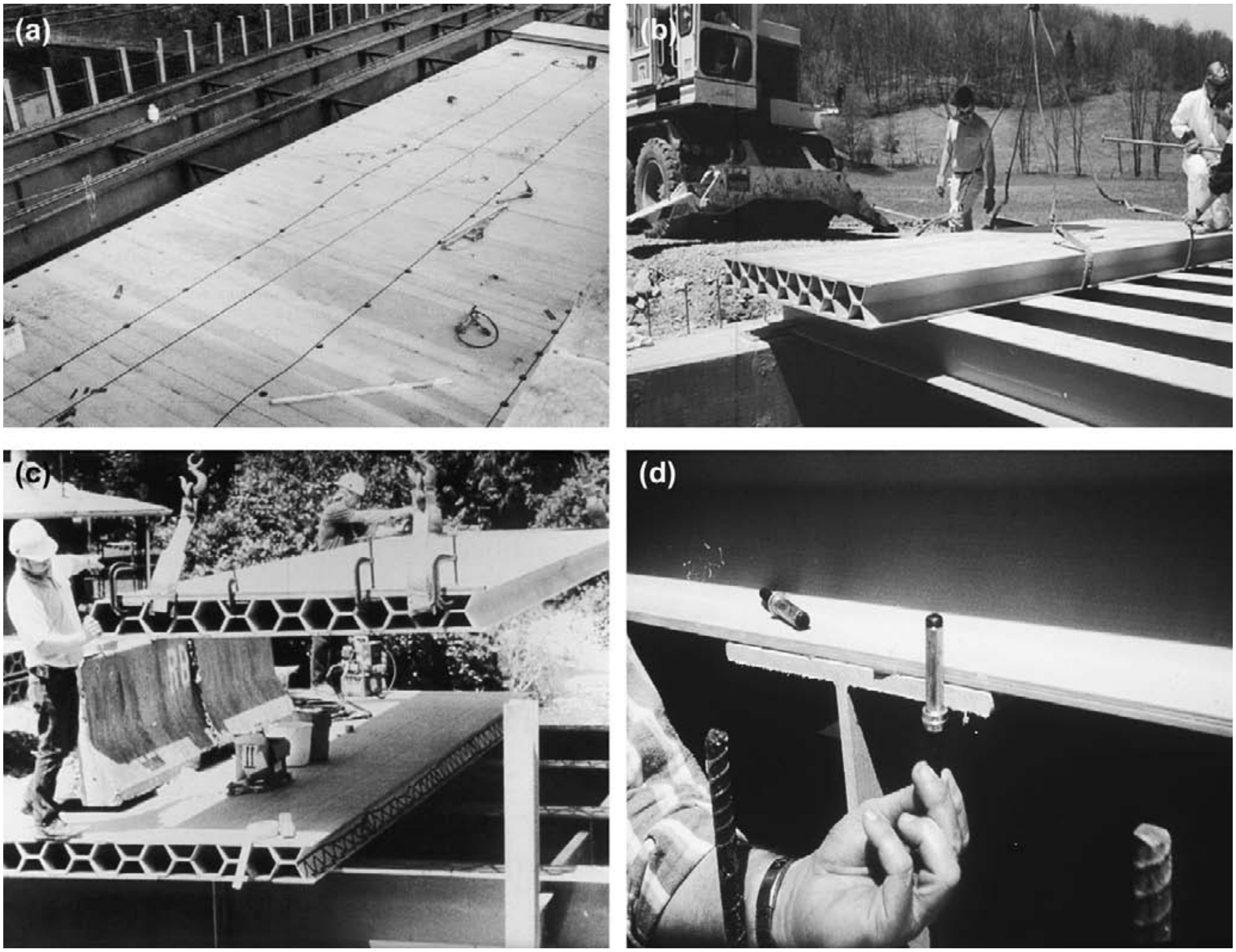

Figure 33.4 Field implementation of FRP composite bridges. (a) Market Street Bridge, Wheeling, WV, FRP deck on steel girders, July 2001; (b–d) Laurel Lick Bridge, Lewis Co, WV, FRP deck on FRP girders, April 1997. *(Photos courtesy of CFC-WVU).*

tongue and groove joints of the first panel and placed on stringers (Figure 33.4c). The panels are connected to stringers using both mechanical fasteners (Figure 33.4d) and adhesive bonding. Sometimes the panels are connected to stringers by shear studs, as was the case in the Market Street Bridge. Once the first deck panel is placed on the stringers and bonded with adhesive in addition to mechanical fasteners, the subsequent deck panel is placed next to the first panel, and the two panels are "squeezed" together to establish good bond, and full shear transfer takes place with the remaining panels. To allow additional curing time for the adhesive, the second panel is lowered and jacked into place and a concrete barrier is placed on the top of the FRP deck to achieve stability and good bond between the panel-to-panel and panel-to-stringer (Figure 33.4c). These bridges are being field monitored for in-service performance [8].

Additional applications of FRP for bridge structures include the use of Carbon FRP (CFRP) cables for suspension and cable stayed bridges, as shown in Figure 33.5. FRP has also been utilized to reduce dead loads, as demonstrated with an inspection walkway for the Blennerhassett Bridge in West Virginia (Figure 33.6).

Similarly, other FRP products (rebar and dowel bars for concrete as shown in Figure 33.7) have been field implemented in lieu of steel reinforcement because they offer unique performance advantages including better thermal and stiffness matching with concrete in addition to non-corrosiveness and higher strength to weight ratio. Also, non-magnetic GFRP rebar in concrete pavement provides a major advantage where toll-monitoring devices are installed at toll booths. Both the FRP rebar and dowel bars have been in-service for several years and functioning well. From Public Roads (Sept/Oct 2008), additional details can be obtained on FRP rebar, reinforcing the continuously reinforced concrete pavements. Similarly, dowel bar performance on the West Virginia Highway System

Figure 33.5 Kleine Emme bridge, Switzerland, with CFRP cables in bottom chord. *(Photos courtesy of Dr. Urs Meier).*

installed over 12 years ago has been found to be performing exceedingly well [9].

FRP modular panels have also been experimented as highway pavement systems (see Figure 33.8). Several major advantages of FRP modular panels are as follows: (1) 40–50 year expected service life, (2) ease and speed of installation with minimal traffic interruption, (3) availability of the panels with rumble strips, paint marks, riding surface and built-in crown from the factory, and (4) cost-effectiveness in relation to continuously reinforced concrete pavements.

33.2.3.1 Bridge substructures

Composites can be used also for piers and abutments in an efficient manner. For example, double-walled cylindrical shells made of glass composites as shown in Figure 33.9 are pultruded up to 24 inches in diameter having strengths of the order of 40,000–50,000 psi. Similarly, carbon composites can be manufactured to sustain 100,000–150,000 psi. Another novel approach to mass produce and erect large size piers or pipes on-site (which can be used as substructural elements or as form work for substructures) is through an infusion process where curvilinear modular panels (Figure 33.10) can be assembled with 8-ft or 10-ft radius of curvature for curved segments having lengths of 100 ft, or built-up sections produced on-site similar to a design for an Ocean Thermal Energy Conversion (OTEC) cold water pipe (Figure 33.11). These composite cylindrical shells are being designed with concrete fill where needed to provide the advantage of mass and resistance against buckling. Composite elements have been used as earth retaining structures, including piles, pile lagging, and retaining walls (Figures 33.12 and 33.13) in an economical manner. Durability of these systems is found to be excellent, especially under corrosive environments. The soil-retaining wall designs can take advantage of the non-corrosive nature of the material as well as its strength to build durable retaining walls 40–50 ft high. The design methodology of such retaining structures can be similar to those for the design of reinforced earth structures [10].

33.2.3.2 Unique bridges

Bridges made of FRP composites can be floating bridges, underwater bridges, and even folding and unfolding bridges. Similarly a number of exotic movable bridges can be developed because of low self-weight (10 lbs/ft^2 or less). However, floating bridges have to be anchored to the seabed or balanced with dampers to minimize excessive movements, especially in the water flow direction. Glass composite materials are ideally suited for anchor cables because of their non-corrosive properties and are being used as anchors for offshore platforms. A novel bridge design is shown in Figure 33.14, which is uniquely suited to be manufactured with composite materials. A wide range of movable or lightweight pedestrian bridges have been developed and field implemented by many engineers including Johannson and GangaRao. A pedestrian bridge built in Germany in the year 2000 is shown in Figure 33.15.

33.2.3.3 Bridging in defense

The US Army has been utilizing advanced bridging technologies to improve the mobility and bridging capability

Figure 33.6 Blennerhassett bridge (WV) FRP inspection walkway composed of rectangular FRP sections (right side). *(Photos courtesy of WVDOT-DOH).*

of heavy armored forces and emergency vehicles. Most of the current bridging systems developed in the 1960s are not capable of carrying many of today's heavier (70−100 ton) wheeled and tracked vehicles. In addition, they are so heavy that they limit the mobility of armed forces [11]. The need to rapidly deploy lightweight bridging becomes more important today than ever before because of the current Army Vision 2010 Transformation. Figure 33.16 shows the latest heavy assault bridge Wolverine, which weighs 24,000 lbs and has a length of 85 ft to cross 75-ft wide gaps under MLC 70 loading conditions [12].

The US Army has been heavily involved in developing new lightweight composite bridges up to 45-ft spans for MLC tanks 70 and 100, for better tactical mobility and rapid deployment/retrievability, which can carry multiple bridges per launcher with minimum profile depth. Kosmatka and his team conducted a pioneering investigation exploring the concept of an all composite army bridge (CAB) as a part of the Defense Advanced Research Projects Agency (DARPA) sponsored Bridge Infrastructural Renewal (BIR) program [11,13]. A composite army bridge made of nearly all graphite design coupled with SCRIMP manufacturing approach was designed, analyzed and laboratory evaluated [14]. The encouraging result was the development of a prototype composite bridge that had a self-weight of 10,500 lb, resulting in a 12.5% weight saving compared to the aluminum bridge of the same span. The static tests showed a design failure load of 75,160 lb versus a proof test load of 116,000 lb. If successful, these CABs will result in about a $50 million market.

Advanced FRP composites also have the potential to revolutionize the design and manufacturing of a new family of bridging for the US Marine Corps [15]. The US Navy is soliciting technologies to design lighter and more compact bridging with less manpower to emplace than the current Marine Assault and Tactical Bridging. Current bridging assets within the US Marine Corps can be grouped into three distinct categories: (1) assault bridging, (2) tactical bridging, and (3) line of communication (LOC) bridging. Assault bridging consists of AVLBs, primarily used for in-stride,

Figure 33.7 Top: FRP rebar for continuously reinforced concrete pavements, Bottom: FRP dowel bars for conventional concrete pavement. *(Photos courtesy of CFC-WVU).*

Figure 33.8 FRP modular panels for pavement project, before and after applying wearing surface. *(Photos courtesy of CFC-WVU).*

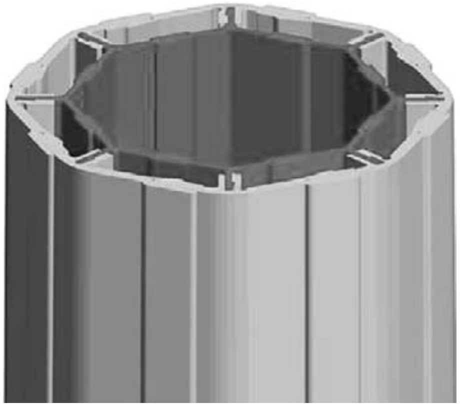

Figure 33.9 Double wall cylindrical shell. *(Courtesy of Hiel [18]).*

short-term breaching purposes for the M1A1 main battle tank, while tactical bridging known as the Medium Girder Bridge (MGB) is a panel type bridge structure designed to be conventionally emplaced from near to far shore, primarily utilizing human assets. As a result, there is no commonality between these two systems regarding interchangeability of parts, concepts of employment, and emplacement and/or displacement. In addition to reaching the end of its service life in 2008, MGB is susceptible to damage if left in place and unmonitored for long periods. It is commented that the current bridging assets within the US Marine Corps are neither capable of being rapidly emplaced nor sufficient in structural capacity to handle the induced stresses of modern wheeled and tracked combat vehicles; hence, the US Marine Corps has been evaluating the use of advanced FRP composite materials and systems to fit their needs for assault and tactical bridging.

Figure 33.10 Curvilinear FRP panel. *(Courtesy of Fiber-Tech Inc.).*

Figure 33.11 Cold water pipe for OTEC. *(Courtesy of Lockheed-Martin).*

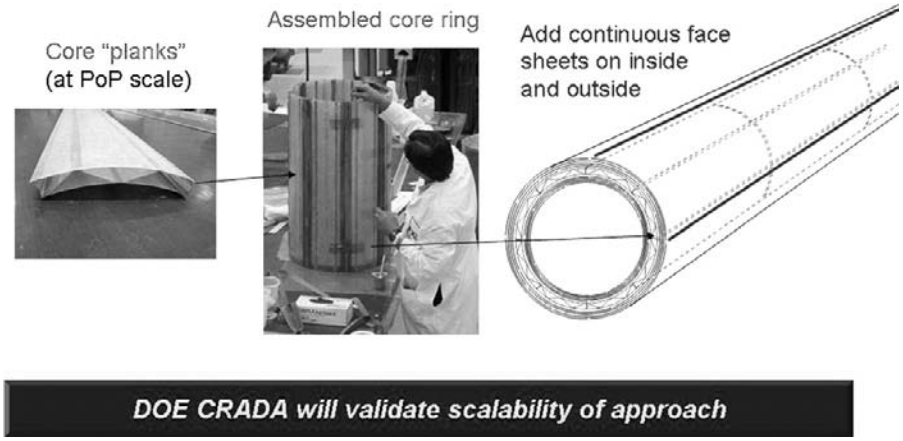

Figure 33.12 Laurel Lick Bridge with FRP piles. *(Photos courtesy of CFC-WVU).*

33.2.3.4 Smart materials for bridges

Typical challenges are to identify proper material systems and processes that are conducive to the following: (1) self-assessing and self-healing materials, (2) coatings that can be used as sensors, and (3) self-cleaning and de-polluting bridges. Bridge decks typically sustain deterioration under environmental attacks as well as fatigue loads, including high stress concentrations under wheel patch loads. Since composites could increase the service life of a bridge deck and save large sums of money, recent development in the use of carbon fibers for the use of sensing and detecting to heal the damage through polymers housed in nano-fibers is being attempted by the US Army. Two examples of smart materials are shown in Figure 33.17, and more can be found through Cornerstone Research Group, Inc. (http://www.crgrp.com).

Coatings consisting of nano-fibers can be used as sensors to detect micro-cracks, fire, and hazardous chemicals. For example, electrically conductive coatings in conjunction with wireless networks are being developed to detect fire and other structural hazards. Inorganic coatings are available for self-cleaning and even cleaning some of the exhaust from traffic forming black soot. The self-cleaning properties improve structural durability by oxidizing pollutants that can potentially cause corrosion-related deterioration. These inorganic polymer coatings can be used on bridges and barriers to clean the structural surfaces and even the environment [7].

Figure 33.13 8-ft high retaining wall. *(Photos courtesy of CFC-WVU).*

33.2.4 Other Structures

Many other FRP composite structures have been field implemented with ease of erection and excellent in-service performance. Some of these other FRP composite structures are as follows: poles, pipes, platforms, wind turbine blades, blast-resistant structures, housing panels, and others. Relevance of these applications with FRP composites, including potential volume of use/application is described below.

33.2.4.1 Poles

Currently, there are 130 million utility poles in-service in the US, with about 98% of them being creosote-treated wood poles and about 2% of steel, composite, or other poles (Figure 33.18). According to a survey of the utility industry [16], more than 70% of the utility poles in use are distribution poles in class 4 or class 5 with 40 ft height or less. These poles sustain a horizontal load of 2400lbs (class 4) or 1900 lbs (class 5) as defined by ANSI O5.1. In addition to a new installation market of $1.2 billion per year, about 4 million poles are being replaced each year, forming a replacement market of US $2.8 billion per year [17,18].

Wood poles typically require treatment with preservatives (e.g., creosote, copper chromium arsenate (CCA), pentachloro-phenol (Penta)) to resist rot, decay, etc., in order to yield a service life of about 30–35 years. Because of preservation treatments of wood poles [19] which are hazardous to humans, the US–EPA regulations have led to evaluating the viability of alternatives to treated wood poles, i.e., steel, concrete, and FRP composite. Recently, through a strong push from the American Composites Manufacturers' Association (ACMA), FRP composite poles have been receiving greater attention from electrical utility and telecommunication companies due to their inherent advantages over poles made of conventional materials.

One of the many reasons to use FRP composite poles as an alternative to wood poles is to improve roadside safety by reducing automobile–pole collision-related deaths, which were reported to be around 1100 people per year [20,21]. The investigation of dynamic response between a vehicle and utility pole has led to the development of breakaway utility poles, which are designed to break from their base at a reduced amount of energy in a plane close to the height of the vehicle bumper from the ground level [16]. Properly

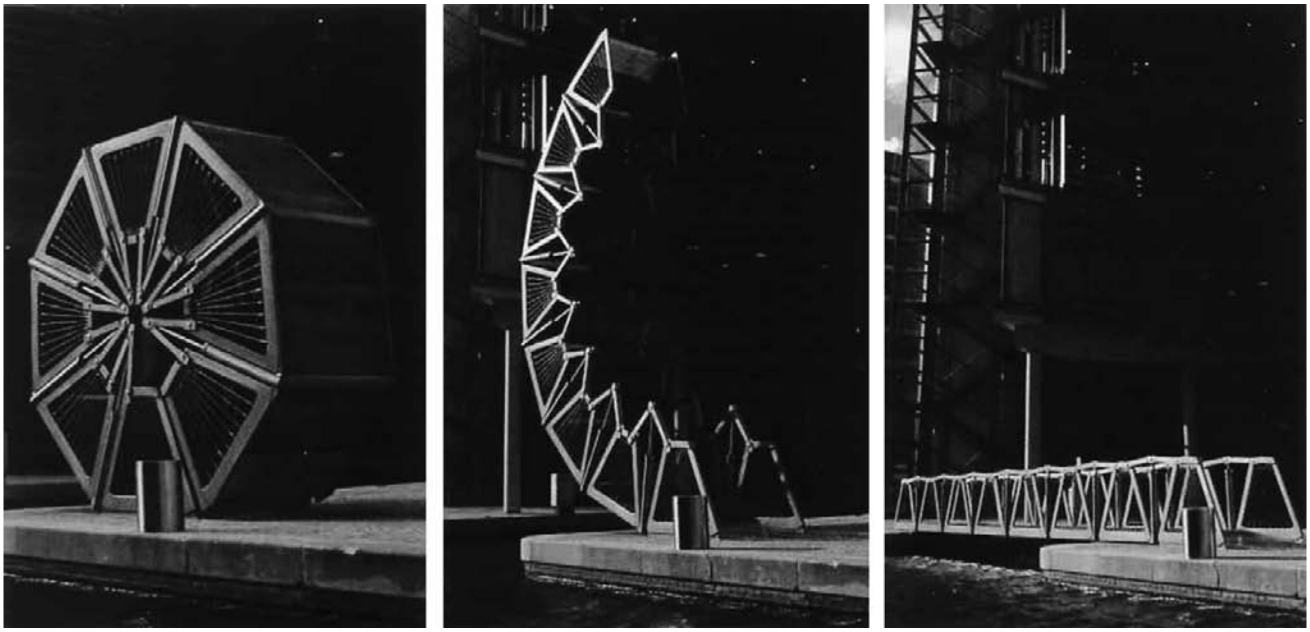

Figure 33.14 Coiling bridge. *(Photos courtesy of 'Bridges', July–August 2005).*

designed FRP composites have superior impact energy absorption. The development and implementation of FRP poles with improved ductility and breakability under impact offers an excellent alternative solution to the problem of utility–pole collision and helps to make the roadway poles more "forgiving," under vehicle–pole collision scenario. More details on the state-of-the-art of FRP poles technology can be found in references [17,22,23]. In the past, the initial cost of FRP composite poles was about three times higher than the treated wood poles; however, recent cost comparisons of FRP poles reveal that they are about 30% higher in initial cost (not including lower handling and durability costs) than wood poles (personal correspondence with BRP, May 2009). By implementing state-of-the-art technology, cost-effective mass production of FRP poles is desired in order to receive a greater market share. Major efforts are underway to accomplish cost-effective mass production processes. For example, a couple of novel approaches especially valid for poles 60-ft to 100-ft are to fill the bottom quarter of the hollow core of a pole with concrete or provide a low-grade insert using recycled thermoplastic. Major advances in lowering costs are being evaluated by Bedford Reinforced Plastics, Inc.

33.2.4.2 Pipes

The pipeline infrastructure in the US is extensive (Figure 33.19). Currently, there are 161,189 miles of liquid pipelines, 307,809 miles of natural gas transmission pipelines and 1,100,855 miles of natural gas distribution pipelines

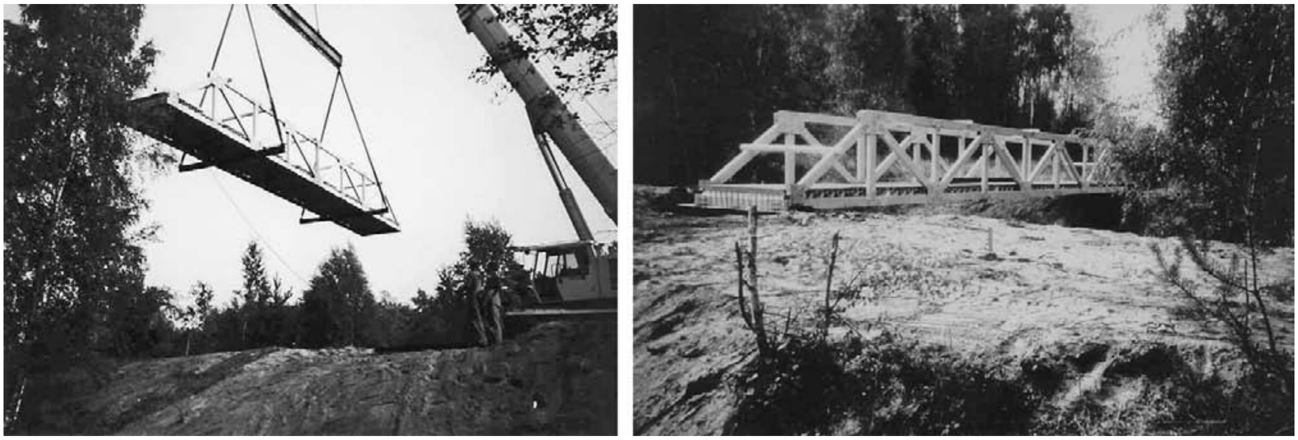

Figure 33.15 Portable bridge built in Germany. *(Photos courtesy of CFC-WVU).*

Figure 33.16 Heavy Assault Bridge System H82510 – XM104 Wolverine. *(Source: FAS [12]).*

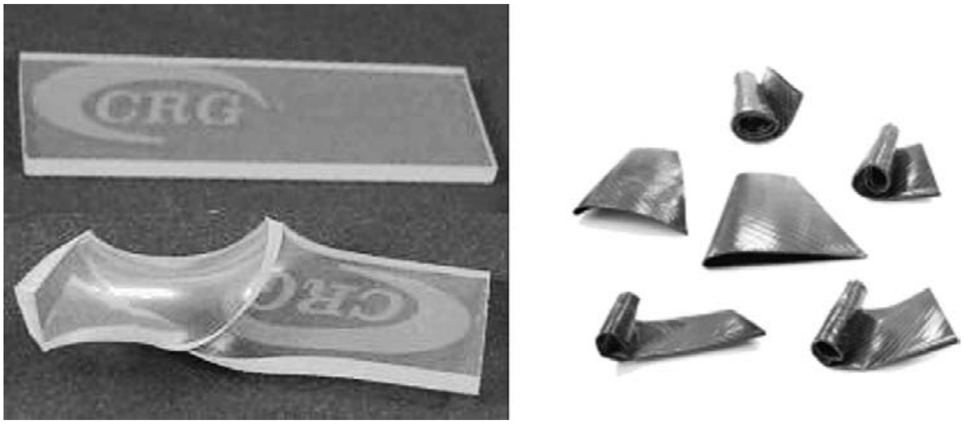

Figure 33.17 Smart Materials. *(Photos courtesy of Cornerstone Research Group, Inc.).*

in-service (US DOT Office of Pipeline Safety Statistics, Jan 2003). Additionally, the large water and sewage systems comprise about 1,500,000 miles of pipes. The existing pipelines are predominantly made of steel, leading to corrosion problems. For example, in 2001, approximately 30% of the total 129 hazardous liquid pipeline accidents were due to corrosion, accounting for over $25 million damages, while there were 209 incidents for natural gas pipelines, accounting for over $37 million damages. The industry is providing in situ repair solutions to corroded pipelines without excavation. These solutions are slip-lining with FRP composite liners of cured in-place linings. Typically reinforced polyvinyl chloride (PVC) or high-density polyethylene (HDPE) are being used as liners. However, Kevlar-reinforced polymer liners are being implemented to resist 350 psi pressure lines such as high pressure water lines. Additional details can be found in Composites Technology Magazine, April 2007.

Thousands of miles of new natural gas pipelines are put in-service each year, while thousands of miles more of deteriorated natural gas pipelines are replaced. It is estimated that between 2001 and 2010, more than 50,000 miles of new transmission pipelines are being built, costing over $80 billion in North America [24]. In order to meet the increased demands, maintain safety and reliability, and be competitive, the pipeline industry is looking at alternatives to conventional steel pipe, for high pressure/high volume natural gas transmission at reduced costs.

Laney [24] evaluated the current and potential use of FRP composite pipe in the natural gas and petroleum pipeline industries. He identified that the small diameter (2–6 inch) composite pipe is being used more frequently for natural gas transportation in flow lines, gathering lines, and distribution lines, while polyethylene pipe is mainly used in distribution pipelines, at both low and moderate pressures. However, only limited testing of a steel/composite hybrid in a natural gas transmission pipeline application has been carried out. "By far the biggest technology challenge is finding stronger, less expensive and longer lasting pipeline materials for larger

Figure 33.18 FRP composite utility pole in-service. *(Photo courtesy of Strongwell, Inc.).*

diameter, high pressure/high volume interstate and intrastate natural gas transmission systems," according to Laney. In order to make FRP composites the material of choice for high pressure large diameter natural gas pipelines, there is a need for further research in the areas of resin/fiber optimization for different applications, manufacturing, joining, material failure through delamination, joint failure, and quality control.

33.2.4.3 Turbine blades for wind energy

Worldwide wind power generation was 121 GW in December 2008, and it amounts to only 1.5% of electricity usage. Wind power usage is growing rapidly, having doubled between 2005 and 2008 (Wind Power—Wikipedia, July 2009). The current annual increase in wind power generation is estimated to be around 31% and it would stabilize to an annual growth rate of 15—16% in the year 2013.

The US is installing 2000 to 3000 megawatts of new wind power recent years with a total capacity of 25,200 megawatts as of 2008. The value of global market for wind turbines (Composites Technology, Dec 2005) is predicted to grow from the current $9.4 billion to $935 billion US dollars in year 2020. Researchers in the US are working toward producing quality turbine blades at minimal cost to reduce power generation costs. In lieu of employing standard composite three-blade rotor mounted turbines, on a horizontally oriented turbine driveshaft, vertical axis turbines are being developed in the UK.

Manufacturing composite blades of lighter weight and greater length will be the primary focus for turbine manufacturers because of certain economic advantages (see, e.g., the scale of LM Glasfiber's 54P/177 ft blade in Figure 33.20). The more efficient windmill energy operations will be derived through longer blade lengths which will be in the range of 200—250 ft, with a root chord width of 14—18 ft. However, one should note that the swept area increases by about the square of the blade length while the self-weight increases approximately by an exponent of 2.5 of the blade length. Hence the real challenge for designers while developing a bigger blade is to strike a balance between self-weight, swept area, and production costs along with the durability of the blade.

Some development work on hybrid blades using glass and carbon fibers is moving forward to control self-weight while enhancing swept area. Typical long blade (185—210 ft) weights range from 30,000 lbs to 40,000 lbs. The depth of

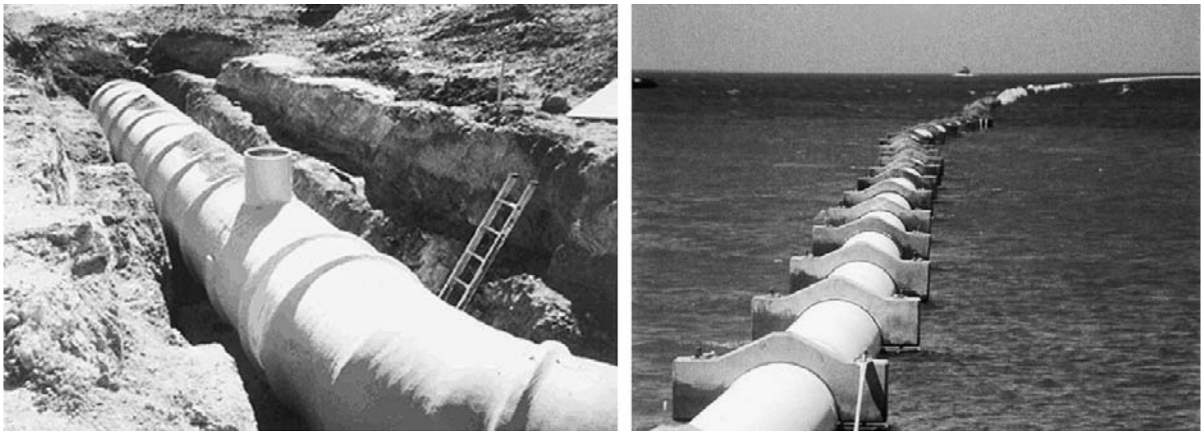

Figure 33.19 Pipelines. Left: FRP pipes for sewerage works, Bolivar Project, Australia; Right: Sea water in-take pipes (www.reinforcedplastics.com).

Figure 33.20 LM Glasfiber's 54P Blade. *(Source: Mason, 2004).*

analysis and design, and even manufacturing procedures are intricate and complex, and require greater understanding of composite material behavior before embarking on any major "leap-frog" technologies for longer size blades. For example, with increasing blade lengths, high amplitude fatigue resistance of hybrid composites becomes a critical factor in design and the durability of the FRP composite blades. The real challenge is to improve the interlaminar shear transfer capability of resins along with improvements in fabric architectures including 3-D stitching so that delamination of the blade can be avoided. Figure 33.21 shows a finite element modeling analysis of the aerodyn 185 ft blade identifying axial strains. Recent advances in urethane technologies coupled with hybrid fabrics with three-dimensional stitching patterns may provide partial answers for future advances. However, one must keep in mind that cost of blades in a windmill system is only around 10% of the total initial cost and in-depth structural optimization of blade alone may not lead to proportionate savings in the overall cost of a windmill system. Therefore, cost-effective solutions have to be found even for windmill towers using composite or hybrid material and structural systems.

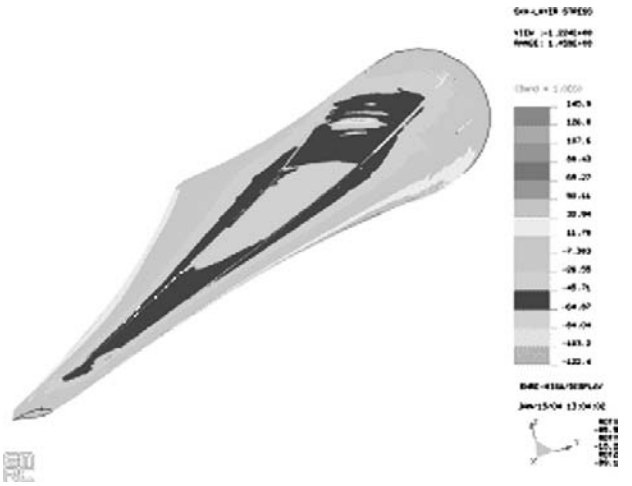

Figure 33.21 Finite Element Analysis of the Aerodyn 56.5 m Blade. *(Source: Mason, 2004).*

Figure 33.22 Armored HMMWV deployed in Iraq. *(Source: Lane [41]).*

33.2.4.4 Blast and fire-resistant structures

Recent terrorist activities spurred a large-scale implementation of fiber composite body armor systems for military and civilian applications [41]. Fiber/fabric composite body armor is designed for an armored vehicle deployed in Iraq as shown in Figure 33.22. Similarly, composite wrapped columns and masonry walls have been designed to resist blast forces and fires by reinforcing the walls with glass or carbon fabric with polymer binder (Figure 33.23).

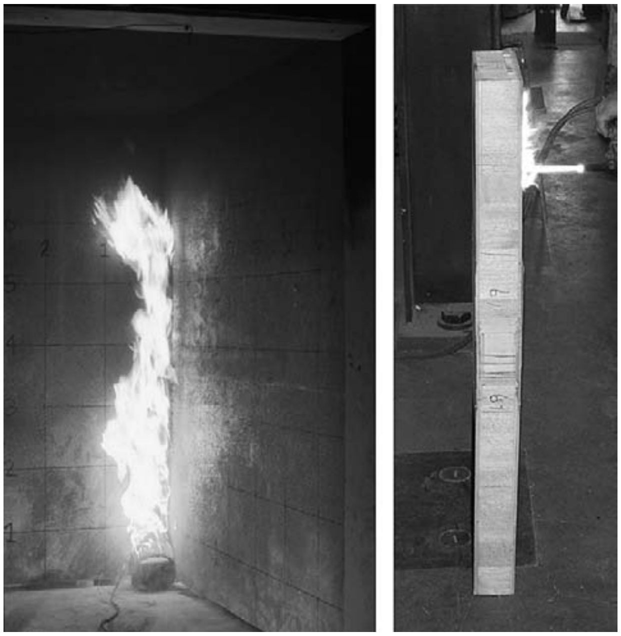

Figure 33.23 Fire testing of FRP composites.

A glass composite panel with fire-retardant resin and wood core was developed for a coal mine "Safe Room" system as a rescue chamber for miners trapped underground [25]. In addition to using fire-retardant resins and intumescent mats integrated into the structural composite reinforcements, the coal mine "Safe Room" system will be coated with intumescent latex, a thin passive fire barrier to further enhance its fire-rating capacity.

Other fibers developed from para-aramid are being evaluated for blast-resistant panel systems because of their high tensile strength. Another notable fiber composite wall panel application to minimize blast effects is an engineered polyurethane foam panel (developed by General Plastics MFG, Tacoma, Washington) tied with adhesive joints and aramid rovings because of high energy absorption of the foam.

33.2.4.5 Energy efficient composite buildings

Housing traditionally has been built from materials such as masonry, timber, steel, and concrete. Fiber-reinforced polymer (FRP) composites were initially used for small components, such as frames for windows, canopies, doors, and other decorative features but, more recently, also for complete buildings to enhance their energy efficiency.

FRP composites have been used to meet some niche applications. For example, Composite Building Systems Inc. [26] (CBS) is manufacturing dome-shaped FRP composite houses as disaster-resistant shelters, because the following features of modular FRP structure make it uniquely suited for such applications: (1) no maintenance (no painting and do not deteriorate from weather, rot, or insect infestation); (2) lower heating and cooling cost (the modular FRP panels have built-in insulations, and the dome shape further increases energy efficiency); (3) high structural strength (the curved surface of the panels reduces wind resistance, enabling the house to withstand hurricanes); (4) quick construction (modular design for ease of erection); (5) earthquake resistance (the FRP panels flex instead of breaking); (6) water resistance (completely sealed from the ground up); (7) portability (an FRP house can be easily disassembled and relocated to a new site).

CBS offers interlocking double FRP composite panels containing thermal barrier inlays (polyurethane foam insulation and optional foil sandwiched between composite skins) and multiple floor plans using modular components. In addition to shelter applications for disaster relief, these systems are applicable for grain storage, fuel storage, cistern and septic tank manufacture, jail facilities, cold storage facilities, military barracks, school buildings, industrial factory and warehouse buildings, large dormitory settings for workers in remote locations, greenhouses, etc.

CFC-WVU designed, manufactured, and constructed the first FRP building in 1995 in collaboration with WV Department of Transportation. A recent inspection revealed that the building has been performing excellently for the past 15 years and looks new, as shown in Figure 33.24.

Currently, FRP modular housing is also being developed for dwellings. FRP composites offer many advantages over traditional materials and lend themselves to prefabricated off-site construction. The prefabrication of wall and floor modules leads to dimensionally accurate, consistent, and reliable quality products in a cost-effective manner and can be assembled at any location and in any climate. This methodology has great potential for the housing market where there is an acute shortage of affordable dwellings and increased pressure to develop sites for residential purposes. FRP modular housing construction approach could be a key to providing quality housing for untold

Figure 33.24 Multi-purpose FRP building, Weston, WV, constructed with modular FRP panels, Nov 1995. *(photos taken on Aug 27, 2009)*

Figure 33.25 FRP composite home being erected at BRP Inc. manufacturing facility.

millions of people who currently live in extreme poverty throughout the world.

FRP modular homes can be installed for permanent, temporary, and semi-temporary purposes. Figure 33.25 shows an FRP composite home being erected at BRP Inc. manufacturing facility. Their modular designs are suitable for speedy construction, as they are lightweight (portable), easy to erect, maintenance free, weather proof, corrosion resistant, extendable, and durable. The panels can be manufactured to be fire retardant, energy efficient (built-in insulation for temperature control) and even integrated with many green concepts for future sustainable buildings, including Trombe wall construction, photovoltaic solar panels, smart windows, natural microclimate creation and use of bio-based resin/fiber composites. Moreover, modular housing can be made in aesthetically pleasing colors and patterns as per customer requirements. The Constructed Facilities Center has been working with Quality Housing Inc. and others to advance the state-of-the-art of modular construction.

33.2.4.6 Platforms

Some of the more exotic applications of FRP composites are as follows: ship-to-shore bridges, fenders, docking systems, aircraft carrier decks, boat/ship hulls, retaining walls, crosswalks, moorings, cables, piles, piers, underwater pipes, railings, ladders, and many others [38,39,42].

According to a survey sponsored by the Office of Naval Research, USDOD, 62% of 11,045 marinas have construction activities, annually costing approximately $100 million for materials. Wood remains the dominant material, while use of composites is about 2% over the past 5 years [27]. An industry study reports that the US decking industry will reach a market potential of $3.4 billion with 5.1 billion board feet of consumption (see Figure 33.26). Such high levels of

Figure 33.26 Marina with composite decking. US Marina decking industry will reach a market of 5.1 billion board feet by 2005. *(Source: www.mbtoday.com).*

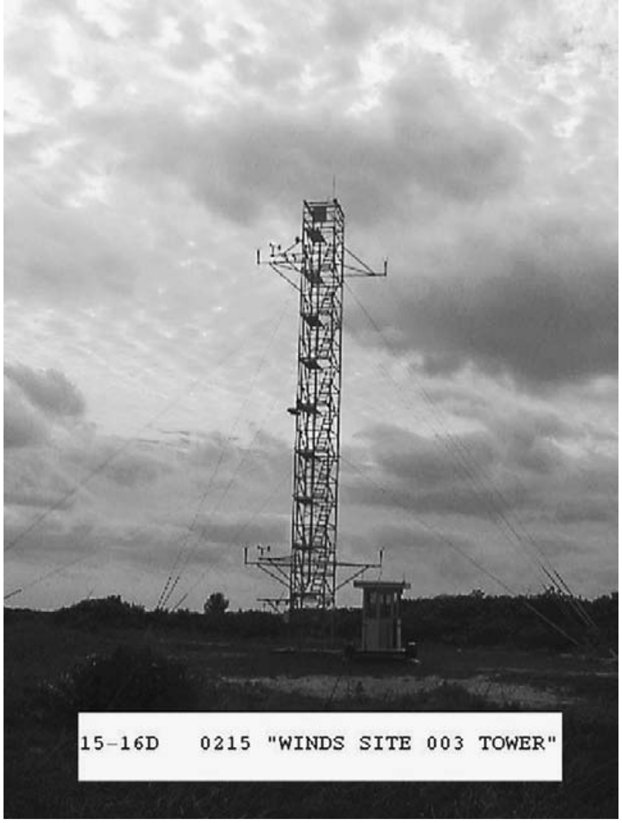

Figure 33.27 Light duty composite tower 215 site 003. *(Source: Air Force, SDR [35]).*

demand are driven by repair and improvement needs as well as the addition of new decks to existing marinas [28,44].

33.2.4.7 Air force radar towers

The US Air Force has thousands of radar towers protecting its assets [29,46], and they are corroding badly because of the primary structural material (steel). Composite tubing products for such tall, narrow structures (Figure 33.27) such as Air Force towers can be mass-manufactured using filament winding, pultrusion, or other techniques such as centrifugal casting. Filament winding is a process where continuous fiberglass rovings are saturated with catalyzed liquid resin and helically wound around a polished steel mandrel. The resin is then cured at elevated temperatures, and the finished product is removed from the mandrel. Pultrusion is a highly automated labor-efficient process for manufacturing FRP shapes and is able to offer higher fiber-to-resin ratio and higher strength parts at a higher production rate, which translates to lower initial costs.

When using pultruded parts in long or tall structures such as monopole towers, an excess amount of material or cross bracing must be used to compensate for the property reductions compared to filament wound composite parts. A low-cost structural composite tubing product is required with significantly improved stiffness and reduced maintenance costs, thus enabling the use of efficient structural system with guyed cables.

Figure 33.28 Bonding issue of wearing surface onto FRP decks.

33.3 Durability of Polymer Composites

Conventional wisdom on the durability of polymer composites is that FRP composite products can be in-service for a very long time unlike steel or concrete. FRP composite materials can provide a longer service life because of lower thermal effects, better mechanical performance, and higher damage tolerance than conventional materials provided they are tailor-made with a high degree of precision in design, manufacture, and assemblage. A lack of understanding of the durability and performance of FRP composite materials under thermo-mechanical loads compared to that of conventional construction materials is a technical obstacle for their high volume usage [30,31].

The aging/durability of a material or structure is identified through its resistance to cracking, oxidation, delamination, and chemical degradation under environmental and/or mechanical loads. Actual data on aging/durability is not well documented, and it is difficult to even access the existing data. Hence, unsubstantiated safety factors have been used in design. These factors have the potential for under-designing and may even lead to catastrophic failures [9]. Figure 33.28 shows a debonding issue of wearing surface on FRP bridge decks, while Figure 33.29 exhibits the severe material degradation under heat/fire for a railroad tie made of reinforced thermoplastic resin system.

The aging response, including durability in polymer composites without load, can vary significantly under environmental fluctuations (no mechanical loading) and it is identified in terms of chemical and physical aging. Chemical aging involves changes in the molecular structure of a polymer such as chain scission, oxidation, or crosslinking. On the

Figure 33.29 Fire of railroad tie made of reinforced thermoplastic.

other hand, in physical aging macromolecules regroup into a new equilibrium state below the glass transition temperature, T_g, for example due to moisture uptake. The durability of FRP composites depends primarily on the pH level, temperature, creep/relaxation, ultraviolet, and externally induced stress, including thermo-mechanical load fluctuations, otherwise known as fatigue [32]. In terms of the above parameters, fluid sorption in and out of FRP composites under freeze—thaw conditions has the highest influence on thermo-mechanical properties. The sorption behavior of fluid into a polymer composite depends on the following: (1) type, temperature, and concentration of the fluid, (2) applied stress, including hydrostatic pressure, (3) state of the material, including voids, and (4) chemical structure [33]. In addition to chemical and physical aging, mechanical load variations under external loads, including fatigue, can influence the durability of FRP composites. This is especially pronounced when chemical and physical aging responses are synergistically acting with mechanical responses. Therefore, an in-depth understanding on chemical and physical aging is essential to realize a durable FRP composite product. For additional details, refer to a technical paper published by GangaRao and Gupta [34].

33.4 Summary

This chapter enunciates the fiber-reinforced polymer composites that are being applied to civil and military infrastructure and also those applications that could be applied in the future. A number of research, development, and implementation issues have been brought out herein, but many more issues need to be evaluated exhaustively before the products can be implemented with ease and economic viability. For example, the following items require immediate attention: (1) durability of composites under harsh environments, (2) development of manufacturing, design, and construction specifications, (3) monitoring of field responses of FRP structures to establish knock-down factors for design, and (4) arriving at life cycle costs of FRP structures and comparing with those infrastructure systems made of conventional materials such as steel and concrete.

Some of the scientific innovations that require urgent attention in mass-manufacturing and design of FRP composites are as follows: (1) through-the-thickness stitching of fabrics [29,46], (2) development of natural resin systems that are ductile and durable, including nano-additives, (3) optimization of connector systems between components, and (4) advancing manufacturing techniques, including rapid prototyping of components, and sub-systems and finally system integration.

Use of composites to rehabilitate existing infrastructure is not dealt with in this chapter due to space limitations. However, readers must note that great strides are being made in applying polymer composite wraps and laminates to reinforce the infrastructure systems in a cost-effective manner so that hundreds of millions of dollars can be saved through the rehabilitation techniques with a simultaneous reduction of user inconveniences.

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34 The Plastic Piping Industry in North America

Thomas Walsh
Walsh Consulting Services, 11406 Lakeside Place Drive, Houston, Texas 77077, USA

34.1 Introduction

Plastic pipe and fittings have been successfully used for a wide variety of piping applications for over 60 years. There are several commonly used thermoplastic materials depending on the particular piping and/or fittings applications:

- Polyvinyl chloride (PVC)
- High-density polyethylene (HDPE)
- Medium-density polyethylene (MDPE)
- Low-density polyethylene (LDPE)
- Linear low-density polyethylene (LLDPE)
- Chlorinated polyvinyl chloride (CPVC)
- Crosslinked polyethylene (PEX)
- Acrylonitrile butadiene styrene (ABS)
- Polypropylene (PP)

Engineered thermoplastic and fluoropolymer materials used in specialty pipe, tubing, and fittings applications include the following:

- Nylons (PA), including nylon 6,6 (PA-6,6), nylon 6 (PA-6), nylon 11 (PA-11), nylon-12 (PA-12), and polyphthalamide (PPA)
- Fluoropolymers, including polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), ethylene chloro-trifluoroethylene (ECTFE), and perfluoroalkoxy (PFA)
- Polysulfones, including polysulfone (PSU) and polyphenylenesulfone (PPSU)
- Polyphenylenesulfide (PPS)

Thermosetting materials used in pipe and fittings applications include the following:

- Epoxies
- Polyesters
- Vinyl esters
- Polyurethanes

The major thermoplastic piping materials used are PVC and HDPE. These materials constitute more than 90% of the total market. The demand for plastic pipe in North America has shown excellent growth over the past 40 years. Common applications for PVC pipe include potable water pipe, sanitary and storm sewer piping, drain-waste-and-vent (DWV) plumbing pipe, and electrical and telecommunications conduit. PE piping dominates land highway drainage piping, gas distribution piping, oil and gas production piping, mining piping, telecommunications conduit, ground coupled heat pump piping, and dredging and marine applications.

There are several piping products that are currently being used, were commonly used in the past, or are being introduced in North America for hot water piping and for higher temperature industrial applications:

- Crosslinked polyethylene (PEX) pipe
- Chlorinated polyvinyl chloride (CPVC) pipe and fittings
- Polypropylene (PP) pipe and fittings
- Polybutylene (PB) pipe (no longer being made in North America)
- Polyvinylidene fluoride (PVDF) pipe and fittings
- Polytetrafluoroethylene (PTFE) tubing
- Perfluoroalkoxy (PFA) tubing
- Multilayer pipe (PEX-Al-PEX), (PE-AL-PE), (CPVC/Al/CPVC), PE/PA, PEX/EVOH
- Composite piping products (PE-GF), glass reinforced, steel reinforced, and fiber reinforced
- Fiberglass reinforced pipe (FRP)

Thermoplastic materials commonly used for higher temperature pipe and fitting products include:

- Chlorinated polyvinyl chloride (CPVC)
- Crosslinked polyethylene (PEX) (extrusion crosslinked or post extrusion crosslinked)
- Polypropylene (PP)
- Polybutylene (PB) (this is no longer used in North America)

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- Fluoropolymers, including polyvinylidene fluoride (PVDF), polytetrafluoroethylene (PTFE), and perfluoroalkoxy (PFA)
- Engineering plastics, including polysulfones, polysulfone (PSU) and polyphenylenesulfone (PPSU) and polyphenylene sulfides (PPS).

34.2 Thermoplastic Pipe and Fittings Materials

34.2.1 Polyvinylchloride (PVC) Materials

Of all thermoplastics, PVC is by far the most widely used in piping applications. Overall, it has excellent basic properties, may be easily processed, and is very economic in cost. PVC is a thermally sensitive thermoplastic to which various ingredients must be added to stabilize it and allow it to be processed. Heat stabilizers are required as well as lubricants, fillers, processing aids, pigments, and impact modifiers. Unplasticized polyvinyl chloride (U-PVC) has excellent chemical resistance, which, combined with the smooth surfaces of the interior pipe wall, minimizes scaling and gives excellent flow characteristics, which remain constant during the pipe's service life. PVC is suitable for conveying potable water due to its low taste and odor properties. PVC pipe has good abrasion resistance, weathering qualities, and good thermal and electrical insulation. PVC is lightweight, easy to handle, and can be installed without great effort. PVC also has very good resistance to weathering, including exposure to ultraviolet radiation in sunlight. Un-plasticized polyvinyl chloride (U-PVC) is quite rigid and is produced in individual lengths of pipe. It is not flexible and is not provided in coils.

34.2.2 Polyethylene (PE) Materials

Polyethylene is the second most widely used thermoplastic in piping applications. Similar to PVC, it has excellent basic properties, may be easily processed, and is economic in cost. PE is more thermally stable than the PVC, but does require stabilizers to prevent damage during processing and in service. Antioxidants and heat stabilizers are required during processing and pigments, and carbon black and/or light stabilizers are needed for weathering protection in storage and in service aboveground. Polyethylene has excellent chemical resistance to both acidic and basic chemicals as well as organic chemicals. PE is much more flexible than PVC and in smaller diameter piping can be coiled. This allows long continuous installations with significantly fewer joints. PE pipe is also suitable for the transport of potable water due to its low taste and odor properties. PE pipe has been very successful in use in oil and gas production piping and in natural gas distribution systems. Historically, PE pipe has also been successful in marine applications, including both submerged pressure pipelines and intake and outfall lines. PE pipe has been used in marine pipeline applications for effluent outfall lines, river and lake crossing pipelines, and fresh water and salt water intake lines since the 1960s.

34.3 New Developments in Polyethylene Materials for Piping

In the late 1980s, new types of polyethylene piping materials were introduced in Europe. These are the bimodal molecular weight distribution PE piping grades. These materials have revolutionized the global PE piping industry and over the past 20 years have penetrated extensively in Europe and the rest of the world, but only to a limited degree in North America. The reasons for this are that under the International Organization for Standardization (ISO) evaluation system, these materials are rated as PE100 cell class materials and they have a 25% strength advantage over the earlier PE80 materials. Because of this advantage in strength and the resulting ability to reduce the wall thickness for equivalent pressure capability, they have gradually displaced the older materials in many applications globally. However, under earlier versions of American Society for Testing and Materials (ASTM) and Canadian Standards Association (CSA) rating systems for polyethylene piping materials, these new grades did not have the same advantages. Both the existing monomodal and the new bimodal HDPE pipe materials fell into the same cell class for their long-term hydrostatic strength, which was an hydrostatic design basis (HDB) of 1600 psi. In order to recognize the superior properties of these newer materials, the US industry has changed the classification system and justified the use of a new safety factor for design and service with these materials in water applications (0.63 vs. 0.50). This has resulted in the hydrostatic design strength (HDS) value changing from 800 psi for water at 73°F for the older PE3408 materials, to 1000 psi for water at 73°F for these classification 4710 HDPE materials. This has been accomplished by replacing the 0.50 safety factor with a 0.63 safety factor.

Recently, polyethylene raised temperature (PE-RT), which is an established hot water piping material in Europe, has been introduced into the North American market. Also, multilayer specialty piping products using PE-RT with various barrier and protective layers have been introduced.

34.4 Chlorinated Polyvinyl chloride (CPVC) Materials

Chlorinated polyvinyl chloride is a direct derivative of polyvinyl chloride (PVC) materials. CPVC materials are made by reacting chlorine with PVC in a secondary reaction process after PVC polymerization (post-polymerization).

The chlorine content by weight of CPVC is increased by this addition of chlorine. Homopolymer PVC grades typically contain 56% chlorine by weight. CPVC contains about 67% chlorine by weight. CPVC materials offer a higher temperature service range. The increase in chlorine content increases the heat deflection temperature at 264 psi from 155°F (68°C) to 218°F (103°C). The chemical resistance of CPVC is similar to or better than that of PVC.

With a maximum service temperature of approximately 210°F, CPVC is an excellent material for hot corrosive liquids and similar applications above the temperature range of PVC. CPVC materials can also be glued with solvent cements or thermally welded. The physical properties at 73°F (23°C) are very similar to that of PVC. CPVC is not recommended for use with chlorinated or aromatic hydrocarbons, and esters or polar solvents such as ketones. Cementing, threading, or flanging can join CPVC.

The use of CPVC in industrial piping applications is widespread and offers several advantages over many traditional piping materials. CPVC piping systems and related components offer exceptional corrosion and chemical resistance, good physical and mechanical properties for many harsh environments, ease of handling, simple reliable joining methods, and long service life. The most beneficial property of CPVC is its resistance to heat while maintaining these other important features. The maximum service temperature for most CPVC products is 200°F. In piping systems, this enables operating temperatures up to 60°F higher than PVC piping products, which broadens the application range significantly for many chemical service requirements. Other benefits include increased hanger spacing at elevated temperatures when compared to PVC piping, as well as low flame spread and smoke generation characteristics.

CPVC pipe has been very successful in industrial applications due to its excellent chemical resistance, and its ability to transport hot fluids. CPVC is used for chemical process piping systems, pulp and paper process piping systems, food processing pipe, and water and sewage treatment piping. In the past 10 years, CPVC piping has begun to penetrate the residential hot and cold-water plumbing markets as well as the industrial and residential sprinkler pipe markets in the US. There has also been some penetration of the hydronic heating market, but it appears that this will be limited due to competition from crosslinked polyethylene piping systems. Pipe, fittings, valves, and pumps represent about 95% of the identified applications of CPVC. CPVC sprinkler pipe has been successfully used for over 25 years in commercial and residential buildings.

34.5 Crosslinked Polythylene (PEX) Materials

Crosslinked polyethylene pipe and tubing have tremendously increased in usage in North America over the past 15 years. This has been due in part to the withdrawal of polybutylene piping materials, which had achieved significant market penetration over a 25-year period, and also due to growth in demand in new applications. Demand growth for in-floor radiant heating and hydronic heating applications has made a major contribution to the rapid growth of PEX pipe and tubing. For hot and cold plumbing pipe and tubing, the maximum service operating temperature is 180°F and the maximum pressure is 100 psi. For radiant in-floor heating systems, the maximum in-service operating temperatures are in the range of 100°F to 120°F and the maximum service pressure is 20 psi. For radiant panel baseboard heating applications, the maximum in-service operating temperatures are in the range of 180°F to 200°F and the maximum service pressure is 20 psi. Crosslinked polyethylene pipe and tubing have also been employed in low temperature liquid cooling systems such as those used in electrical power conversion units.

34.6 Crosslinking Technologies

There are three main crosslinking chemical methods: azo, peroxide, and silane crosslinking. There is also physical or radiation crosslinking, which involves either exposure to nuclear radiation or electron beams to generate free radical species for the crosslinking reactions. All these methods produce a crosslinked polyethylene, whose molecular chains are chemically linked together and physically or mechanically intertwined (tangled). The benefits provided in the final crosslinked products include improved elevated temperature performance, improved resistance to stress cracking, improved chemical resistance, reduced deformation under load (creep), increased abrasion resistance, and improved impact properties.

34.7 Polypropylene (PP) Materials

Polypropylene is a crystalline polymer with a melting point of 330°F (165°C). It is the lightest of the most common thermoplastics with a specific gravity of 0.90 g/cc if unmodified. The key properties in addition to this are its high heat resistance, stiffness, and chemical resistance. It may be useable for low stress structural applications up to 275°F (135°C), but for piping applications, it has an upper limit of 212°F (100°C). Although excellent in chemical resistance with respect to handling caustics, solvents, acids, and other organic chemicals, it is not recommended for use with oxidizing type acids, detergents, low-boiling hydrocarbons, alcohols, and some chlorinated organic materials. Un-pigmented, natural polypropylene is degraded by UV light unless it is shielded, pigmented, or otherwise stabilized. The heat deflection temperature of PP ranges from 195°F (91°C) to 240°F (116°C), which is higher than that of other commonly used piping plastics.

In some cases, polypropylene is actually a combination of PE and PP, which is accomplished during the second stage of polymerization. This is called impact copolymer PP, and gives the plastic much less brittle characteristics than homopolymer PP, which contains no PE molecules. Impact copolymer PP withstands impact forces down to −20°F (−29°C) whereas homopolymer PP is very brittle below 40°F (4°C). While PP has a useful temperature range from −20°F to a maximum 180°F, at this higher temperature, PP is recommended for use only with water or drainage. Polypropylene pipe is resistant to organic solvents, acids, and alkalis. It is not recommended for oxidizing acids, chlorinated hydrocarbons, or aromatic chemicals. PP pipe can be joined by fusion welding, threading, or flanging.

34.8 Polybutylene (PB) Materials

Polybutylene base polymers are semi-crystalline isotactic thermoplastic polyolefins. They are derived from the polymerization of butene-1 monomer with or without other alpha-olefin monomers utilizing Ziegler-Natta type of catalyst. Their unique crystallization behavior means longer open times of adhesive and sealant formulations compared to other commonly used polymers such as polyethylene and ethylene-vinyl acetate copolymer (EVA). Polybutylene (PB), also called polybutene-1 or poly-1-butene, is different from polybutenes or polyisobutylenes (PIB). PIB are amorphous and rubbery, and come in the form of a viscous liquid or big hard block (6 in. in length and width or could be higher). PB base polymers are supplied in the form of small pellets (about 1/4 in. in diameter) or nibs.

Polybutylene piping was used extensively in the manufacture of water supply piping from 1978 until 1995. Due to the low cost of the material and the ease of installation, polybutylene piping systems were viewed as “the pipe of the future” and were used as a substitute for traditional copper piping. It is most commonly found in the “Sun Belt,” where residential construction was heavy through the 1980s and the early-to-mid 1990s, but it is also very common in the Mid Atlantic and Northwest Pacific states. PB piping systems were used for underground water mains and as interior hot and cold water distribution piping. Industry experts believe it was installed in at least 6 million homes, and some experts indicate it may have been used in as many as 10 million homes. Most probably, the piping was installed in about one in every four or five homes built during the years in which the pipe was manufactured. PB plumbing pipe is a flexible, easy-to-cut, gray, plastic pipe with joints secured with either epoxy or insert fittings and metal crimp rings. PB was less expensive in material cost and easier to install than traditional copper plumbing and was widely used.

It is generally accepted that oxidants in the water supplies such as chlorine and chloramine reacted with the polybutylene piping and acetal fittings causing them to scale and flake and become brittle. Micro-fractures resulted, and the basic structural integrity of the system failed. Such failures occurred without warning, often causing significant damage to buildings and personal property. It is believed that other factors such as improper installations may also have contributed to the failure of polybutylene systems.

34.9 Acrylonitrile Butadiene Styrene (ABS) Materials

Acrylonitrile butadiene styrene (ABS) is a lightweight thermoplastic material that is used to make DWV plumbing pipe and fittings. ABS piping systems are lighter, easier, and less expensive to install than metal DWV piping. ABS pipe and fittings are also resistant to corrosion. ABS pressure pipe is also available for specialized applications.

34.10 Nylon (PA) Materials

Nylon-11 (PA-11) and Nylon-12 (PA-12) have been introduced for use in gas distribution piping. PA-11 is also used in multilayer steel reinforced offshore risers and flowlines for the production of deep water oil and gas deposits. Nylon-6 (PA-6) is being used as a permeation barrier layer in multilayer PE/PA piping for crude oil and gas production piping. Nylon 6-12 is just now being introduced for piping applications.

34.11 Fluoropolymer Materials

Polytetrafluoroethylene (PTFE) is made in larger amounts than any other fluoropolymer. It is resistant to practically every known chemical or solvent. In addition, it has the highest useful temperature limit of all commercially available plastics. Fabricated PTFE products have a melting point of 620°F (327°C) and a useful temperature range of −436°F (−260°C) to 500°F (260°C). PTFE grades used in plastics applications have a very high molecular weight, which results in a melt viscosity much higher than what is acceptable for conventional thermoplastic processes. As a result, the usual processing techniques are not possible. PTFE resin is pressed into useful shapes under high pressure at room temperature and then heated to 700°F (371°C) to complete the molding (sintering) process and adjust the crystalline content. Ram extrusion of granular PTFE resin is used to make tubing and other continuous shapes. PTFE is used to make tubing products.

Polyvinylidene Fluoride (PVDF) is a thermoplastic fluoropolymer with a melting point of 352°F (178°C) and a wide usage range from −40°F (−40°C) to 302°F (150°C). It has a very linear chemical structure, and it is similar to PTFE with the exception of not being fully fluorinated. Its drawbacks in the area of chemical resistance include unsuitability with strong alkalis, fuming acids, polar solvents, amines, ketones, and esters. It has a high tensile strength as well as a high heat deflection temperature. It is readily weldable, offers high purity qualities, and is resistant to permeation of gases. PDVF piping is widely used in the chemical process industry and also in the semiconductor manufacturing industry where ultra-pure water is required. PVDF corrugated duct and conduit are used for its flame-retardant properties in plenum space applications to protect telecommunication cables. PVDF is also used in multilayer steel reinforced offshore risers and flowlines for the production of deep water oil and gas deposits.

One of the disadvantages of PTFE is that it is not melt-processable. In 1960, DuPont introduced fluorinated ethylene propylene (FEP), which was chiefly designed to provide melt processability. In 1972, DuPont introduced another fully fluorinated polymer, Perfluoroalkoxy (PFA), which is also melt-processable, with better melt flow and molding properties than FEP. Although PFA has somewhat better physical and mechanical properties than FEP above 3000°F (1490°C), it lacks the physical strength of PTFE at elevated temperatures and must be reinforced or designed with thickness to compensate for its softness. The heat deflection temperature of PFA is the lowest of all fluoropolymers. PFA is used to make tubing products.

Ethylene chloro-trifluoroethylene (ECTFE) is a partially fluorinated melt-processable polymer that is intermediate in performance between fully fluorinated polymers (PTFE) and PVDF. It has excellent chemical resistance to oxidizing chemicals and is used in chemical piping applications for severe environments.

34.12 Engineering Plastic Materials

Polyoxymethylene (POM) or acetal was used for hot and cold water plumbing fittings in conjunction with polybutylene pipe and tubing. Disinfecting oxidizing chemicals in potable water supplies such as chlorine and chloramine reacted with the acetal fittings and caused them to scale and flake and become brittle. Micro-fractures resulted, and the basic structural integrity of the fittings failed and caused leaks. There was a class action lawsuit and both polybutylene and acetal were withdrawn from this application.

Sulfone polymers have gradually replaced brass and acetal for fittings for hot water applications over the past 15 years. Sulfone polymers have low shrinkage and can be injection molded to close tolerances and exhibit excellent creep resistance under load and at higher temperatures typical of hot water service conditions. Combined with this, their excellent resistance to oxidation and to chlorine and chlorinated chemicals in hot water has facilitated their acceptance in plumbing applications. Polyetheretherketone (PEEK) and Polyphenylene sulfide (PPS) polymers have been introduced for oil and gas production piping applications both for onshore and offshore use.

34.13 Mulitlayer Piping Products

Aluminum-plastic composite water piping is made of an aluminum tube that is laminated to interior and exterior layers of plastic. It provides the advantages of both plastic and aluminum such as light weight, flexibility, strength, and corrosion resistance. Brass fittings, tees, elbows, and couplings are used to complete the system. In addition to domestic water supply systems, aluminum-plastic composite piping can be used for under-floor heating, ice melt systems in sidewalks and driveways, air conditioning systems, geothermal heat pumps, and compressed air distribution. Multilayer constructions include polyethylene-aluminum (PE-AL-PE), crosslinked polyethylene-aluminum (PEX-AL-PEX), raised temperature polyethylene-aluminum (PE-RT-AL-PE-RT), and most recently chlorinated polyvinylchloride-aluminum (CPVC-AL-CPVC). Polyethylene-nylon-6 (PE/PA) multilayer piping is being used for oil and gas production piping.

Multilayer flexible steel pipes with polyethylene inner and outer layers (PE-Steel-PE) are used for oil and gas production piping as well as transmission piping. These are piping products produced by winding interleaved steel strips around a thermoplastic inner liner and then applying an external thermoplastic layer using crosshead extrusion. These pipes range from 2 to 6 in. in diameter and are delivered in large coils. Steel mechanical couplings are used to connect the individual strings of piping.

34.14 Composite Piping Products

Multilayer glass fiber, carbon fiber, aramid fiber, and steel reinforced composite thermoplastic piping products have been in service for the past 15 years for oil and gas gathering pipelines and are now being introduced for oil and gas transmission pipelines. The reinforced thermoplastic piping (RTP), also referred to as spoolable composites or spoolable piping, consist of thermoplastic pipes or liners with exterior layer(s) of reinforcing materials. There are several variations of the basic structure, including wrappings with continuous glass or carbon fibers, wrappings with and without thermosetting resin matrices encapsulating the fibers, and reinforcing layers of steel strips and high strength thermoplastic or glass fiber fabric wrappings. The thermoplastic pipe or liner is typically between 0.08 and 0.2 in. in wall thickness, and the laminate structure is varied to produce the required strength. Glass and aramid fibers or glass and high strength thermoplastic fabrics are used as the reinforcing layer and wound atop polyethylene liner pipes. Structures made with higher performing thermoplastics such as crosslinked polyethylene (PEX), nylon (PA-11), polyphenylene sulfide (PPS), and polyetherether ketones (PEEK) have also been produced. In general, these products are categorized as "spoolable composite pipes." Steel mechanical couplings are used to connect the individual strings of piping.

More than two million meters of these pipes have been installed in North America over the last 10 years. These pipes currently are manufactured in diameters from 1¼ to 6 in. and pressure ratings from 750 to 3000 psi. The unique feature of this composite pipe is that it is spoolable and comes in coils up to 6 miles in length in the smaller diameters. Also being introduced are larger diameter (from 8 to 24 in.) high strength reinforced thermoplastic composite pipes for pipeline insertion for the rehabilitation of deteriorated oil and gas transmission pipelines.

Composite glass reinforced polyethylene (PE-GF) piping products, where short glass fibers are mixed directly into the polymer matrix in polymer extrudate, are a recent development and have been introduced for large diameter piping applications, up to 120 in. diameters and even larger, in Europe and in North America.

Composite spiral wound steel reinforced drainage pipes have also been developed in Japan and Australia and have been recently introduced in North America. These are used for larger diameter piping products for storm drainage and sanitary sewer piping applications.

34.15 Fiberglass Reinforced Thermoset Piping

Fiberglass reinforced thermoset piping includes Fiberglass Reinforced Plastic (FRP), Glass Reinforced Plastic (GRP), Reinforced Thermosetting Resin Pipe (RTRP), and Reinforced Thermosetting Mortar Pipe (RTMP). Fiberglass reinforced epoxy, polyester, and vinylester pipe is a standard material for transporting corrosive liquids, and is in wide use in the chemical, oil, paper, power, municipal water, sewage, and many other industrial applications. GFRP, or simply fiberglass pipe, is a piping product containing continuous glass fiber reinforcement embedded or encapsulated in a cured thermosetting resin. The composite structure may contain a thermoplastic or thermosetting liner pipe. GFR pipe has excellent chemical resistance both to acidic and basic chemicals as well as crude oil and natural gas. GFR pipe is used in oil and gas production from 2 in. up to 24 in. diameters, at higher pressures (up to and >450 psi), and for higher temperature applications (up to 212°F, 100°C).

High pressure glass fiber reinforced thermoset piping is widely used in oil field applications, mainly for oil and gas gathering pipelines, well casings, and down-hole tubing and for piping for water injection wells. Typically, epoxy thermoset piping is not resistant to acid environments and so has not been widely used in oil and gas gathering pipelines unless in combination with a thermoplastic liner, which provides resistance to corrosive chemicals. GFR piping is also used as acid, alkali, and salt medium transportation pipe in the chemicals process industry as well as for aboveground pipelines such as fire pipelines. GFR liners are also used in production pipelines in very corrosive environments and where the internal protective coating (IPS) has failed.

High pressure thermoset FRP pipe is a type of composite piping where continuous glass fibers and epoxy resin are combined for pipe winding and curing. In the pipe winding process, the glass strands wind continuously around a mandrel at a constant winding angle. The axial strength and hoop strength of the finished pipe are determined by the accuracy of the winding pattern and the winding angle. The curing process is the key technology for higher pressure FRP pipes due to the strength of the interface between the glass fiber and the thermosetting resin.

FRP piping is commonly available in size ranges from 1 to 24 in. diameter and can be fabricated in much larger diameters with the limiting factor being the ability to safely and economically transport the larger pipes. Most FRP piping systems are available in various pressure ratings depending on the application. The two most commonly used joining methods for FRP are adhesive bonding for bell and spigot ends (mostly used on pipe diameters 12 in. and below) and butt-strap adhesive, used mainly for larger diameter or specially formulated piping systems.

34.15.1 Cured-in-Place Piping

Cured-in-place-piping (CIPP) was introduced over 35 years ago for the rehabilitation of deteriorated sanitary sewers. Since that time, CIPP technology has been extended to the rehabilitation of storm sewers, drainage pipes, culverts, sewer laterals, potable water pipe, gas distribution pipe, and oil and gas transmission pipelines. The dominant cured-in-place piping systems employ either a non-woven felt bag or woven polyester fiber hose, impregnated with either an epoxy or vinyl ester thermosetting resin, with an impermeable membrane on one side of the bag or tube. The impregnated liner is either inverted or pulled into the host pipe using cold water. The host pipe must be thoroughly cleaned prior to inserting the liner. The inversion process results in the resin adhering to the walls of the host pipe and the impermeable membrane is on the inside of the new pipe. Once in place, the resin is cured, typically using hot water or steam. The liner can be designed for full structural, semi-structural, or non-structural capabilities. Thermoset resins for potable water applications must meet National Sanitation Foundation and local health authority approvals. The fabric material of the liner can be factory tailored to fit the diameter of the host pipe. Cured-in-place liners can negotiate up to 90^o bends within the host pipe.

34.16 Pipeline and Piping Rehabilitation Technologies

34.16.1 Cured-in-Place-Piping

Cured-in-place-piping (CIPP) was introduced over 35years ago for the rehabilitation of deteriorated sanitary sewers. Since that time, CIPP technology has been extended to the rehabilitation of storm sewers, drainage pipes, culverts, sewer laterals, potable water pipe, gas distribution pipe, and oil and gas transmission pipelines. CIPP is a continuous pipe-within-a-pipe used to rehabilitate pipes ranging in diameter from 3 to 120 in. diameters. CIPP has applications in water, sewer, gas, and chemical pipeline rehabilitation. The dominant cured-in-place lining systems employ either a non-woven felt bag or woven polyester fiber hose, impregnated with either an epoxy or vinyl ester thermosetting resin, with an impermeable membrane on one side of the bag or tube. The impregnated liner is either inverted or pulled into the host pipe using cold water. The host pipe must be thoroughly cleaned prior to inserting the liner. The inversion process results in the resin adhering to the walls of the host pipe and the impermeable membrane is on the inside of the new pipe. Once in place, the resin is cured, typically using hot water or steam. The liner can be designed for full structural, semi-structural, or non-structural capabilities. Thermoset resins for potable water applications must meet National Sanitation Foundation and local health authority approvals. The fabric material of the liner can be factory tailored to fit the diameter of the host pipe. Cured-in-place liners can negotiate up to 90^{o} bends within the host pipe.

Cured-In-Place-Pipe (CIPP) is the most commonly used piping system employed for the rehabilitation of deteriorated sanitary sewer pipelines. Service laterals can be restored internally with robotically controlled cutting devices. The rehabilitated pipe is then inspected by closed-circuit television (CCTV).

34.16.2 Sliplining

Sliplining involves removing a portion of the existing pipeline for access, and then pulling a new pipe into the existing main. Several types of thermoplastic piping products are typically used with HDPE pipe being the most common. One disadvantage to sliplining is the loss of internal diameter and the resulting reduction in hydraulic capacity of the pipeline. Reduced friction factors for thermoplastic piping helps compensate for the reduced inner diameter of the new pipeline. Another disadvantage is the inability to negotiate elbows and bends in the pipeline. At valves, wyes, and elbows the pipeline must be exposed and opened up. Once the host pipe is lined the liner pipe must be corrected and the pipeline reinstated. Service connections must also be exposed to make the connections to the new pipeline.

34.16.3 Fold and Form or Deformed and Reformed Piping

This is a modified version of sliplining, which involves the insertion of a liner pipe where the diameter of the pipe has been partially collapsed into a “C” or “U” shape (folded or deformed shape) and then reeled into a coil. At the insertion site, the folded liner pipe is pulled into the existing deteriorated main and then reformed by a variety of methods (hot water, steam pressure, pulling a reforming plug through the pipe, etc.). Fittings and service connections have to be reinstated after the liner pipe is reformed against the inner surface of the host pipeline. Fold and form systems are available generally in coils in diameters up to 18 in. Most applications are for smaller diameters. Larger diameters can and have been rehabilitated with this technology, but this generally involves fusion welding of individual lengths of pipe and deforming and inserting the folded liner pipe on-site. Both PE and specially formulated PVC pipes have been used in these applications. More recently, this technology has been extended to high strength composite piping for the rehabilitation of deteriorated high pressure oil and natural gas transmission pipelines from 6 in. diameter up to 24 in. diameter.

34.16.4 Tight Fit Piping

Tight fit or roll-down lining systems use the viscoelastic response of thermoplastic materials in compression to reduce the outside diameter of the plastic pipe by a small amount and then sliplining the reduced diameter pipe into a deteriorated main. The inserted liner is then expanded, or allowed to recover its original diameter, to fit tightly against the host pipe. HDPE pipes are predominantly used with this technique.

34.16.5 Formed-in-Place-Liners

Another technology being used for the rehabilitation of both non-pressure and pressure piping systems is the Formed-In-Place-Liner (FIPL). This technology employs a thin thermoplastic liner with protrusions, which is fused into a tube shape, inserted into the host pipe, and inflated against the inside surface of the host pipe with the protrusions pointed outward against the host pipe forming an annular space. Once in place, flowable grout is pumped into the annular space created between the liner and the host pipe by the protrusions on the inside surface of the liner. Once the grout has set, the FIPL provides a semi-structural pipe-within-a-pipe.

34.16.6 Epoxy Spray Coat Lining

The epoxy lining process involves the application of a very thin layer (1mm) of resin and hardener to the host pipe wall. One application method involves computerized machinery with heating devices to achieve the appropriate mixture and temperature of the resin and hardener that is critical for durability and cohesiveness. For internal lining application, the equipment used is similar to that used for cement mortar coatings. After lining, the ends of the pipeline are capped and the resin is allowed to cure. After the curing process is completed (normally 16 hours), the pipe should be inspected visually or by CCTV.

34.16.7 Internal Joint Sealing

An internal joint seal makes the inside surface of leaking pipeline pressure tight. The pipe joints must be cleared of debris and dust and the area on either side of the joint prepared, after which the seal is positioned to span the gap and kept in place by stainless steel retaining bands. The seal's flexibility allows a bottle-tight seal around the entire pipe joint, while its low profile and graded edge permit water to flow without creating turbulence. Internal joint seals are made of ethylene propylene diene monomer (EPDM) synthetic rubbers. To date, this technique has only been applied to larger diameter man-entry pipes. The development of new robotic techniques will allow the extension of this technique to smaller diameter pipes.

34.17 Plastic Pipe and Fittings Manufacturing Processes

34.17.1 Thermoplastic Pipe Manufacturing

Plastics extrusion is generally described as the conversion of plastic powder or pellets or granules into a continuous uniform melt and then forcing this melt through a die, which converts the melt into the desired shape. In the manufacture of thermoplastic pipe products, raw thermoplastic pellets or flake are gravity fed into the extruder from a top mounted hopper. Additives such as process stabilizers, long-term antioxidants, lubricants, colorants, and UV inhibitors are often used and can be mixed in with the plastic material either at the hopper, prior to arriving at the hopper, or as a masterbatch or concentrate using the same plastic.

The mixture enters through the feed throat of the extruder, which is an opening at the top of the extruder near the rear of the barrel and comes into contact with the screw. The rotating screw forces the plastic pellets or mixture of resin and additives forward into and against the heated barrel. The barrel is then heated to the desired melting temperature of the molten plastic. This can range from generally from 390°F (200°C) to 527°F (275°C) depending on the polymer. The plastic pellets or flake are allowed to melt gradually as they are pushed through the barrel. More heat is generated by the mechanical shear contributed by the pressure and friction as the plastic is forced against the barrel by the screw. In most extruders, cooling by fans or chilled water is used to keep the temperature of the melt below a set value. If too much heat is generated, the melted plastic can be degraded.

There are compositional differences between polymers, especially between polyvinyl chloride and chlorinated polyvinyl chloride, which are more susceptible to degradation in processing and require higher levels of processing stabilizers, and polyolefins, which must be stabilized for processing stability as well as for protection into the service environments. There are also differences in material handling as PVC is converted from a reactor flake product, while CPVC, PE, PP, and other materials are converted from pelletized compounds.

In the manufacture of solid wall thermoplastic piping, the downstream sizing, cooling, and takeoff equipment plays a very important role. Generally, the pipe is formed to the specific diameter in the vacuum cooling tank immediately after the extrusion die. The molten parison is pulled by the applied vacuum against a series of sizing sleeves while the parison is being cooled. This sizes the pipe and begins the solidification process. The speed at which the pipe is pulled into the vacuum tank and through any succeeding cooling tanks is a function of the takeoff or puller. This equipment controls the speed of the extrudate as it proceeds through the downstream equipment. Where vacuum sizing is used to form the pipe, this pipe is described as outside diameter controlled pipe.

The manufacture of corrugated piping is typically done with large external molds to which the molten parison is either formed against using air pressure or vacuum. Dual wall corrugated pipe includes a co-extruded smooth inner layer. Triple wall corrugated pipe includes the addition of a smooth outer layer over the corrugations.

Both of these production methods make continuous lengths of piping and smaller diameters are coiled while larger diameter pipes are cut into individual lengths.

Another method of manufacture of solid wall pipe is to extrude and wrap molten sheets or strips of thermoplastic around the outside surface of a tubular mandrel. Where this method is used, this pipe is manufactured to a controlled inside diameter. Continuous fiberglass reinforced thermosetting resin pipe is generally manufactured in this manner. Some types of spiral strip-wound composite piping are manufactured by being formed against the inside surface of a tubular fixture.

34.17.2 Thermoplastic Fittings Manufacturing

Thermoplastic pipe fittings may be injection molded, fabricated, rotomolded, or thermoformed. Injection molded fittings are generally made in sizes through 12 in. nominal diameter. Typical molded fittings are tees, 45^{o} and 90^{o} elbows, reducers, couplings, caps, flange adapters, stub ends, branch saddles, service saddles, and self-tapping saddle tees. Electrofusion couplings and fittings are made either by injection molding or machined from pipe stock. Electrofusion fittings and couplings are made with a coil-like integral heating element incorporated into the fitting. Joining with these fittings uses an electrical fusion device that provides electricity into the heating element, which melts the adjacent thermoplastic material and creates a fusion welded joint.

Larger diameter fittings exceed the capabilities of injection molding and are typically fabricated. Rotomolding is used for the manufacture of polyethylene large diameter (up to 60 in.) and custom fittings for polyethylene corrugated drainage piping applications.

Thermoformed fittings are made by heating a section of the pipe and then using a forming tool to reshape the heated area. Examples of thermoformed fittings are sweep elbows, swaged reducers, and forged stub ends. Some polyethylene corrugated pipe fittings and appurtenances are also thermoformed.

34.17.3 PVC Pipe and Fittings Manufacturing

PVC resin is typically received by the pipe converter in powder form. It is then mixed with stabilizers, lubricants, processing aids, and other additives, and dry blended with intensive mixing to form a compound. PVC pipe extrusion generally uses twin screw extrusion to melt, plasticate, and feed the hot melted plastic into the die. In the die, the molten PVC is formed into a tubular shape. Upon exiting the die, the hot parison is fed into a vacuum sizing and cooling device, where the pipe is squeezed against sizing sleeves that form the parison into a controlled outside diameter pipe. Wall thickness is normally adjusted by controlling the haul-off or line speed, which pulls and stretches the molten parison as it exits the die. The final PVC formed pipe may be drawn through one or more water immersion or water spraying cooling cabinets until the pipe is cooled sufficiently. It is then drawn through the pulling device and fed into a cutting device, which cuts the pipe into specific lengths. A marking device can also be incorporated into the pipe production line to print a line onto the pipe identifying it.

Although several techniques have been developed for sizing tubular products, most pipes are produced by vacuum sizing or external sizing tube techniques. Regardless of the sizing technique, the high molecular weight resins give the best pipe performance characteristics. Pressure sizing has been used, but is not very common today.

Both CPVC compound and CPVC resin are provided for conversion into pipe. CPVC pipe production is very similar to PVC pipe production.

Small diameter PVC and CPVC fittings are typically manufactured using injection molding. Larger diameter fittings are fabricated.

34.17.4 PE Pipe and Fittings Manufacturing

PE resin is received not as reactor flake but as pelletized compound whether un-pigmented or pre-pigmented. Generally, it is combined with a color concentrate or masterbatch in the extruder, melted and plasticated, and fed into the die. Similar to PVC, molten PE is shaped into a tubular shape in the die and then fed into a vacuum sizing and cooling cabinet. Smaller diameter flexible pipes may be wound onto coils providing up to several thousand feet of continuous pipe or tubing on each coil. PE pipe up to 6 in. in outside diameter is currently being coiled. Small diameter PE fittings and couplings are typically manufactured using injection molding. Larger diameter fittings are fabricated.

34.17.5 PEX Pipe Manufacturing

34.17.5.1 AZO crosslinking

In AZO crosslinking, polyethylene resin is mixed with an organic AZO chemical (i.e., a chemical compound containing the structure $-N{=}N-$) and then extruded into tubing at a temperature below the temperature at which the AZO compound will undergo decomposition. The extruded tubing is placed in a salt bath and raised in temperature until the AZO compound reaches the point where it decomposes and forms two free radical species and a nitrogen molecule. The free radical species thus formed abstract hydrogen atoms from the backbone of the polyethylene molecule and initiate the crosslinking reactions. A relatively high temperature is required to initiate the decomposition of the AZO chemical and start the crosslinking reactions. AZO crosslinking is not commonly used for the production of PEX pipe and tubing.

34.17.5.2 Peroxide crosslinking

In the Engel process, polyethylene base resin along with antioxidants and other additives is mixed with an organic peroxide additive and fed into a chamber where a reciprocating piston generates pressure in excess of 29,000 psi (2000 bar). This results in an almost instantaneous rise in temperature sufficient to melt the polyethylene. Frictional heating in the die provides further heating as the sintered polymer mass is forced along the mandrel. The Engel process is essentially a sintering process with the crosslinking reaction occurring as the molten polymer is forced through a heated die. In the Engel process, the crosslinking reaction occurs above the melting temperature of the polyethylene. When the polyethylene is in a molten state, the polymer chains are in an amorphous state. It is argued that with the Engel process, the crosslinking occurs homogeneously distributed throughout the macromolecular structure of the polymer, as the crystalline regions do not exist in the molten state. When crosslinking is conducted at temperatures below the melting point of polyethylene, the formation of microcrystalline regions tends to push the additives and the other foreign materials out of these regions and into the amorphous areas. Thus, the crosslinking reactions occur more in the amorphous regions and much less in the crystalline regions and the crosslinking is not consistent throughout the polyethylene material. The peroxide crosslinking process depends upon the decomposition of the organic peroxide under the influence of heat to generate free radicals, which, in turn, abstracts hydrogen atoms from the backbone of the polyethylene chain.

The Pont-à-Mousson method involves the extrusion of a polyethylene base resin with organic peroxide added. The extrusion process shapes the PEX tubing, and the crosslinking reaction occurs in a fused salt bath at the temperature at which the organic peroxide decomposes. The formed tubing is placed in a fused salt bath at temperatures between 4800°F and 5400°F (2500°C−2800°C). Compared with the Engel process, the Pont-à-Mousson process uses a larger amount of peroxide and initiates the crosslinking reaction at higher temperatures. Profile stability and surface finish are potential problems in the Pont-à-Mousson Method due to the high temperatures involved.

In the Daoplas process, the tubing is extruded first and then subsequently allowed to absorb the peroxide followed by crosslinking under the influence of temperature and pressure.

FASTPEX is a faster Engel manufacturing process for PEX tubing. The normal Engel process is a very slow extrusion process and it has productivity disadvantages compared with the newer silane crosslinking processes. The Engel process is controlled by the very low Melt Flow Rate (MFR) (vs. high MW) of the PE flake used. For the FastPEX process, a new PE base resin with a higher MFR was developed.

34.17.5.3 Silane crosslinking

Dow Chemical developed silane crosslinking in the 1960s and there are two main processes: the Sioplas process, which is a two-step process, and the Monosil process, which is a one-step process. In the Sioplas process, there is an initial reactive compounding step in which an organic silane is grafted onto a polyethylene resin. The compounding extruder is typically a single screw extruder of 25:1 length to diameter ratio and the reactive compounding is conducted at temperatures between 1900°C and 2200°C. A separate catalyst chemical is compounded as a masterbatch onto a separate polyethylene resin. The tubing manufacturer then mixes the silane graft copolymer material with the catalyst copolymer masterbatch in a 95 to 5% ratio and extrudes the tubing product. Typical extrusion temperature conditions range between 190°C and 220°C. The crosslinking or curing is performed on the extruded polyethylene pipe after it has been extruded and coiled. Typically, the pipe is exposed to circulating hot water or low pressure steam to initiate the crosslinking reaction and to carry off any side products of the crosslinking reaction. The pipe may also be cured by exposure to a high moisture environment. The silane crosslinking reaction depends upon moisture exposure and will proceed even without a catalyst. The amount of crosslinking eventually does not depend on the catalyst.

In the Monosil process, the polyethylene resin is mixed with organic peroxide, a liquid silane, and catalyst in the hopper of the extruder. The tubing is then extruded and subsequently cured by exposure to moisture or steam.

There is also the Siloxane process, which simply mixes the various additives (silane chemicals, crosslinking agents, antioxidants, catalyst, colorants, etc.) along with the polyethylene base resin using a high intensity mixer prior to feeding the mixture into the pipe extruder. The Siloxane process requires a special type of extrusion screw.

With silane crosslinking processes, the crosslinking reactions occur while the polymer is in the solid state. As such, the polyethylene material exists with both the crystalline and the amorphous regions being present. There will be differences in the degree of crosslinking occurring in the crystalline regions as compared to the amorphous regions.

34.17.5.4 Radiation crosslinking

Radiation or physical crosslinking processes rely on the use of an external source of high-energy radiation to create intermediate excited transition state species, which can decompose and create hydrogen atoms and organic free radical species. Typically, electromagnetic radiation (γ radiation) from a radioactive isotope or high-energy electrons (β radiation) from an electron accelerator is used to transmit energy into the polyethylene molecular chain. These two different processes are referred to as "Nuclear" and "Electron Beam", respectively. These processes are carried out at room temperature on extruded polyethylene tubing products. The crosslinking reactions tend to be concentrated in the amorphous regions of the polyethylene material and thus the initial degree of crystallinity in the polyethylene tubing is effectively retained.

All these methods produce a crosslinked polyethylene whose molecular chains are chemically linked together as well as being physically or mechanically intertwined (tangled). The benefits provided in the final crosslinked products include improved elevated temperature performance, improved resistance to stress cracking, improved chemical resistance, reduced deformation under load (creep), increased abrasion resistance, and improved impact properties. Because of the different crosslinking methods, there are three different manufacturing technologies commonly used for PEX pipe and tubing.

PEX is not used to manufacture fittings or couplings for PEX pipe and tubing. Fittings and couplings for use in PEX piping systems are typically made of brass or injection molded PVDF or Polysulfone plastics.

34.17.6 Fiberglass Reinforced Thermosetting Pipe Manufacturing

There are two main manufacturing processes for fiberglass reinforced thermoset piping (FRP). Most thermoset piping systems are manufactured using a filament winding process for applying the reinforcement. This process impregnates the glass fibers with the thermosetting resin and applies the wetted fibers to a mandrel or a liner under controlled tension in a predetermined pattern. Multiple layers of fibers may be applied. FRP is also produced by a centrifugal casting process, where glass fiber mat, woven roving, or chopped glass strands are placed in a mold, which is rotated at high speeds. Catalyzed thermosetting resin is injected into the mold wetting out the reinforcing materials. Fittings are manufactured using compression molding, filament winding, spray-up, contact molding, and mitered processes. Compression molding is typically used for the smaller diameter fittings and filament winding is used for larger fittings, generally 8–16 in. diameter (200–400 mm). The spray-up, contact molding, and mitered processes are used for complex or custom fittings. The mitered manufacturing process is more commonly used for on-site modifications.

34.18 Long-Term Strength Testing of Thermoplastic Piping Materials

In order to design a thermoplastic material for piping applications, the long-term strength of the particular material needs to be estimated. This is necessary because thermoplastic materials demonstrate time-dependent material properties due to their linear viscoelastic responses. To properly design using such materials and to ensure adequate service life for the plastic piping products, some type of long-term testing protocol must be used. This testing protocol along with some method of analysis of the resulting data must allow a projection of the estimated long-term strength at or near the projected service life limits required for the particular application. For pressure piping applications with thermoplastic piping materials, there are two similar but differing analysis methods that have been developed and modified over the past 50 years. These are the American Society for Testing and Materials (ASTM) D2837, "Standard Test Method for Obtaining the Hydrostatic Design Basis for Thermoplastic Pipe Materials," and the International Organization for Standards (ISO) Technical Report TR9080, "Thermoplastics Pipes for the Transport of Fluids – Methods of Extrapolation of Hydrostatic Stress Rupture Data to Determine the Long-Term Hydrostatic Strength of Thermoplastic Pipe Materials." Both of these documents set out analysis protocols for the development of long-term projections for test data developed by the stress rupture testing of specimens of thermoplastic piping.

The commonly used thermoplastic piping materials are viscoelastic materials and they demonstrate time-dependent physical properties. These materials include unplasticized polyvinyl chloride (u-PVC) and polyethylene (PE), as well as the more specialized thermoplastic piping materials, chlorinated polyvinyl chloride (CPVC), polypropylene (PP), crosslinked polyethylene (PEX), acrylonitrile-butadiene-styrene (ABS), and the various fluoropolymers (polyvinylidene fluoride (PVDF), tetrafluoroethylene (TFE), ethylene-chloro-trifluoroethylene (ECTFE), and per-fluoroalkoxy (PFA)). Stress rupture test data, when analyzed and plotted on a logarithmic basis, produce a straight-line plot over short testing times. This enables a linear regression analysis to be carried out and the long-term strength of these materials to be projected to 100,000 hours and also to 438,000 hours (50 years).

One of the underlying assumptions of this analysis is that there is only a single failure mechanism occurring. This is generally true of the vinyl polymers and also of the fluoropolymers, but may not be true depending on the basic material properties of polyethylenes, polypropylenes, and crosslinked polyethylenes. Polyolefin materials will exhibit a change in the failure mode from a ductile failure to a brittle or slit type failure depending on the fundamental material properties of the particular grade and on the environmental conditions used for the testing. This transition from ductile to brittle failure mechanisms can vary tremendously. When this change in failure mode occurs, there is a drastic change in the slope of the regression line of the long-term stress rupture testing and the projected long-term strength of the particular material decreases rapidly as the testing is continued in time or if the testing is done at higher temperatures. Figure 34.1 shows an example of hydrostatic stress rupture curves (time to failure vs. hoop stress) for a typical PVC piping compound.

Figure 34.2 shows an example of hydrostatic stress rupture curves (time to failure vs. hoop stress) for a typical polyethylene piping material where elevated temperature testing demonstrates this change in failure mechanism. Figure 34.2 shows the development of a second type of failure mechanism (brittle or slit failures) for the higher temperature testing data (60°C and 80°C). The ambient temperature test data (23°C) will show a similar downturn of the curve as a similar transition from ductile to brittle failure mechanism also occurs. But this does not happen until much longer test times beyond the 10,000 hours typically used to evaluate these materials. Figure 34.2 demonstrates how changes in temperature change the onset of the transition from a ductile failure mechanism to a brittle or slit failure mechanism for polyethylene materials. Changes in the fundamental properties of a polyolefin material such as molecular weight, molecular weight distribution, and density

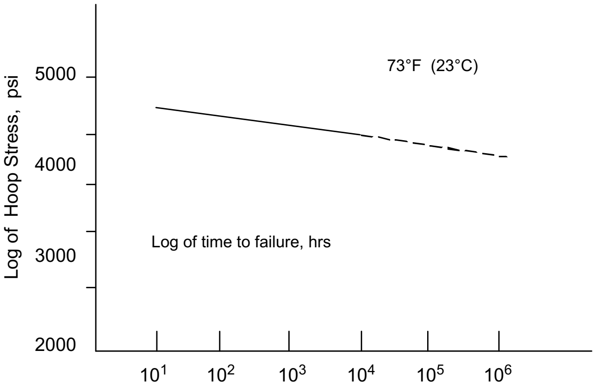

Figure 34.1 Typical stress rupture testing curves for a polyvinylchloride pipe material.

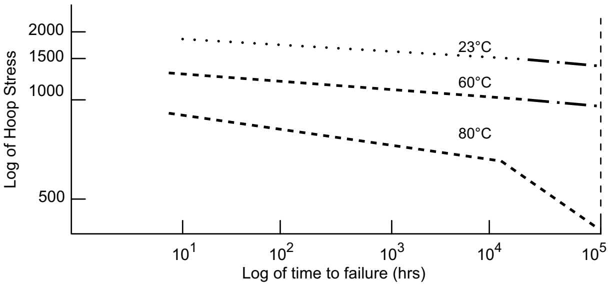

Figure 34.2 Typical stress rupture testing curves for a polyetylene pipe material.

or degree of crystallinity, can also affect the onset of this change.

Changes in the testing temperature causes two distinct changes to the stress rupture testing curves. Again, because of the viscoelastic nature of these materials, as the temperature increases the tensile strength decreases. That is, at higher temperatures, the portion of the curve representing the ductile behavior of the material demonstrates a lower hoop stress value and a lower projected long-term strength.

The change in failure mechanism represents the effects of chemical-oxidative attack on the polymer material. As this is a chemical process, it is dependent on the temperature at which the test is carried out. With very few exceptions, the rate of reaction increases with an increase in the temperature. In 1889, Arrhenius pointed out that a reasonable equation for the variation of the rate constant of a chemical reaction with temperature would be the following:

$$\begin{aligned} \mathrm{d}\ln k &= Ea \\ \mathrm{d}\,T &= RT^2 \end{aligned} \tag{34.1}$$

where k is the rate constant for the reaction; T is the temperature (degrees Kelvin); Ea is the activation energy of the reaction; R is the gas constant; and ln is the natural logarithm.

If Ea is not temperature dependent, Equation (34.1), upon integration, yields the following:

$$\ln k = \begin{array}{l} -Ea + \ln A \\ RT \end{array} \tag{34.2}$$

where A is the constant of integration.

This equation is also written as the following

$$k = Ae^{-\in/kT} \tag{34.3}$$

where k is the average rate constant for the reaction; A is the per-exponential factor, frequently termed the frequency factor and is independent of temperature; $\in a$ (Ea) is the Arrhenius Activation Energy and provides a value for some characteristic energy that must be added to the reactants for the reaction to occur.

From Equations (34.2) and (34.3), it follows that a plot of the logarithm of the rate constant against the reciprocal of the absolute temperature should be a straight line. The slope of the plot will yield the activation energy of the reaction and the frequency factor can be found from the intercept. As the equations imply, reaction rates increase as the temperature increases. A useful rule of thumb is that the reaction rate doubles for every 10°C increase in the temperature of the reaction.

Because the basic failure mechanism of brittle failure in polyolefin piping materials is a chemical process (chemical-oxidative attack on the polymer backbone), then this process will follow the Arrhenius equation and occur much faster at elevated temperatures. This allows accelerated testing at elevated temperatures to be used to model and project the longer-term ambient temperature behavior. This has been well demonstrated experimentally by the polymer industry over the past 50 years.

Thus, when a polyolefin pipe material is evaluated by linear regression analysis in order to project the long-term strength, this projection is only valid with certain boundaries. Where a second failure mechanism is known to occur, a straightforward extrapolation of the test data developed out to 10,000 will give an erroneous long-term value at 100,000 hours and at 438,000 hours (50 years). The long-term strength of the material will be significantly overestimated and there develops a significant risk of early failure of pipe made with this material depending on the stresses and environmental factors encountered in service. Where a change in the physical state of the material occurs over the range of temperatures tested the linear regression cannot be applied. A change in the physical state of the material would be a phase transition, reaching the glass transition or changes in the crystallinity of the material.

34.19 Test Methods for Determining Long-Term Hydrostatic Strength

ASTM D2837, "Standard Test Method for Obtaining Hydrostatic Design Basis for Thermoplastic Pipe Materials," describes a procedure for analyzing stress rupture pipe test data in order to extrapolate a long-term strength value for the material being tested. ASTM D2837 is the preferred method for establishing the HDB for thermoplastic pipe materials throughout North America and also for much of Central America and South America. ASTM D1598, "Standard Test Method for Time-to-Failure of Plastic Pipe Under Constant Internal Pressure," describes how to test individual pipe specimens, and is applicable to both thermoplastic and reinforced thermosetting/resin pipe materials. ASTM D2837 requires that a minimum of 18 failure points as well as a specific distribution of failure points be obtained to develop a full hydrostatic stress rupture curve for a material at a specific temperature. This distribution is shown in Table 34.1.

Thus, to develop a full stress rupture plot at ambient temperature at least 18 failure points distributed over 10,000 hours must be obtained. Spreading the failures out over three long decades as required by ASTM D2837 adds to the statistical significance of the linear regression analysis. It also provides an opportunity to look for indications of the occurrence of a second failure mechanism. The occurrence of a second failure mechanism increases the variance in the data.

For materials that demonstrate a single failure mechanism during stress rupture testing and meet the analysis requirements in D2837, establishing the long-term hydrostatic strength is a simple matter of performing a linear regression analysis of the test data as per D2837 and PPI TR-3 and extrapolating the 100,000 hour intercept of the projected failure data. However, with some materials, there exists the potential of a second failure mechanism occurring, which invalidates the fundamental assumptions of D2837 and TR-3 that there is only one failure mechanism occurring. With these types of materials (polyethylene, polypropylene, and crosslinked polyethylene, for example) additional testing requirements have been introduced to ensure the validity of the long-term strength projection.

Table 34.1 Required minimum distribution of failure points

Hours	Failure Points
<1000	At least 6
10 to 1000	At least 3
1000 to 6000	At least 3
>6000	At least 3
>10,000	At least 1

34.20 Validation of Polyethylene Pipe Materials

In order to address the possibility of loss of ductility in polyethylene piping materials, the Hydrostatic Stress Board of the Plastics Pipe Institute developed the validation testing concept to ensure that polyethylene piping products would remain ductile and not undergo a ductile to brittle transition leading to premature failures due to Slow Crack Growth (SCG) while in service. Slow Crack Growth or more commonly Environmental Stress Cracking (ESC) is the most common failure mechanism for thermoplastic piping materials. This validation testing protocol is included in ASTM D2837 and PPI Technical Report TR-3, "Policies and Procedures for Developing Hydrostatic Design Basis (HDB), Hydrostatic Design Stresses (HDS), Pressure Design Basis (PDB), Strength Design Basis (SDB), and Minimum Required Strength (MRS) Ratings for Thermoplastic Piping Materials or Pipe." A validation of the 50-year LTHS is required in ASTM D2513, "Standard Specification for Polyethylene (PE) Gas Pressure Pipe, Tubing, and Fittings." The protocol requires additional stress rupture testing at elevated temperatures to confirm that the polyethylene piping material remains ductile throughout the timeframe of the extrapolation of the ambient temperature testing data. It is this extrapolation to 100,000 hours, which is used to establish the LTHS and the resulting HDB cell classification.

34.21 Popelar Shift Function Calculations for PE Pipe Materials

The shift functions developed for high-density polyethylene (HDPE) and medium-density polyethylene (MDPE) piping materials by Popelar, Kenner, and Wooster were used to calculate the duration of short-term elevated temperature stress rupture testing required to confirm the 100,000-hour long-term hydrostatic strength or to confirm the 50-year (438,000 hour) long-term hydrostatic strength. These requirements have been incorporated into the PPI Technical Report TR-3 and into ASTM D 2837, Standard Test Method.

Popelar, Kenner, and Wooster related the stress rupture performance of polyethylene materials measured at elevated temperatures to that occurring at the operating or reference temperature of the system by using the classical time-temperature superposition principle, whereby elevated temperature data are translated but along both the time axis (horizontal shifting) and the stress axis (vertical shifting) to form a smooth master curve. The amount of the shift at each temperature establishes the shift function. A necessary condition for the validity of this procedure is that the resulting shift function must be independent of the specific mechanical test. Popelar et al. found that these shift functions could be used to develop a coherent master curve for the time to failure as a function of the hoop stress in the long-term hydrostatic pressure testing of a HDPE pipe. The shift functions for both HDPE and MDPE were found to be essentially identical. Popelar developed two reduction equations, one for temperature reduction factors and a second for stress reduction factors. Popelar's work provides the following shift functions:

$$\begin{aligned}\alpha\tau &= \exp[-0.109(T - TR)] \\ \beta\tau &= \exp[-0.0116(T - TR)]\end{aligned} \tag{34.4}$$

The time to failure t_f of PE depends upon the applied stress (σ) and the temperature (T).

where

$$\sigma(TR) = \sigma(T)\beta\tau \quad \text{and} \quad t_f(TR) = t_f(T)/\alpha\tau \tag{34.5}$$

where T = testing temperature (°K), TR = reference temperature (°K), and (T − TR) is the difference between the two temperatures. σ (TR) = stress at the reference temperature; σ (T) = stress at the testing temperature; t_f (T) = time to failure at the testing temperature; and t_f (TR) = time to failure at the reference temperature.

Popelar proposed in his paper that times to failure of 650 hours at 80°C would be sufficient to establish the 50-year Hydrostatic Design Stress at 20°C. He also stated that these shift functions could consolidate data irrespective of type of MDPE or HDPE gas pipe material and that this signified that these functions are universal for these materials. This work was used to develop accelerated testing requirements for polyethylene piping grades.

34.21.1 Application of Shift Functions to PE Piping Materials

A minimum of 200 hours on test at 176°F (80°C) or 70 hours on tests at 194°F (90°C) would confirm the Long-Term Hydrostatic Strength (LTHS), which is the extrapolation to 100,000 hour LTHS at 73°F (23°C).

A minimum of 1000 hours on test at 176°F (80°C) or 300 hours on tests at 194°F (90°C) would confirm the extrapolation to reach 50 years (438,000 hours) at 73°F (23°C).

To validate the 140°F (60°C) HDB or the LTHS values at 100,000 hours, a minimum of 11,300 hours of elevated temperature testing at 176°F (80°C) without any brittle failures or a minimum of 3,800 hours at 194°F (90°C) is necessary.

34.22 Ductile-to-Brittle Transition and Failure Mechanisms

The key property in the long-term testing of plastic piping materials is the retention of ductility. This is one of the basic assumptions of ASTM D 2837, Standard Test Method for Obtaining Hydrostatic Design Basis for Thermoplastic Pipe Materials or Pressure Design Basis for Thermoplastic Pipe Products." In constant-tensile load testing, the onset of the "ductile-to-brittle transition" is the important parameter. This corresponds to the area of the stress vs. the time plot in which a downward inflection point or "knee" is observed. This represents the region of the stress-rupture plot in which the ductile/creep deformation failure ends and brittle/stress cracking failure begins. The later this transition occurs, the better the resistance of the plastic material to Slow Crack Growth (SCG) or Environmental Stress Cracking (ESC). Retention of ductile performance is also the basis for the validation testing requirements for PE piping grades.

34.23 Long-Term Strength Testing of Reinforced Thermosetting Piping

ASTM D2992, "Standard Practice for Obtaining Hydrostatic or Pressure Design Basis for "Fiberglass" (Glass-Fiber-Reinforced-Thermosetting Resin) Pipe and Fittings" sets out the testing and analysis protocols for the development of long-term projections for test data developed by the stress rupture testing of pipe specimens similar to the requirements of ASTM D2837 for thermoplastic piping.

34.24 Long-Term Strength Testing of Reinforced Composite Piping

These products are being tested by both systems depending on the individual pipe construction.

Spoolable composite reinforced thermoplastic pipes are being tested per the requirements of ASTM D2837, while spoolable composite pipes with reinforced thermosetting resin layers are being tested per ASTM D2992.

34.25 Design of Plastic Piping Systems

Once the HDB has been determined for a particular thermoplastic piping compound or for a thermosetting composite pipe, it is necessary to establish the allowable working stress for long-term design. This needs to be done to ensure that the plastic pipe will operate under pressure over the desired service life. While the experimental testing tests the plastic pipe's ultimate strength to failure (HDB), plastic pipes in service must endure additional stresses beyond just the internal applied pressure of the fluid being transported. These stresses include, for example, soil loads, bending stresses, joint loads, rock impingement, soil shifts, dynamic loads under roadways, cyclic loading, surge pressures, etc. In addition, the design factor is intended to take into account the normal variables that occur in the manufacturing of the raw materials (base plastic material, additives, colorants, etc.), in the pipe manufacturing process itself, in transportation, in storage, in handling, in joining, and during installation. The maximum allowable operating stress or the HDS is obtained by multiplying the HDB by a strength reduction factor called the Design Factor (DF).

$$\mathrm{HDS} = \mathrm{HDB} \times \mathrm{DF} \tag{34.6}$$

where HDS = hydrostatic design stress, psi; HDB = hydrostatic design basis, psi; and DF = design factor (a number less than one).

The definition of the HDS in ASTM D2837 is the following: "The estimated maximum tensile stress the material is capable of withstanding continuously with a high degree of certainty that failure of the pipe will not occur. The stress is circumferential when hydrostatic water pressure is applied."

It is not the hoop stress from internal pressure that will determine the service life of a plastic pipe, but rather how the material responds to other induced stresses during service and the corresponding stress intensification (point loading, fatigue, surge, etc.). Ductile materials will shed these stress concentrations by distributing the stress into the surrounding matrix, while more brittle materials will tend to be further affected and result in a reduced service life.

The original design factors for plastic pipe for water service were established after extensive research and discussions within the plastic pipe industry in the 1950s and 1960s. The design factor for plastic piping for water service is 0.5.

34.25.1 Joining

PVC pipe and fittings products are joined using solvent cemented joints, gasketed joints, fusion welded joints, and mechanical couplings and appurtenances. PE pipe and fittings are joined using fusion welding, electrofusion, gasketed joints, and mechanical couplings and appurtenances. PEX pipe and tubing are joined using mechanical couplings and injection molded fluoropolymer and polysulfone fittings. PP pipe and fittings are joined using fusion welding, gasketed joints, and mechanical couplings. ABS pipe and fittings are joined using solvent cemented joining. Fluoropolymers are joined

34.26 Specifications, Product Standards, Test Methods, and Codes

The American National Standards Institute (ANSI) serves as the administrator and coordinator of the US private sector voluntary standardization system. ANSI oversees the creation, promulgation, and use of product specifications, standards, and guidelines that cover a wide variety of American manufactured products. ANSI facilitates the development of American National Standards (ANS) by accrediting the procedures of standards developing organizations (SDOs). These groups work cooperatively to develop voluntary national consensus standards. Accreditation by ANSI signifies that the procedures used by the standards body in connection with the development of American National Standards meet the Institute's essential requirements for openness, balance, consensus, and due process.

There are several North American organizations, some of which are ANSI accredited, and which develop and publish product standards, test methods, and practices for plastic piping systems. These include the following:

- The American Society for Testing and Materials (ASTM)
- Canadian National Standards Association (CSA)
- NSF International (NSF)
- Underwriters Laboratories (UL)
- Factory Mutual (FM)
- American Water Works Association (AWWA)

The International Organization for Standardization (ISO) publishes internationally recognized standards and test methods for plastic piping systems.

There are also several American codes bodies that publish model plumbing codes:

- International Association of Plumbing and Mechanical Officials (IAPMO), which publishes the Uniform Plumbing Code
- The International Code Council (ICC) was founded in 1994 by the Building Officials and Code Administrators International, Inc. (BOCA), the Southern Building Code Congress International (SBCCI), and the International Conference of Building Officials (ICBO). The ICC publishes the International Plumbing Code, the International Building Code, the International Fuel Gas Code, the International Mechanical Code, and other codes.
- The Council of American Building Officials (CABO), which publishes the One-and Two Family Dwelling Code
- National Association of Plumbing, Heating and Cooling Contractors (NAPHCC), which publishes the National Standard Plumbing Code

34.27 Regulatory

The most important regulatory environment is the regulation of oil and gas pipelines. The Department of Transportation's (DOT) Pipeline and Hazardous Materials Safety Administration (PHMSA) regulates the operations of the nation's onshore pipelines. PHMSA performs the following activities:

- Collects and reports data on pipeline operations annually
- Analyzes pipeline safety and reported accident data

- Evaluates which safety standards need improvement and where new rulemakings are needed
- Sets and enforces regulations and standards for the design, construction, operation, maintenance, or abandonment of pipelines by pipeline companies
- Educates operators, states, and communities on how to keep pipelines safe
- Facilitates research and development into better pipeline technologies
- Trains state and federal pipeline inspectors
- Administers grants to state and localities for pipeline inspections, damage prevention, and emergency response

Regulations for Integrity Management of hazardous liquid pipelines have been in effect since 2001 and natural gas transmission pipelines since 2002. PHMSA has recently published a proposed rulemaking that would extend the Integrity Management Program requirements to the gas distribution pipeline industry.

While PHMSA is the federal pipeline safety authority, there are other agencies having responsibilities or interests in pipelines. The Department of Homeland Security (DHS) Transportation Security Administration (TSA) has responsibility for coordinating security for all transportation-related operations, including pipelines. Both the Department of Energy (DOE), with responsibilities for energy supplies and refinery operations, and the Federal Energy Regulatory Commission (FERC), with responsibilities for natural gas regulations, have interest in the nation's pipelines. PHMSA works with DOE, DHS/TSA, and FERC, as well as the states and the local governments and the pipeline industry to ensure the safe operation of these pipelines.

Federal regulatory approval is not ordinarily required for the development of new hazardous liquids (oil) pipelines, unless it will cross federal lands. Generally, state and local laws are the primary regulatory factors for construction of new hazardous liquid pipelines.

PHMSA has the primary responsibility for the issuance of DOT Special Permits and Approvals to the Hazardous Materials Regulations (HMR). A Special Permit or Approval is a document that authorizes a person to perform a function that is not currently authorized under the authority of the HMR. Also, in many instances, the Regulations require approvals and/or registrations prior to transportation in commerce. At present, installation of these newer composite pipes in regulated pipelines requires special permits for each project.

In addition to the federal regulatory agencies, there are also state regulatory agencies that oversee pipelines. In Texas, the Railroad Commission of Texas regulates and monitors pipeline operations. The Railroad Commission of Texas (RRC, Commission) is the state agency with primary regulatory jurisdiction over the oil and natural gas industry, pipeline transporters, natural gas and hazardous liquid pipeline industry, natural gas utilities, the LP-gas industry, and coal and uranium surface mining operations. It is also responsible for research and education to promote the use of LP-gas as an alternative fuel in Texas. The Commission exercises its statutory responsibilities under provisions of the Texas Constitution, the Texas Natural Resources Code, the Texas Water Code, the Texas Health and Safety Code, the Texas Utilities Code, the Coal and Uranium Surface Mining and Reclamation Acts, and the Pipeline Safety Acts. The Commission also has regulatory and enforcement responsibilities under the federal law, including the Surface Coal Mining Control and Reclamation Act, the Safe Drinking Water Act, the Pipeline Safety Acts, the Resource Conservation Recovery Act, and the Clean Water Act.

While gas transmission, crude oil pipelines, and hazardous materials pipelines are generally regulated by PHMSA, there are a significant number of oil and gas gathering pipelines that are not regulated and do not report their operational data to the PHMSA. Generally, these are operations that are away from high consequence areas such as cities, towns, and areas of habitation and, as a result, represent much lower risk to the general public.

Simply, gas gathering operations away from habited areas are unregulated until the product is delivered into a transmission or product pipeline for transport off the property into the pipeline system. There have been ongoing discussions for PHMSA to extend its regulatory reach into these unregulated operations, but this does not appear imminent at this time.

Potable water applications require testing and certification by NSF International.

34.28 Applications of Thermoplastic Plastic Piping

PVC piping is typically used for:

- DWV pipe
- Sanitary sewers
- Storm water drainage
- Water mains
- Water service lines
- Irrigation piping
- Electrical and telecommunications conduit
- Various industrial installations

PVC piping can be used both underground and aboveground and inside buildings. It can be used outdoors if the pipe contains stabilizers and UV inhibitors to shield against ultraviolet radiation and it is painted with a water-based latex paint. PVC materials are resistant to many ordinary chemicals such as acids, bases, salts, and oxidants.

PE piping is typically used for:

- Gas distribution piping
- Oil and gas production piping
- Sanitary sewers
- Marine outfalls
- Storm water drainage
- Storm water retention systems
- Agricultural drainage
- Marine outfalls
- Water mains
- Water service lines
- Irrigation piping
- Geothermal piping
- Electrical and telecommunications conduit
- Industrial installations
- Fire mains
- Mining pipe
- Chemical process industry piping

CPVC piping is typically used for:

- Hot and cold water plumbing pipe
- Fire sprinkler piping
- Chemical process industry piping

PEX piping is typically used for:

- Hot and cold water plumbing pipe
- Radiant heating application piping
- Fire sprinkler piping

PP Piping is typically used for:

- Corrosion-resistant DWV piping
- Chemical process industry piping
- Hot and cold water plumbing pipe
- Radiant heating application piping

ABS piping is typically used for:

- Drain, waste, and vent pipe (DWV)

PVDF Piping is typically used for:

- High purity water piping systems
- Chemical process industry piping
- Corrosive-resistant DWV piping

34.29 Installation Using Thermoplastic Pipe for Pipeline Replacement

34.29.1 Open-Cut Installation

The most common method for the construction of a new main in a new trench usually parallel to the old main is the conventional open-cut excavation method. Less frequently the old main can be dug up and removed and a new pipe installed in the same trench.

34.29.2 Horizontal Directional Drilling (HDD)

Horizontal directional drilling consists of several installation steps. First, a pilot bore is made with a suitable-sized drilling rig. The bore is steered to create an initial hole at the required line and grade. Successive reamers are then pulled back to enlarge the bore diameter to the desired size. During the last stage of reaming, the service pipe is pulled back into the bore. HDD is often employed when an open cut excavation is unsuitable such as at a railway crossing or river crossing. Most pipelines installed by this process are fusion welded continuous HDPE pipes, although steel, ductile iron, and PVC pipes are also installed by this process. The recent introduction of fusible PVC piping has allowed PVC piping to be more widely used in HDD installations of water pipe, telecommunications, and electrical conduit that were previously dominated by PE pipes.

34.29.3 Pipe Bursting

Pipe bursting employs a specially designed bursting head larger than the old pipe, which cracks, splits, or bursts the old pipe as it is pulled through and pushes the pieces of the old pipe outward into the surrounding soil. The new pipe is attached to the rear of the bursting head and is pulled into the space left by the broken old pipeline. It is possible to significantly increase the diameter of the pipeline being replaced with pipe bursting. This tends to be limited by soil conditions, the proximity of other buried utility lines, and the depth of cover. The pulling force of the bursting unit must be maintained at a value less than the tensile strength of the replacement pipe to avoid over stressing the replacement pipe. The replacement pipeline must be installed in one continuous length. Fusion-welded polyethylene pipe is the most commonly used material for replacing gas distribution lines, water mains, and sewer pipes. Mechanical-joined PVC pipe and fusion welded PVC pipe are also used in sewer line and water main replacement, but to a much smaller extent. Pipe bursting tools include static, pneumatic, hydraulic, and cutting heads.

34.30 Applications of Composite Piping

34.30.1 Applications of Fiberglass Reinforced Thermosetting Resin Pipe

Fiberglass reinforced thermosetting pipe and fiberglass thermosetting resin pipe can be used for a variety of applications above and under the ground, including sanitary sewer systems, wastewater treatment plant piping, industrial piping, firewater piping systems, cooling water piping systems, potable water piping systems, oil and gas production piping systems, and underground structures, including manholes, oil/water separators, sumps, and risers.

34.30.2 Multilayer and Composite Plastic Piping Products

Multilayer composite piping products in oil and gas production applications are still in their infancy. Initial applications have been almost completed for composite spoolable thermoplastic pipe products. There are several North American manufacturers (Fiberspar Spoolable Products, Flexpipe Systems, Future Pipe, Polyflow, and Prime Flexible Products) and also European manufacturers such as Pipelife. These piping products are used at higher operating temperatures. For example, the Pipelife Soluforce pipe system has a maximum service temperature of 65°C and a project lifetime of greater than 20 years. External fiber reinforced thermoplastic spoolable composite piping is used for oil and gas production piping and aboveground transport of crude oil and natural gas. These are products using mainly HDPE as the liner pipe, but there are products that use PEX-B for the liner pipe, where higher temperature fluids are being transported. The external reinforcements are typically polyester fiber, glass fiber, carbon fiber, aramid fibers, and interleaved steel strips.

35 PET Use in Blow Molded Rigid Packaging*

Dan Weissmann
DW & Associates, Simsbury, CT 06070, USA

35.1 Introduction

PET blow molding into containers was the last to join other polyester established applications like fibers and films. Polyester fiber development dates back to the early 1940s with a major push after World War II, and the biaxial oriented films go back to the 1960s. These films were the first to facilitate the use of polyester in packaging. PET containers were developed and commercially produced starting in the mid-1970s. Since then, PET containers have gained an impressive position in the field of packaging. PET gains came not only at the expense of glass, but also by replacing other plastics like PVC, PS, and HDPE, and, to a limited degree, metal cans. Total polyester production and the division into the main areas of application are shown in Figure 35.1 and the global breadth of PET manufacturing is shown in Figure 35.2 [1].

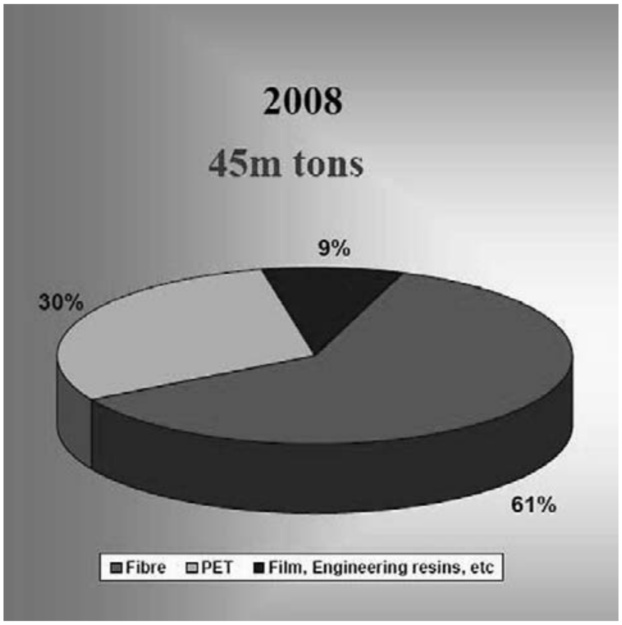

Figure 35.1 Global polyester uses 2008.

Of the total polyester production, about one-third or 15 m tons is PET for packaging. Five hundred billion containers are produced annually around the world, accounting for about two-thirds of the PET packaging resin. PET packaging covers a myriad of products, both liquid and solid, in all categories.

35.1.1 The Development of PET Blow Molding Technology

PET bottles were commercially introduced to the market place for the first time in 1976, by Pepsi Cola. The bottles were supplied by Amoco from their Seymour, IN plant, blown on Cincinnati Milacron machines, from preforms molded in molds supplied by Broadway Mold in Dayton, OH. The PET bottle introduction coincided with the FDA-forced withdrawal of the Monsanto supplied Coca Cola ANS bottles, making it the only plastic carbonated soft drink (CSD) bottle on the market. Figure 35.3 shows a Continental Can Company (CCC) bottle produced in the company's first

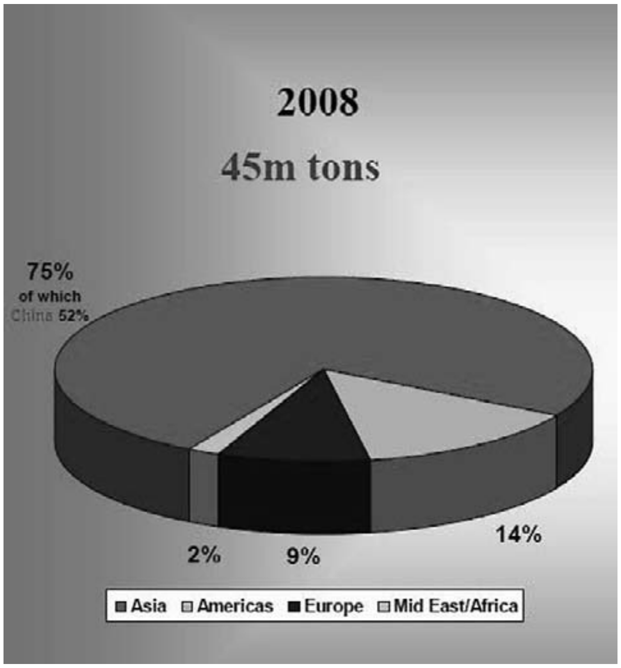

Figure 35.2 Polyester global production by world regions.

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* This chapter is dedicated to the memory of Samuel L. Belcher.

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Figure 35.3 First production Pepsi Cola bottle.

Figure 35.4 Early hot fill bottle by Yoshino, Japan 1982.

PET bottle blow molding plant in 1977. A second important milestone was the introduction in Japan by Yoshino in 1982 and in the US by Monsanto in 1985, of bottles suitable for hot filling, a typical filling method for perishable beverages like juices. The Yoshino and the Monsanto bottles are shown in Figure 35.4 and Figure 35.5, respectively.

Since its market introduction, PET containers have enjoyed impressive growth, not only in numbers, but also in the range and variety of products packaged and in container configurations. Today, besides various soft drinks, liquor wine and beer are packaged in PET, as well as edible oil, salad dressing, and other sauces, health and beauty products, household chemicals, automotive fluids, and a variety of other goods like nuts, candy, mayonnaise, jelly, apple souse, and spaghetti sauce, all packaged in wide mouth jars. Even tennis balls are packaged in cans made of PET.

Figure 35.5 First commercial hot fill bottle USA 1985.

The availability of virgin as well as recycled PET made it a more common material in thermoforming, which can be found in a variety of other packaging formats like tubs and blister packs. Crystallized PET trays, which can be heated in conventional or microwave ovens, are a typical part of prepared food packages.

Fundamentally, the basic blow molding technology has remained the same over the years. Progress manifested itself in refining package design, the manufacturing processes, and the machinery to produce lighter weight containers and higher production rates both in injection and blow molding. In the 1970s, the basic blow molder was the Cincinnati Milacron RHB-V producing 2400 bottles per hour, whereas today's machines can reach 72,000 bottles per hour or 1.5 million bottles per day. Depending on the design of the preforms, injection machines can produce over 500 million preforms per year. Along with improvements in basic production equipment, came the developments of a variety of auxiliary equipment, both upstream and downstream, leading to highly specialized and optimized production systems. Of major importance were the gains made in handling empty bottles at high line production rates.

The origin of blow molding process is in the Wyeth patent [2], where the properties of bottles were detailed and their dependence on the processing of the material and the achievement of desired morphology to improve the physical and the barrier performances were outlined. During the development of the blow molding machine at Cincinnati Milacron, the process was changed from the extrusion-orientation process, which was covered in a subsequent patent [3], to the reheat of pre-molded preforms. Broadway Mold designed and built the first PET preform mold and successfully molded the first preform, keeping the material amorphous and avoiding crystallization, a must for subsequent reheating and blowing. The PET was supplied by Goodyear, which became a major material supplier. The Goodyear PET business later became a part of Shell Company and now is a part of M&G.

35.1.2 PET—The Packaging Material

Balance of properties is what makes PET the major packaging material it is. Inertness, toughness, and reasonable level of barrier to CO_2, oxygen, and water vapor transmission, combine in protecting and preserving the content, maintaining appealing appearance and freshness, and preventing spoilage.

Additionally, PET morphology is successfully used to modify material properties to meet various package demands. Orientation is used to enhance impact resistance while increased crystallinity raises PET thermal range. Both orientation and crystallinity reduce permeation.

Table 35.1 compares PET with other common materials used in packaging. Polyolefins, the other major material group used in packaging, provide advantage only in lower water vapor transmission in comparison to PET.

Structural integrity depends on material property, container geometry, and wall thickness. Impact strength after orienting PET is high and most containers will survive impact from 1.8 meters.

Table 35.1 Permeation factor of common packaging materials

	Oxygen	Carbon Dioxide	Water Vapor
PET amorphous	10.4		
PET heat set bottle	5.5	20	2.5
PET double blow bottles	4.3	9.0	1.2
PVC	8–15	20–40	2-3
LDPE	480	1500	1.5
HDPE	95	580	0.3
PP	150	450	0.5
PS	416	1250	13
PC	225	550	14
ANS (Barex)	1.1	3.1	6.1

Note: Permeability rates at 25 °C (cm^3)(mil)/(24 hour)(100 in.^{2})(bar) ASTM D1434.
Water vapor transmission at 38 °C 50–100% RH (g)(mil)(24 hour)(100 in.^{2}) ASTM E-96.
The data in the table is based on Barrier Polymers [35] and other information provided by Morris Salame and elsewhere.

Table 35.2 Typical properties of PET

Tensile modulus	2760 MPa
Tensile strength	45 MPa
Elongation	250–500%
Melting point	257 °C
Glass transition temperature	75 °C

Source: Cleartuf PET Product Manual, (The Goodyear "Blue Book"), 1976.

Typical properties of amorphous PET are given in Table 35.2.

35.1.3 PET Structure and Manufacturing

PET monomer structure is given in Figure 35.6. The monomer being the chemical building block of the polymer, it is responsible for most of the material properties.

Of great importance is the glass transition temperature (T_g), where a polymer changes its behavior from a very rigid glass to a pliable rubber-like material. The structure of the Mer is a major factor in determining where the T_g occurs. A material with a similar structure only without the benzene ring has a T_g, which is 140 degrees Celsius lower than PET [4].

PET is produced by a reaction of Terephthalic Acid (TPA) and Ethylene Glycol (EG) in condensation polymerization as shown in Figure 35.7. A catalyst is used to drive the reaction to high molecular weight, with Antimony compounds being the most common one. Germanium compounds as catalyst are believed to produce PET with better color and clarity. Thermal stabilizers are deployed to prevent degradation and color formation at the high temperature of the reaction. High vacuum must be applied at least toward the end of the process to remove water and other volatiles, and facilitate the molecular weight build-up.

Intrinsic viscosity (IV) is the common measure of the molecular weight of PET. Usable range of IV for packaging is between 0.7 and 1.04. At the high end, extrusion blow molding grades are possible, but this process makes it very difficult to attain orientation, hence it never took hold in the industry. Other polyesters are available for extrusion blow molding; however, the modifications made to facilitate parison extrusion and prevent crystallization change their properties significantly from standard PET.

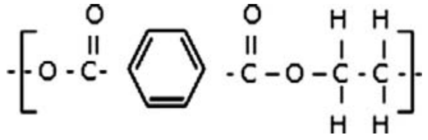


Figure 35.6 PET monomer.

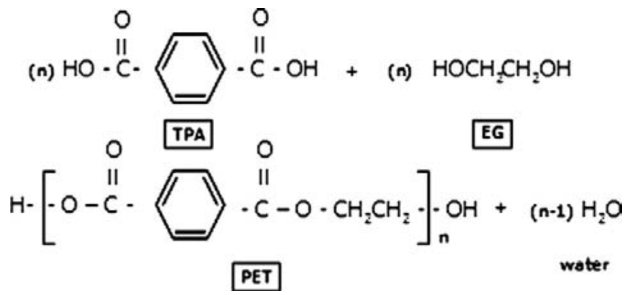


Figure 35.7 PET polymerization reaction.

There are two routes to polymerize PET as shown in Figure 35.8. The majority of the PET is produced via the purified TPA route. The by-product of the polymerization is water as seen in Figure 35.7. Hence, in the presence of water and high temperature, break-up of the molecule occurs. This mandates extreme drying conditions on the material before any melt processing.

Production of PET is done mostly in continuous reactors with batch operation left only for special products. There are two parts to the process. In the first, the chemical reaction is taking place where the polymer reaches an IV of about 0.55. On leaving the reactor, the polymer is pelletized. It is then transferred into another reactor where Solid State Polymerization (SSP) takes place and the IV is raised to the final product level. Before the low IV pellets can be solid stated, they first must be crystallized to prevent them from sticking and fusing together. Crystallization is done while the pellets are kept moving through a high level of agitation or a fluidized bed system. An added benefit of solid stating is the ability to further remove any residuals or by-products. Acetaldehyde (AA), CH_3CHO, or MeCHO is one of the compounds being formed in the polymerization of PET manufacturing as well as during melt processing. Although it does not pose any health risks as it is found abundantly in fruits, it does impart a sweet taste, hence possibly affecting the taste of the content. It is highly undesirable in water and in some other beverages. AA is closely monitored and usually reported with other properties of the material. The key to keeping AA level low is to start with a low AA resin and control the injection process in a way that minimizes its formation. It is important to use the right injection molding machine screw configuration and well-designed injection mold manifold.

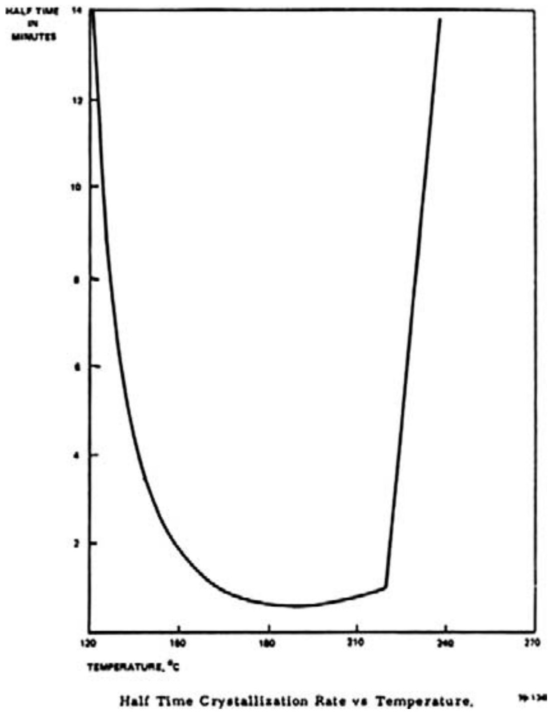


Figure 35.9 Half life crystallization time of PET.

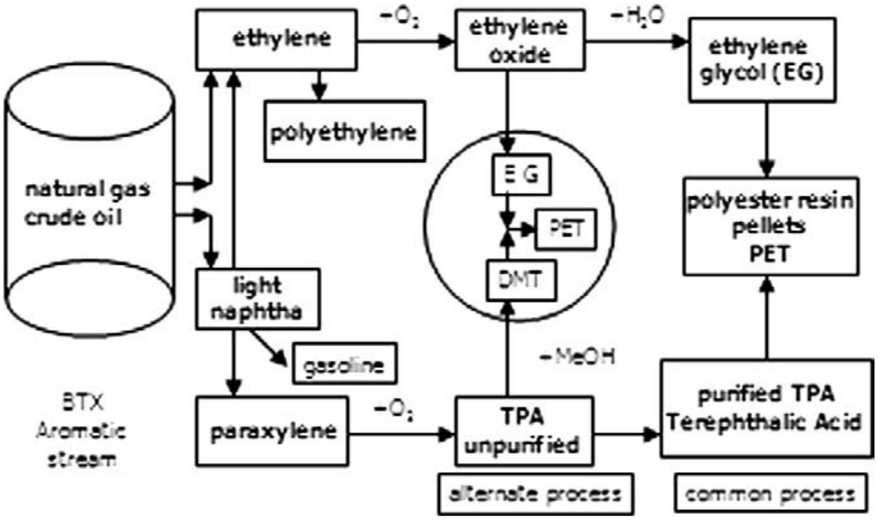


Figure 35.8 ET manufacturing routes.

PET, on cooling from the melt, will tend to crystallize. The tendency is very strong, hence the need for quenching when amorphous morphology is sought on cooling from the melt. Figure 35.9 is the half time crystallization rate vs. temperature for PET [5]. Minimum half life time, or conversely maximum crystallization rate, is achieved in a temperature range of 170−190 °C. The crystallization time is in terms of seconds. The rate of crystallization slows down with increase in molecular weight, co-monomer content and type, residual catalysts [6], and diethylene glycol (DEG) that is formed during the manufacturing of PET [7]. Hence, the curve of Figure 35.9 shifts upward to longer times.

Crystallized PET does not exhibit a glass transition any more and would not become really pliable until the crystals start softening on approaching the melt region. Hence, crystallized preform cannot be blown into bottles unless special means are used. To slow down crystallization, the polymer is usually modified into a co-polymer or by additives. Co-polymers are formed by using diacids, glycols, or cyclohexane dimethanol (CHDM) [8]. In all cases, retardation of crystallization opens a window for molding amorphous preforms. The crystallinity level in preforms is usually less than 4%.

Lately, new processes have been developed where the product reaches its final IV in a single step system and no solid stating takes place. When the system end-products are PET pellets, the system is also referred to as “Melt to Resin” (MTR). When the resin is fed directly to downstream production like the injection molding of preforms, it is referred to as “Melt to Preforms” (MTP).

Figure 35.10 is a schematic representation of a conventional 4 Reactor System and the direct to final IV system, the 2 Reactor system, developed by Uhde Inventa-Fischer.

Both systems require pellets crystallization step. In the 4 Reactor system before the SSP step, and at the end of pellet production in the 2 Reactor system. The pellets must be crystallized to enable drying which is required before any processing of the PET.

35.1.4 Morphology: Orientation and Crystallinity

The ability to change the morphology of PET, and with it its properties, is critical to the performance of PET in packaging. Orientation raises mechanical properties to the level needed to support stresses due to the carbonation in CSD bottles. Crystallinity content in the material elevates the thermal resistance of PET so that packages that undergo thermal filling survive the exposure to relatively high temperatures, certainly above the glass transition temperature of the amorphous PET.

Manufacturing processes have been established so that the desired morphology change is taking place during the forming of the molded article.

The effect of orientation on various PET properties is summarized in Table 35.3.

The orientation process takes place while the bottle is blown from the preform into its final shape. The stretch ratio from the preform to the bottle, the rate of stretching, and the temperature affect the level of orientation achieved. The stretch leading to orientation is associated with generating residual stresses in the container wall. Unless the temperature is lowered rapidly, relaxation will take place and the orientation will dissipate. The relaxation rate is high above the glass transition temperature and slows down significantly below it.

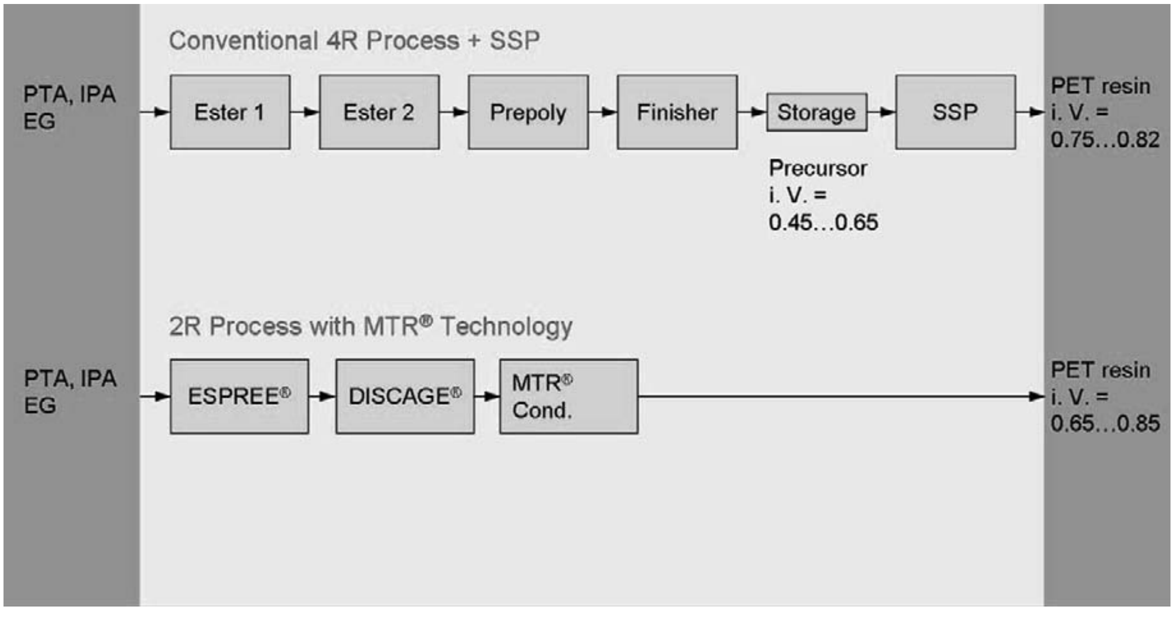


Figure 35.10 PERT manufacturing processes comparison.

Table 35.3 Orientation effect on mechanical properties of PET

	Amorphous	Uniaxially Orientated	Biaxially Oriented
Tensile strength	48.2 MPa	248 MPa (longitudinal) 68.9 MPa (traverse)	4172 MPa
Modulus	2761 MPa		4130 MPa
Elongation to break	250–500%	60% (longitudinal) 150% (traverse)	100%

Uniaxial stretch 375%, Biaxial stretch 300 × 300%.
Ref: Cleartuf PET Product Manual (The Goodyear "Blue Book"), 1976.

Hence, the requirement to run the blow molds at low temperatures to lock in the orientation when desired.

The orientation process aligns the molecules and makes it easier to form crystalline domains. The crystalline structure is the preferred state to which PET will revert unless molecular motion is restricted. The typical level of crystallinity in cold mold blown bottles, like CSD bottles, is 20–25%. This crystallization is formed as the material is being stretched and is referred to as strain-induced crystallization (SIC). The crystallites formed under SIC conditions are numerous and remain small and therefore different from those formed under thermal crystallization conditions, which result in large spherulites. Spherulites will grow until they impinge on one another. At a certain size, the spherulites start to scatter incident light and will appear opaque white rather than the clear colorless amorphous PET. To preserve bottle clarity, the crystallites must remain small.

The crystalline structure being highly organized results in increase in the density of the material. Typical value of the crystalline domain density is 1.455 while the amorphous domain density is 1.335. The level of crystallinity can be measured directly by various analytical techniques like x-ray diffraction, or derived from the material density using a simple mixture calculation. A common way to determine a sample density is through the use of a density column [9] with the right mixture of chemicals to cover the intended density range.

Higher levels of crystallinity are achieved if the molecule segments remain free to move, as is the case when the preform is heated to its highest possible temperature and the blow mold temperature is high. The amount and the rate of the increase in crystallinity depend on material IV, temperature, and time. The blowing process that intentionally drives the crystallinity up to create hot fillable, thermally stable bottles is called heat setting. In a typical heat setting process, the level of crystallinity reached is 30 – 35%. Higher levels, into the mid-40% range, can be achieved through the double blow blowing process.

The temperature range for maximum crystallization rate, as shown in Figure 35.9, is also the range which will yield the higher crystalline content in bottle blowing, hence, mold temperature is raised toward this range. This has to be tempered with the fact that unless some cooling is applied at some point, the container may be too soft to exit the molds without the risk of distortion or deformation.

The level of crystallinity attained is also a function of the initial blow ratio—draw ratio from preform to bottle. At low levels of draw ratio, a low degree of crystallinity is induced with no increase in annealing. At moderate draw ratios, a higher level of crystallinity is induced and annealing will raise it further. At the very high draw ratios, the crystalline level is high but no growth is added on annealing [10]. This means that for heat setting only, a moderate blow-up ratio should be used. The typical blow-up ratio for heat set bottles is 7:1 compared with 15:1 for CSD bottles.

Figure 35.11 shows the shrinkage behavior of bottles on hot filling as a function of the original bottle blow-up or draw ratio [11]. The shrinkage behavior follows the three regions of crystallinity formation as described above. The shrinkage is rather high at low and high draw ratios because at these levels, no crystallinity build-up has taken place. With only little crystallinity at the low draw ratio, no real thermal resistance above the T_g has developed. At the high draw ratio, significant levels of oriented material remain, which is highly stressed and leads to high levels of shrinkage.

An added benefit of exposing the bottle to temperatures above the glass transition is that molecular relaxation takes place at the same time crystallinity is building up. Both depend on molecular movement freedom for a molecule to either get into the crystalline structure or slip by other molecules out of the oriented state. This facilitates the dissipation of the orientation and the residual stresses associated with it. Residual stresses are ultimately responsible for any deformation of

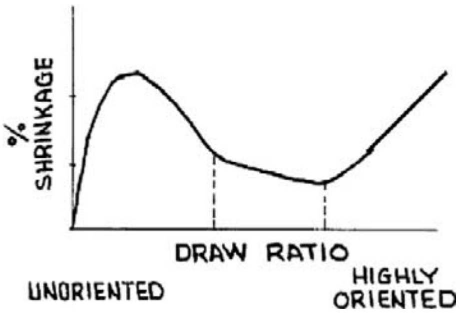


Figure 35.11 Draw ration (BUR) effect on bottle shrinkage on heating.

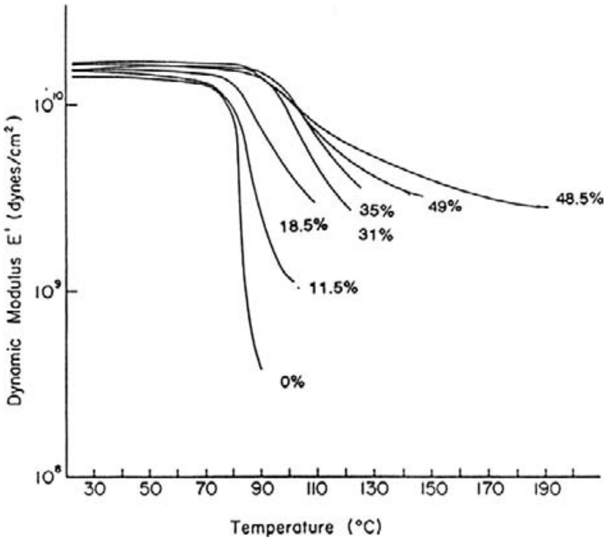


Figure 35.12 Shift in glass transition temperature with increase in crystallinity.

a product on reheating above the glass transition temperature, like shrinkage or warpage in hot filled bottles.

The dynamic modulus for PET at various levels of crystallinity is shown in Figure 35.12. The deflection point, where the modulus starts dropping, is the glass transition temperature, indicating the shift from the glassy to a rubbery state and a significant loss of mechanical performance. As indicated in Table 35.2, the amorphous glass transition is at about 75 °C. With the increase in crystallinity, the glass transition shifts to higher temperatures, hence, providing higher thermal resistance.

The ability to crystallize PET can also be utilized in stabilizing the finish against exposure to high temperature. The finish is formed while injection molding the preform and it remains amorphous, hence, it is likely to become pliable if exposed to temperature above the glass transition temperature—a plausible scenario when hot filling and a certain situation if containers are retorted. Neck crystallization is a process where the neck is heated to force thermal crystallization. The optimum temperature is derived from the crystallization half time shown in Figure 35.9. As pointed out previously, the large spherulites scatter incident light to make the finish appear opaque white, as shown in Figure 35.13. The technology was developed by Yoshino and covered in a 1983 patent [12] and subsequent other patents covering improvements.

35.1.5 Permeation and Barrier

The preservation of packaged food is the main concern to the food industry. Shelf life of a product in a package is defined as the time during which it is safe to use such products. Obviously, it is in the interest of any company to extend the shelf life as long as possible. Products can be shelf stable or require specific storage conditions like refrigeration.

Figure 35.13 Crystallized finish.

The shelf life of shelf-stable products is controlled by the way the food is processed, specific additives, thermal stabilizers, anti-oxidants or UV absorbers, and the packaging methods. Such methods may include thermally processing the content before it is put into the container like hot filling or after filling and sealing the container like retort or pasteurization. However, only in a few cases can an indefinite shelf life be reached. Usually, deterioration processes will start after filling. The deterioration processes can vary from color change to microbiological activity leading to spoilage. In all cases, they are affected by the environment inside the container or by exposure through the container wall and closure.

Plastics, including PET, let most gases pass through them. The rate of permeation of such gases depends on the chemical structure of the particular gas and of the package material [13].

Permeation characterization of various materials is expressed by their Permeability Factor (P_{factor}). Total flow through the wall of a package takes into account surface area, thickness, and the difference in partial pressures of the gas between the inside and the outside of the wall, in addition to the P_{factor} and obviously the exposure time. Usually, the time in terms of shelf life will be the sought-after answer given a particular set of package structure and exposure conditions. To arrive at shelf life, the sensitivity of the packaged content must first be defined. This is typically given in terms of P_{critical}. The basic relationship governing permeation is given in the equation below:

$$\dot{q} = P_{\text{factor}} \times (A/L) \times \Delta p \tag{35.1}$$

Where $\dot{q}$ is the rate of gas transmission, A is the surface area, L is the thickness of the package wall, and Δp is the partial pressure difference. Shelf life is derived by dividing the critical level by the transmission rate. Rise in temperature and moisture level of the container wall will increase permeation rates through it, as will the increase in concentration of the permeant. Hence, storage conditions of the package affect the package shelf life significantly.

In addition to the chemical structure, PET's morphological state also contributes to barrier performance. Increasing levels of both crystallinity and orientation will raise barrier levels. The permeation factor relation to crystallinity is given in the following relation:

$$P_{\mathrm{sc}} = P_{\mathrm{a}} \times (1 - X_{\mathrm{c}})^2 \qquad (35.2)$$

P_{sc} is the permeation factor of the material; the notation sc refers to semi-crystalline. P_{a} is the permeation factor of the amorphous phase and X_{c} is the crystalline content fraction [14]. Experimental data is presented in Table 35.4 for both thermal and strain-induced crystallinity in terms of oxygen ingress to the package.

As the crystallinity increases, the yearly oxygen ingress is reduced, meaning that the permeation factor becomes smaller. The reduction in permeation is in good agreement with Equation (35.2) for thermally-induced crystallinity. However, the drop in permeation is faster when the crystallinity is strain-induced. The crystalline domains created by stress-induced crystallization are smaller than those produced thermally; hence, there must be more crystalline entities to reach the same levels of total crystalline content. The higher number of domains seems to be more effective in reducing oxygen transmission through plastics.

Even though PET barrier is better than many other plastic materials and is farther enhanced by crystallinity, the barrier to transmission of oxygen, CO_2, light, UV, and water vapor, is still very limiting in many cases of food packaging. Several materials and compositions are being used for barrier enhancement. Those can be divided into homogenous or multi-layer—multi-material wall materials. Homogenous wall structures include PET, which is blended with barrier enhancing materials. In a multi-layer wall, a separate high-barrier material is added within the PET, in effect creating a three-layer wall. In a few cases, two barrier layers are embedded in the PET to create a five-layer wall. High-barrier materials and their properties are listed in Table 35.5.

Blending of a high-barrier material into PET requires that the material processing temperature be compatible with the PET temperature. Nylon MXD6 is a high-barrier material that meets this criterion and is frequently found in barrier-enhanced formulations. However, it produces a pearlescent shiny appearance and haze at relatively low loading levels unless special means are undertaken to make the Nylon MXD6 more optically compatible with PET [15]. Having a compatible process temperature is beneficial even when Nylon MXD6 is added as a separate layer as it makes hot runner manifold construction simpler.

Enhancing barrier materials can provide either a passive or an active barrier. While a passive barrier just reduces the permeation through the wall, an active barrier is a scavenger, which reacts chemically with the permeating gas. All active barrier materials for PET are geared to react with oxygen before it reaches the packaged content. Only passive barrier is used to cut down on CO_2 losses. Several suppliers offer oxygen-scavenging resin systems for PET. Many of the compositions are based on Nylon MXD6 oxidization in the presence of Cobalt, which serves as a catalyst [16]. It was first developed in the mid-1980s at CMB and later became commercially known as Oxbar. Several improvements in the composition were commercialized subsequently, mostly to reduce the haze in the blend, which limited the use to about 2% loading. Other developments include additional scavenger-based systems other than Nylon/Cobalt. Another advantage of using a scavenger system is that it also reacts

Table 35.4 Oxygen ingress as function of crystalline content

Crystalline Fraction (%)	Thermally-Induced Crystallinity	Stress-Induced Crystallinity
04	42	
12	36	
15		25
24		19
26	24	
36	17	12
42		10
45		9
50	10	

Note: Bottle: 2 l 0.45 mm thick. Source: Morris Salame.

Table 35.5 Barrier material permeation factors

	Oxygen	Carbon Dioxide	Water Vapor
ANS	1.0	3.0	5.0
Nylon MXD6	0.45		1.6
EVOH F (68%VOH)*	0.07	0.05	3.8
EVOH E (56%VOH)*	0.02	0.20	1.4
PEN	1.1		
PGA	0.05		

Note: Permeability rates at 25 °C (cm^3)(mil)/(24 hour)(100 in.^{2})(atm) ASTM D1434.
Water vapor transmission at 38 °C 50–100% RH (g)(mil)(24 hour)(100 in.^{2}) ASTM E-96.
EVOH at 20 °C and 65% RH [36].
**EVOH barrier vary strongly with moisture level.*

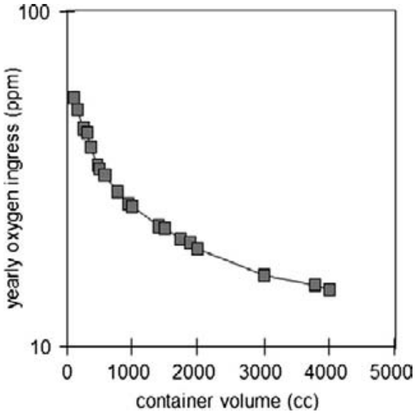


Figure 35.14 Oxygen ingress as function of bottle size.

with the oxygen in the package wall or inside the container, in effect lowering the total oxygen from the level immediately after filling and sealing the container [17,18].

Another class of barrier enhancements is coatings. A coating can be applied internally or externally to the containers. SiOx are the most common plasma coatings applied inside the container. The two major commercial systems in use are Actis by Sidel and Plasmax by KHS. Plasma coatings are the most diverse in terms of providing barrier to oxygen and CO_2 as well as flavor and aroma scalping off the product. External coating includes Bairocade by PPG and the APT's flow coating [19]. Both are epoxy-based and after applying must be cured by the application of heat. The APT system is unique as it is applied to the preforms rather than to the blown bottle. Early commercial applications of the ATP coating were directed at reducing CO_2 permeation from CSD bottles.

The enhancement of the barrier provides compensation for the effects of reduced wall thickness in lighter weight packaging and smaller-size containers. The wall surface area per unit of the content is inversely related to container size. Figure 35.14 shows the effect in terms of yearly oxygen ingress under constant permeation conditions, P_{factor}, and wall thickness.

35.1.6 Commercial Manufacturing Processes

Blow molding of PET containers starts with the injection molding of a preform. Various preforms are shown in Figure 35.15. The preforms, after conditioning to the proper blow molding temperature (100−110 °C), are blown into the final container shape.

There are three basic manufacturing processes for PET bottles, as listed below:

1. Injection blow molding (IBM)
2. Injection stretch blow molding (ISBM)

Figure 35.15 Typical PET preforms.

3. Preform injection followed by reheat stretch blow molding (RSBM)

Figure 35.16, Figure 35.17, and Figure 35.18 show schematically the main section and function performed in each of the blowing systems.

IBM and ISBM machines are also referred to as One Step (or stage). It is in reference to the fact that in both systems, the preform and the blow molding take place at the same time; however, at different stations of the machine. The machine indexes the preforms from the injection position to the blow position. The injection plus the RSBM is referred to as the Two-Step system. The preforms are molded independently of the blowing in a conventional injection molding process.

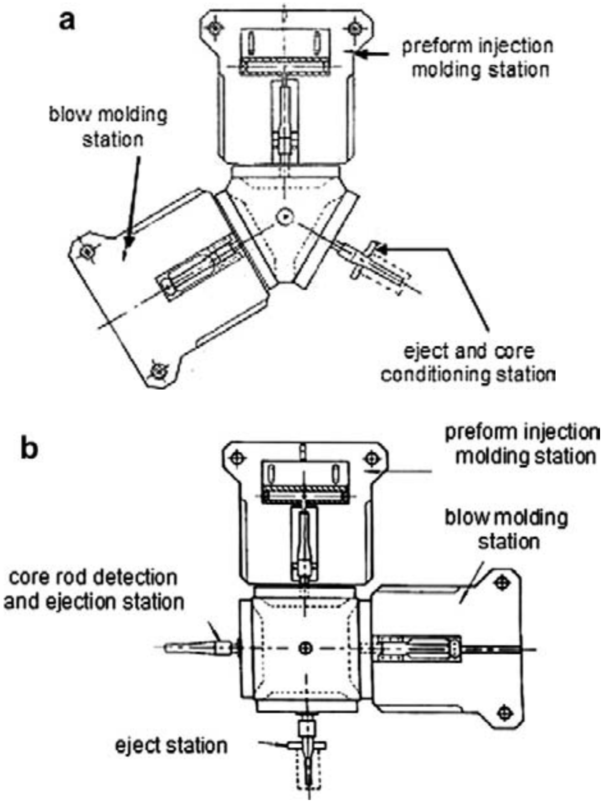


Figure 35.16 Injection blow molding (IBM) a. three position system. b. four position system.

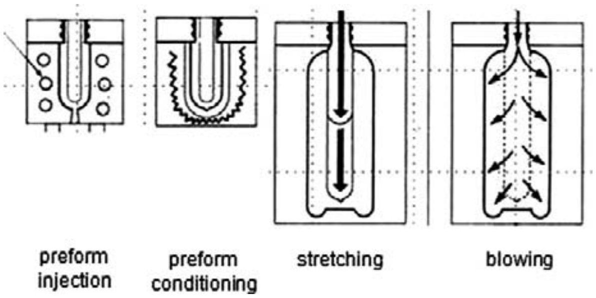


Figure 35.17 Injection stretch blow molding (ISBM).

Those preforms are utilized as needed for the blowing of the bottles. As the preforms are fed to the blow machine, nominally, at room temperature, they must first be reheated to the blow temperature; hence, a reheat oven is an integral part of the RSBM machine. Another distinguishing aspect is that both IBM and ISBM follow a "Cool Down" process. The cool down process makes reference to the fact that the preforms reach the blow molding temperature through cooling down from the melt temperature about 255 °C encountered in the injection step. In contrast, the RSBM is a "reheat" process as preforms are heated up to the blow temperature.

Depending on the ISBM machine configuration, the cooling and conditioning of the preforms can be done entirely while the preforms are still in the injection mold, or can be divided into in-mold cooling followed by indexing the preforms to a specific conditioning position before indexing again into the blowing position. Typical of the in mold cooling and conditioning are the Aoki "Direct Heatcon" machines while Nissei machines represent the independent condition station configuration. In the IBM process, cooling and conditioning of the preforms take place only in the injection mold. In the four-station configuration, the additional position is used to condition the core rod temperature so that it is the same at the start of every cycle and also to make sure that the product was stripped off the rod successfully. There are other configurations of the IBM system where the preforms are shifted in a vertical or horizontal direction between the injection and the blow position, or swung around between them.

Another system, "integrated two step" or "one and one half step," yields higher productivity as compared to one-step machines by exploiting the fact that the blow molding cycle time is much shorter than preforms injection cycle. In each machine cycle, the number of preforms being molded is a multiple of the number of blow cavities. After removing the preforms from the injection cavities, they are staged and advanced into blowing in groups matching the number of blow cavities. Hence, every group of preforms is held for a different number of machine cycles before being blown. Additional preform conditioning is applied prior to the transfer of the preforms into the blow mold. Typical of this system configuration is the SIPA ESC Integrated System machines.

Figure 35.19 demonstrates graphically the temperature history from the pellet to the final products for both the one and the two-step processes.

The IBM process does not involve any real axial stretch of the preform. The preform is transferred from the injection station into the blow mold on the core and is blown off it. Both ISBM and RSBM utilize a stretch rod to start the blowing process by stretching the preform in the axial direction. The blow pressure comes on either at a point during the stretching or after the stretching has been completed. The exact rate of stretch and the timing of the blow air and its pressure help in distributing the material from the preform to the container, usually in an attempt to reach a uniform wall thickness. Typically, the pressure will be increased toward the end of the preform inflation as material stiffness rises with the increase in orientation and the decrease in temperature.

Preform injection molding is a highly technical field as economics demand the use of very high cavitation molds. For high production, 192, 144, and 96 cavity molds are standard. To facilitate short cycle time, most systems are equipped with post-mold cooling devices, which hold the preform under

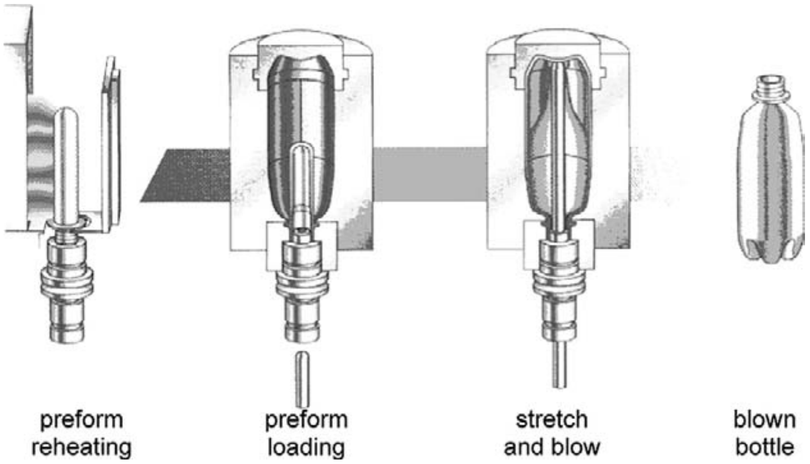
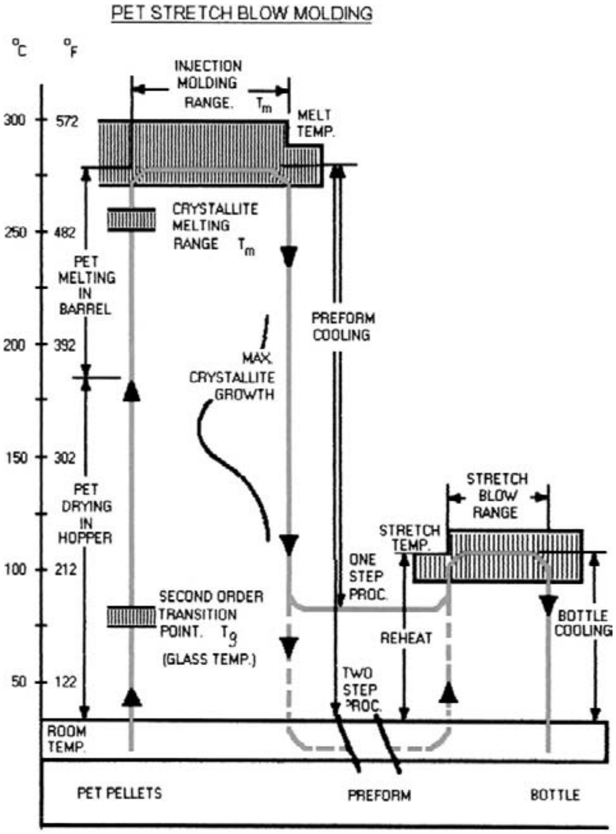


Figure 35.18 Reheat stretch blow molding (RSBM).



(AMERICAN HOECHST - ADAPTED)

Figure 35.19 Thermal history: pellet to bottle.

forced cooling conditions for an additional time. Half-liter water bottle preforms weighing 10—12 g are routinely molded at sub-10 seconds cycle time.

35.1.7 Container and Preform Design Fundamentals

Any container development starts with graphic design. The visual aspects of the entire package including the container, the cap, and the label represent the product and must attract customer attention. Other design aspects are derived from performance criteria. Additional constraints are imposed by materials and process capabilities.

Two distinct groups of bottles are commonly being produced. Group I includes bottles that are cold or warm filled. Group II includes bottles the filling of which involves a thermal-high temperature treatment of the content.

Group I can be divided further into still and pressurized content. The majority of pressurized containers are for carbonated soft drinks and beer bottles with some other products like aerosol containers. Non-pressurized containers are the least demanding from a performance and design point of view; however, the move to lighter-weight bottles resulted in many bottles, which otherwise would not be pressurized, being packaged now with nitrogen over pressure. The pressure in the bottle provides for stiffer behavior for both handling and load support when stacked in storage. It also facilitates the use of light weight bottles in vending machines. Nitrogen capping is used in almost all water bottles and many other products [20].

The carbonation level in the bottles is determined by the amount of CO_2 gas dissolved into the packaged content and is expressed in container volume equivalent. One volume of CO_2 is nominally equivalent to 0.00196 g of CO_2 per milliliter (ml) liquid. The amount of dissolved gas depends strongly on temperature and will stabilize when the partial pressure of the dissolved gas in the liquid is in equilibrium with the gas pressure in the head space. One volume of CO_2 at 15.5 °C will result in one bar pressure in the container. Each additional volume increases the pressure by another one bar. The carbonation level in beer bottles is about 2.5 volumes. Most CSD bottles are nominally at 4 volumes; however, some like tonic water or seltzer may be as high as 5.5. The gas pressure results in creep expansion of the container with time. The creep will increase if the temperature rises, first because of the increase in pressure due to the change in the equilibrium pressure and the thermal expansion of the gas. The loss of carbonation in CSD bottles is a result of both bottle expansion due to creep and permeation losses through the side wall and the cap. There are specific limits for allowable carbonation losses before bottles are deemed unsaleable. The effect of nitrogen use in the bottle is similar except that the pressures used are relatively low, about 0.3 bar, and the egress is slow as the difference in partial pressures between the inside and the outside of the container is small.

Group II includes containers, which, as part of their filling, undergo a thermal sterilization process. There are four thermal filling processes: hot filling, pasteurization, retort, and aseptic filling. The most common for PET containers is hot filling, which is used in the packaging of juice, isotonics, and many of the enhanced water products. Hot fill temperatures are between 81 °C and 95 °C, pasteurization takes place at a lower temperature, and the nominal retort temperature is 121 °C.

For design consideration, group I bottles exhibit a high orientation level while group II exhibits a high crystallinity level.

PET bottles are blown almost exclusively through first injection molding preforms. There is a unique relationship between the preform and the blown container as the most common goal is to reach a uniform wall thickness throughout the container, which guarantees the use of a minimum amount of material.

The advance in Computer Aided Engineering (CAE) using Finite Element Analysis (FEA) methods makes virtual design and development of containers possible. Stress level under top load, internal pressure, or vacuum can be evaluated. Additionally, the blowing process can be simulated, and material distribution and wall thickness throughout the container can be estimated [21,22]. The blow simulation is also used to evaluate and optimize the preform design.

The ability to distribute material from the preform to the bottle is controlled, in addition to the nature of the material itself, by the preform design and the process parameters, namely average preform temperature, temperature profile along the preform, pressures, timing, stretch rod speed, and mold temperature. The preform design is derived from the container shape and the anticipation of the blowing characteristics of PET, most notably PET's ability to undergo strain hardening. Preform expansion starts with the formation of a local aneurism. The section affected blows out and thins out. The thinned-out area stops expanding and stabilizes when the increased strength of the material due to orientation, crystallization, and cooling provides sufficient resistance to the blow pressure. From this point, the edge of the aneurism, where a large change in the thickness occurs, starts to propagate and thin out similar to necking and shoulder propagation in uniaxial stretching of test specimen in a tensile testing machine. The propagation will take place in the radial direction first, because of the prevailing stresses, and then progress longitudinally along the mold [23]. The stretch of the preform, which is mechanically driven, helps lower the pressure needed to initiate the aneurism and also helps shift the material along the bottle, depending on the speed with which it moves.

A major constraint in the design of preforms is that they must reliably be injection-molded, preferably in the shortest possible cycle time. The finish, the open end that frequently includes a thread portion, needs special considerations as it is likely to be the thinnest section of the preform and as it is the last to fill while including critical dimensions.

Figure 35.20 illustrates both a preform and a bottle, identifying the major sections of the preform and pointing out a typical material movement from the preform to the bottle on blowing [24].

There are four distinct sections to the preform: the finish, the taper, the body, and the end-cap. Similarly, the bottle sections are: the finish, shoulder, the body, and the base. There is a loose relationship between the sections of the preform and the corresponding sections of the bottle.

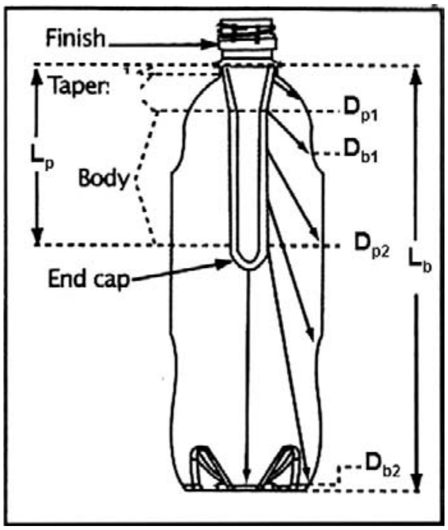


Figure 35.20 Preform to bottle relationship.

For preform design purposes, three relationships are used: the axial or longitudinal stretch ratio (SR_l), the circumferential or hoop stretch ratio (SR_c), and the blow-up ratio (BUR), which are defined below:

$$SR_l = \frac{L_b}{L_p} \tag{35.3}$$

$$SR_c = \frac{D_b}{D_p} \tag{35.4}$$

$$BUR = SR_l \times SR_c \tag{35.5}$$

The BUR represents the area extension ratio from the preform to the bottle. There are variations in defining the preform and bottle variables that are used in calculating the stretch ratios. The outside preform diameter can be replaced by the inside diameter or mid-thickness diameter when calculating the circumferential stretch ratio. The inside preform length can be substituted for the outside length. Another possibility is the use of a contour line from below the finish to the center of the base both on the preform and the bottle in the longitudinal ratio calculations. Figure 35.20 actually defines two different circumferential ratios: one at the upper part of the preform and the bottle and the other at the bottom. It is important to check the stretch ratio for the inner diameter as it may be significantly larger than the outside stretch ratio [25]. Figure 35.21 is a map of stretch ratio for a typical product group of PET bottles. The axial stretch ratio of 1 represents the IBM process.

35.1.7.1 Preform profiling

Profiling the preform either by selectively adding thickness or by programmed heating is a way to improve availability of the material for blowing into critical or deficient

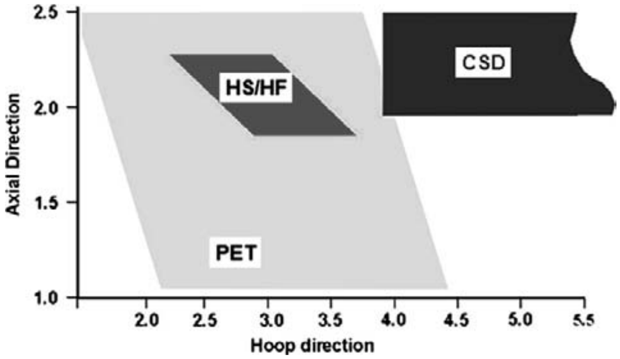


Figure 35.21 Stretch ratios design domain for PET.

areas of the blown article. The underlying principle is that heavy areas stay hotter than thinner areas and hot areas will stretch more readily than the cooler ones.

The ability to program the preform through profiled wall thickness is very important in IBM as conditioning of the preform temperature in the injection cavity is limited due to the physical limitation of independent cooling circuits and especially when trying to minimize cycle time. The longitudinal parting line of the cavity provides a high level of flexibility in the design as it can tolerate negative angles due to adding material on the cavity side. Thermal profiling is accomplished in the mold and/or in the conditioning step in the one-step systems and by-lamp setting along the preform in the reheat oven in the RSBM process.

Circumferential profiling is used in the production of oval or rectangular containers where there is a large difference in the stretch of the two main perpendicular directions. Preferential thickness is created by adding material to the preform on the core side. When a conditioning station is used, additional thermal profiling is possible. In RSBM, circumferential profiling is done through preferential heating. When circumferential programming is used, the preform must be orientated correctly in relation to the bottle cavity.

35.1.7.2 Critical design areas

Critical design areas of the bottles depend on the application. For cold fill, non-pressurized bottles, the base is the main area of concern to avoid drop impact failure. The center of the base and the preform gate vestige remain relatively thick and essentially amorphous due to the lack of any stretch. Two principles guide base design. First, the thickness reduction from the center to the average base thickness should take place within a distance of less than 1/3 of the base radius from the center and second, the gate vestige must be elevated to create a space, known as Base Clearance, off the seating level of the container. Figure 35.22 represents a still or low pressure base.

Figure 35.22 Still liquid and low pressure bottle base.

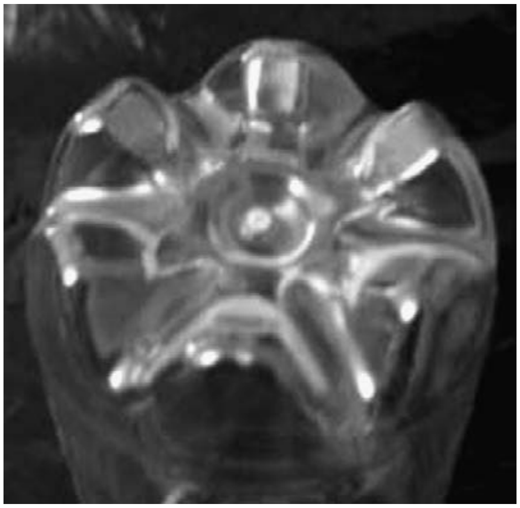


Figure 35.23 CSD pressure base.

Almost all CSD bottles have a footed base design similar to the one shown in Figure 35.23. Champagne type bases have been used in small diameter CSD bottles successfully; however, they were phased out in favor of the footed design, which uses less material in the base. To facilitate the blowing of the champagne bases, a special preform design has been developed by Devtech Labs, which increases the thickness at the end-cap section that creates a step inside the perform [26].

The base must not deform under pressure, and should continue to support the bottle upright, hence, the exact geometric design, especially of the straps between the feet, is very important. Numerous base designs and their attributes can be found in patents. A balance must be struck between the tendencies to place the feet as far out as possible in order to improve bottle stability, and the difficulty to blow them out and keeping sufficient wall thickness at the farthest points.

The base area, in addition to being susceptible to impact failure, can fail catastrophically from environmental stress cracking. Such cracking is a function of exposure to chemicals, which attack the plastics, and a biaxial stress field, which exists in the base. For PET, the main concerns are soaps used on filling line conveyors for cleaning and line lubrication, generally known as Line Lubes, and the hardness-alkalinity of the water. It is therefore important to thin out the wall in the base in the shortest possible distance from the center and build-up as much orientation as possible in this area. The specified base clearance must take into account that it is reduced from the molded dimension due to deformation and bottle creep under the carbonation pressure.

Hot filled packages end up under vacuum after returning to room temperature due to the thermal shrinkage of the content. Regular PET containers will collapse by buckling under the vacuum. Special features must be incorporated into the design to mitigate the effect of the vacuum. The major feature in reducing vacuum stresses in the container is the incorporation of vacuum panels, which move inward preferentially to their surroundings because of the pressure differential between the outside and the inside. A typical design of vacuum panels is shown in Figure 35.24. Most common in round bottles are six vacuum panels. It is not unusual to find reinforcing ribs above and below the vacuum panel section. Round bottles are also designed with a rather heavy rib about their waist line providing stiffness against the possibility of the bottle ovalizing when deforming, as clearly shown in the bottle of Figure 35.25.

Similarly, the base, as shown in Figure 35.26, is designed to pull inward under vacuum. Several ribs bridge from the outside to the center of the base. The reinforcement is needed to prevent deformation of the center under the hot fill temperature as the center remains amorphous and with heavy wall, because only limited stretching reaches this area during blowing.

Recently, several designs were introduced where the vacuum absorption is done exclusively within the base. The impetus to the design is to have a smooth label area and a glass-like look. The first of these designs, shown in Figure 35.27a, was the Powerflex developed by Amcor.

The base design incorporates a relatively easy moving diaphragm which deforms inward as the pressure inside the container becomes negative. The base diaphragm functions so effectively in reducing the vacuum that the final vacuum level in Powerflex bottles is lower than in bottles of conventional hot fill designs. Figure 35.28 shows a comparison of the vacuum evolvement on cooling for glass, conventional round, and Powerflex bottles, all filled at 85 °C.

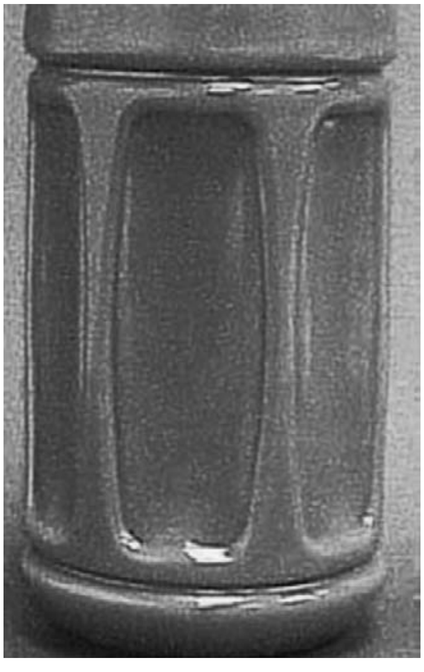


Figure 35.24 Vacuum panels and reinforcing ribs.

Figure 35.25 Hot fill bottle with waist reinforcing rib.

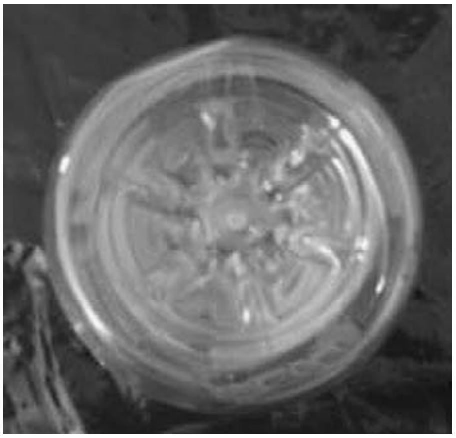


Figure 35.26 Hot fill bottle vacuum base.

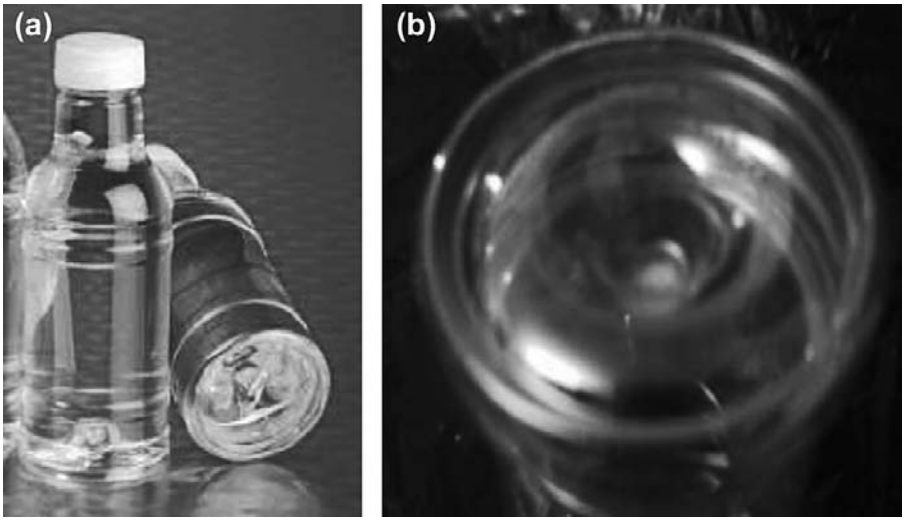
The final vacuum level in the Powerflex bottle is 60% of the conventional bottle and less than a third of a glass bottle.

Wall thickness in all containers is continuously being lowered as container weights fall to reduce material usage. This implies less stiffness for mechanical performance. The most effective way to recover stiffness is through the use of ribs. While plain circumferential or longitudinal ribs are effective, they may not provide the visual effect desired for the package. One way to meet the visual requirements is by disguising the ribs within an overall embossed wall design. A good example of such design is the water bottle shown in Figure 35.29.

35.1.7.3 Finishes and caps

A critical area in all containers is the finish. Unless the applied cap seals the container properly, the package cannot

Figure 35.27 a. Powerflex bottle b. base details.



function as intended. A large variety of caps are used on PET containers. Material-wise, there are metal and plastic caps and even a combination of both. Metal caps in use are crown cap or roll-on caps. Crown cap usage on PET is limited and can be found on some beer bottles. Roll-on caps, used extensively on CSD bottles and phased out by the plastic caps, are reappearing on wine bottles. Roll-on caps start as thin metal cylinders, closed on one end. After being placed on the bottle, a set of rollers iron the metal against the finish threads to form the cap threads and at the same time sealing the bottle. Plastic caps are injected or compression molded to fit packaging of various end-products. Caps can be snapped into the containers or threaded. The design could be a single or continuous tread (CT) or have two or more leads, depending on their diameter. A multi-lead cap requires less of a turn to apply. Many caps have pilfer-proof rings, which are separated from the rest of the cap on first opening, serving as a security measure against product tempering. Beverage caps can be classified by those which must contain positive pressure or vacuum and by the temperature at the time of application and use. One-piece caps are those where the seal is made directly with a feature of the cap shell, like an internal lip, without an additional liner/gasket. Caps can also be classified by the way they interact with the container to create the seal. Some are designed to seal on the top surface of the finish or

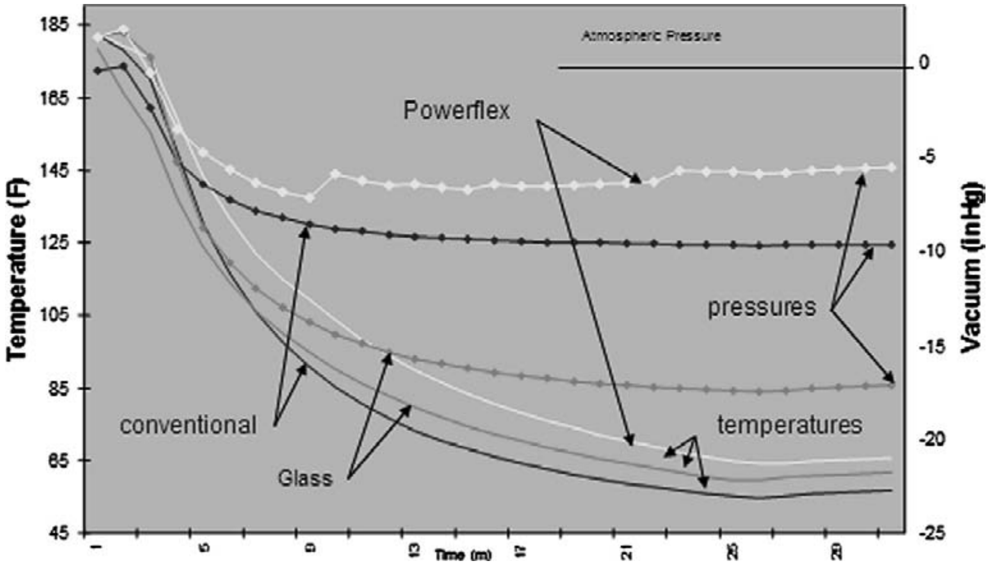


Figure 35.28 Vacuum level comparison of Powerflex glass and standard PET.

Figure 35.29 Creative stiffening of light weight bottles.

alternatively on the outside or the inside. Other caps may have multiple sealing interfaces with the container.

A unique feature of the cap/finish used in CSD bottles is the interrupted threads. The interrupted threads create a vent slot, which provides an escape route for the gas in the bottle immediately on slightly turning of the cap. The force on a standard 28 mm diameter cap, at room temperature, is about 15 Kg$_f$ and can more than double at temperatures reached in storage or while in transport.

In some applications, an aluminum foil is bonded to the container by induction heating and a plastic cover is provided to reseal the package after first opening.

In all cases, the containers as well as the caps must meet stringent design standards for them to work together. There are standard cap designs and dimensions, which provide the basis for most finish/cap designs. The gate keeper for all finish and cap design information in the US is CCMA − Closure & Container Manufacturing Association. Another professional organization ISBT—International Society of Beverage Technologies is also involved in reviewing and consolidating design standards. Similar standards can be found in other geographic regions of the world.

35.1.8 PET Processing

The intention of this section is to review only unique topics in the processing of PET, including material handling, preform molding, and blow molding.

35.1.9 Injection Molding

35.1.9.1 Drying

PET processing, if not adequately dried, will result in significant IV drop. PET pellets equilibrium moisture, as shown in Figure 35.30, depends on the humidity in the environment. The moisture absorbed can reach as high as 0.7% with 80% of the equilibrium level reached in the first two weeks of storage.

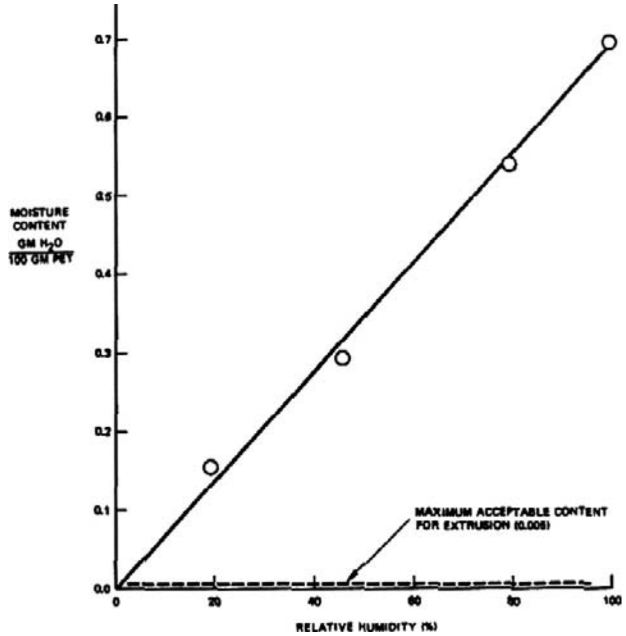


Figure 35.30 PET equilibrium moisture.

Recommended PET maximum moisture for melt processing is 0.005% (50 ppm). PET is typically dried in a desiccant dryer at about 165 °C for a period of 4−6 hours. Raising the temperature can shorten the drying time needed; however, exposure to high temperatures could result in yellowing of the resin. Extremely dried PET will regain moisture, exceeding the maximum moisture level recommended, in a matter of a few minutes as illustrated in Figure 35.31.

The IRD (Infra Red Dryer) provides a new method for drying PET, where heat radiated from IR lamps is used for drying. Of specific interest for PET is the ability of the system to also crystallize, and effectively dry a mixture of pellets and regrind. The IRD overcomes the typical low mix limits applied in order to prevent the entire hopper load from fusing together, once the temperature increase above 60 °C.

The main part of the system is a rotating drum with a spiral channel around the circumference of it. The IR array is mounted at the center of the drum. The resin keeps dropping to the bottom as the drum is turning, hence, continuously mixed and exposed to the IR heat. The spiral channel advances the resin from the loading end of the drum to the exit. Air flow through the drum removes the moisture driven off the resin out of the system. The IRD still utilizes a relatively small hopper dryer downstream of the IR unit to provide for surge capacity and flow regulation with demand. Drying time is very short, a total of one hour and 15 minutes in the IR drum and 45 minutes in the desiccant hopper compared to 4 to 6 hours in standard desiccant dryers. A typical set-up of the IRD system is shown in Figure 35.32.

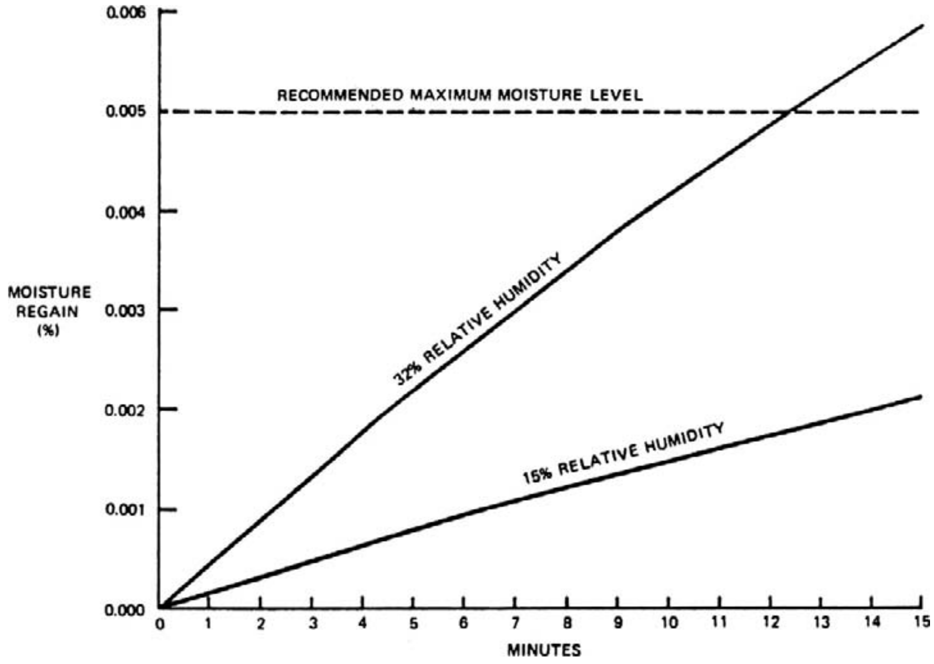


Figure 35.31 Moisture regain rate for PET.

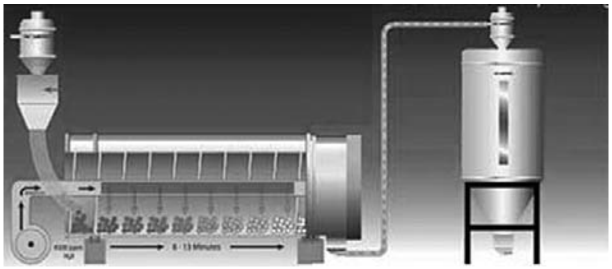


Figure 35.32 IRD drying crystallizing system.

35.1.9.2 Preform cooling

Fast cooling is a must in order to prevent the preforms from crystallizing. Molds are operating at a temperature of about 5 °C. Additionally, post-mold cooling is used on the take-out system of high production machines enabling the shortest in mold cooling time. Preforms stay under forces cooling for up to three additional cycles before being discharged. The Husky Index system provides a unique set-up for preform cooling. The machine is equipped with two or four sets of cores, which index each injection cycle. The preforms stay on the cores after being extracted from the cavity until the cores are in a position to engage the cavities again. Additional cooling is applied from the outside at other index positions.

35.1.10 Blow Molding

35.1.10.1 The blow pressure curve

The preform blowing into a bottle can be best followed up by analyzing a pressure curve, which is a recording of the transient pressure in the blowing article as a function of time. A typical blowing curve for a hot fill bottle, which includes internal post cooling of the bottle, known as Balayage, sweeping, or flushing air, is shown in Figure 35.33.

The curve can be divided into three regions. The first is the formation of the bottle on the pressure curve from the start of blowing to the point where maximum pressure is reached. The second is the cooling or heat setting in the case of hot filled bottles where the curve is at a constant high pressure. The third region on the curve is where the pressure drops as the air is exhausted all the way to atmospheric pressure or with a short interval at an intermediate pressure when internal cooling is applied, again only in the case of hot filled bottle blowing. The intermediate pressure is associated with adiabatic cooling. Final exhaust occurs when the blow valve is closed and the air is released out of the container so that the mold can be opened to release the blown article. The time intervals shown are for a particular preform/bottle case and will be different for other bottles and machine rates. Also, the blow curve represents only the mold locked time, which is only a part of the total cycle. Additional time is required for mold opening, bottle extraction, preform loading, closing, and latching, which account for about 15% of the total cycle.

The drop in pressure in the first region shortly after applying the air corresponds to the formation of the aneurism. The pressure drop occurs because the incoming air cannot flow in fast enough to match the expansion of the preform and the volume increase once the aneurism is formed and starts to propagate. When the bottle reaches the mold wall, the volume stabilizes and the pressure builds up to match the supply pressure.

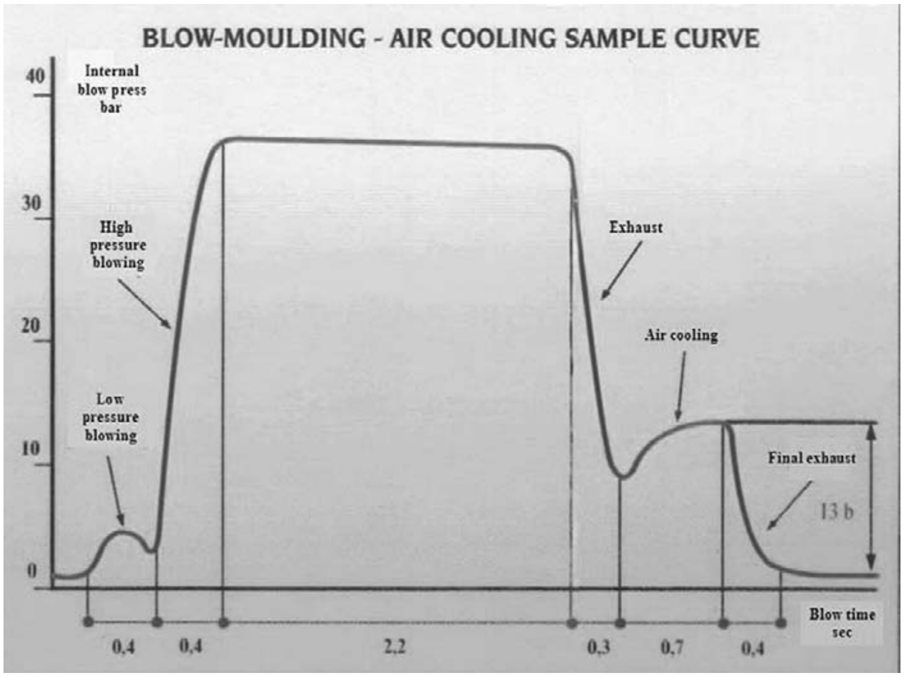


Figure 35.33 Blow pressure curve (heat set bottles).

Blow air is applied first at a low pressure, and is followed by high pressure toward the end of the forming process. As can be seen from the blow curve in Figure 35.33, the expansion of the preform into the bottle happens rather fast. The high rate of strain gives rise to the formation of crazes, also known as stress whitening, which are micro-cracks in the material that scatter incident light, hence appearing white. As pressure is the main driver of the rate of expansion, lowering the initial pressure prevents the crazing from happening. The low pressure is in the range of 7—10 bars, and the final pressure is in the range of 15—40 bars depending on the bottle being blown, the machine, and run conditions.

35.1.10.2 Internal cooling (hot fill bottles)

To maximize crystallinity build-up in hot fill/heat set containers, the blow mold temperature used is very high, about 150 °C. Internal cooling is used at the end of the blow

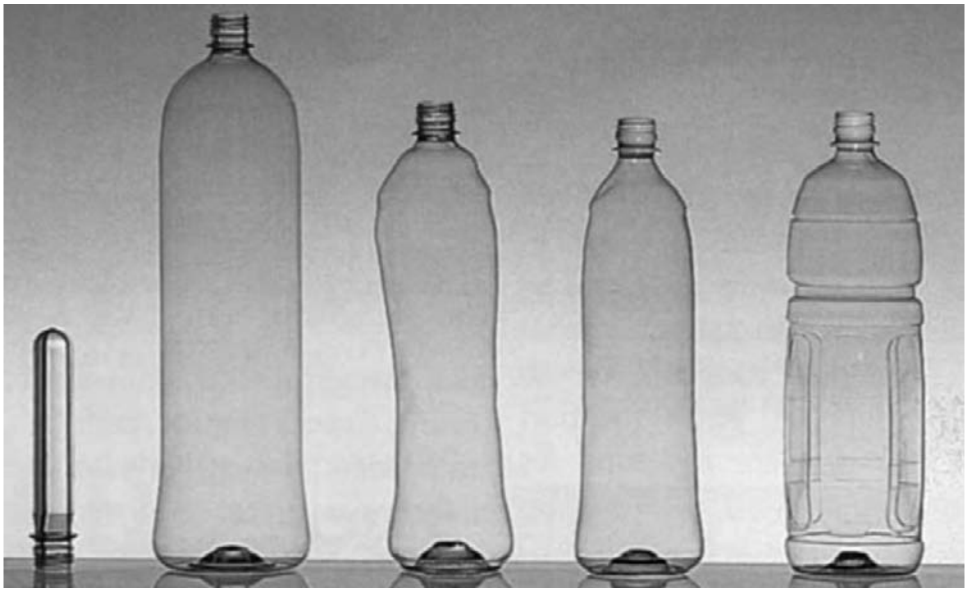


Figure 35.34 Double blow article sequence.

Figure 35.35 Wide mouth jar preform.

cycle. By letting air out of the container while the inlet valve stays open, the pressure drops and the incoming air expands adiabatically and cools the inside of the container. Typical pressure while the purging air is on is about 13 bars. The air is introduced through holes drilled in the stretch rod, which point the air to critical areas of the container.

35.1.11 Special Blowing Processes

35.1.11.1 Double blow

Double blow is a process that produces bottles with higher heat stability than heat set-hot fill bottles covered by Yoshino patents [27,28]. The process involves the additional steps of relaxation and final blow following the initial blowing. The intermediately blown article of the first blow is sized to be about 15–25% larger than the final container size. In the relaxation oven, the intermediate article is shrunk to a size slightly smaller than the final container. The second blow stabilizes the size of the bottle to the designed volume and dimensions. Figure 35.36 shows article progression from a preform to the final product.

The process produces a higher level of crystallinity in the containers. The relaxation step releases the molecules from the remaining oriented domains and enables further creation and growth of the crystalline region. Crystallinity reaches 40–45% vs. the 30–35% level reached in a typical heat setting process. The higher crystallinity increases the barrier and reduces oxygen ingress as indicated in Table 35.4.

35.1.11.2 Wide mouth jars and cans

The production of wide mouth jars and cans follows the same process as any other PET container starting from a preform. However, the use of large size finish, larger than 38 mm, significantly penalizes the productivity of the injection molding of preforms, except in one-step processes. In the injection step of a two-step process, the larger finish preforms must be spaced farther away in the mold, hence, fewer cavities can be arranged at the same mold size compared with small diameter or narrow neck preforms.

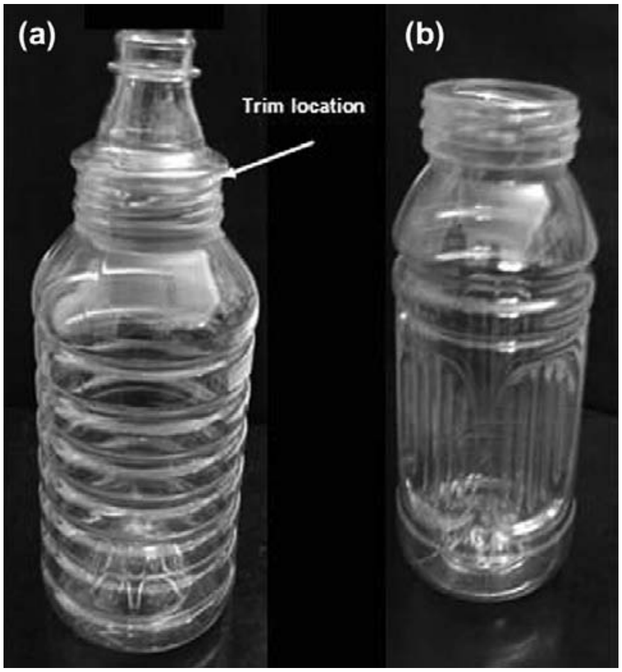


Figure 35.36 Blow and trim wide mouth jars before trimming and finished jar.

While many types of jars are blown in one step, higher production demands shift the manufacturing to a two-step process. Wide mouth preforms have a conical section, as shown in Figure 35.35, which replaces the body of the preform or is a transition to the conventional body section. In extreme cases, the preforms are just the finish and a flat wall, perpendicular to the finish.

An alternative process is the Blow and Trim process. In this process, preforms are narrow neck. The blown article is the wide mouth container plus a moil section on top, which is trimmed off in a subsequent step. The finish is blow molded, rather than injection-molded, similar to what is done in extrusion blow molding. Figure 35.36 shows on the left the "as blown" article, with the moil and the finished jar after trimming on the right.

35.1.12 Recycling and Sustainability

The use of recycled material is not new in the blow molding industry. Extrusion blow molding, which involves trimoff and punch-outs of various sections of the blown article, makes it an economic necessity to reuse the material. A large body of experience in using recycled material back into new production has been established over the years. For PET, the use of recycled material from internal plant sources, like un-blown preforms, rejects, and the like, started almost immediately after establishing PET production facilities.

In the beverage industry, the introduction of the first plastic bottles by Coca Cola included a commitment to post consumer recycling (PCR). The bottles were called "Easy

Goer" and the Monsanto product/material name was "Cycle Safe."

In 2008, 650,000 tons of PET was recycled in the US out of 2.44 million tons used. The recycling rate of 27%, highest in recent times, was driven partially by reduction of consumption [29]. The majority of the recycled PET ended in applications other than food containers. Such applications are less likely to produce an economic value as high as returning the materials into food packaging. Notwithstanding the economic value, other outlets for recycled material are a must as not all the material can be converted back to meet the rigorous requirement of food packaging. Typical food grade output of recycling facilities is about 70−85% of the total material input.

While in-plant recycling has to deal only with the thermal history and possible degradation of the material, normally affecting physical performance and color, post consumer recycling presents an entirely different issue especially where the intended end use is food packaging, referred to as suitable for Food Contact Articles. Post consumer recycling must meet not only the general regulations in place for the particular plastics, but must also ensure that the material is safe from any possible contamination encountered while in use as a container.

35.1.12.1 Regulatory approval

The use of PCR material for food contact packaging involves a governmental approval of the recycling process ability to decontaminate the material. In the USA, it takes the form of a No Objection Letter (NOL) being issued by the FDA after reviewing submitted data of decontamination. The FDA lists about 125 NOL, all but a few are for PET. The first PET NOL was issued in 1991 to Hoechst Celanese, an early supplier of PET resin.

To prove effective decontamination, the FDA requires a "Challenge Testing"—a controlled contamination of PET before getting treated in the process under review followed by analytical testing, which is capable of detecting the contaminants at very low levels [30]. Typical contaminants and their concentration are listed in Table 35.6, taken from the FDA website.

The FDA makes other allowances for the use of recycled material like restricted source, the position of the material in the structure of the package, the type of food being packaged, and limitation of use [30].

35.1.12.2 Processing post consumer recycled PET

Recycled material is typically delivered in bails. Beside the PET containers, there are caps, labels, and glue. The process steps include extraction of obvious contamination, electronic sorting for PET or other known rejects like PVC, sorting and diverting by color, followed by grinding and washing, separation of the various materials, and ultimately drying and removing grinding dust, ending up with the PET flake. Residual PVC, even in very small amounts, label glue, and other contaminants will contribute greatly to yellowing of the material, limiting its further use.

Table 35.6 Contaminants surrogate for decontamination evaluation

Contaminant	Concentration
Chloroform (volatile polar)	10% v/v*
Toluene (volatile non-polar)	10% v/v
Benzophenone (non-volatile polar)	1% v/v
Tetracosane or lindane (non-volatile, non-polar)	1% w/w†
Copper(II) 2-ethylhexanoate (heavy metal)	1% w/w
Balance: 2-propanol (as solvent for Cu(II) 2-ethylhexanoate) Hexane or heptane (as overall solvent for cocktail)	10% v/v 68% v/v

**v/v − volume of contaminant per unit volume of entire cocktail.*
†w/w − mass of surrogate per unit mass of entire cocktail.

The washing process can be followed by various types of cleaning processes. One is a chemical process, which etches the surface of the material to remove the previous contact layers [31]. Decontamination can be accomplished by applying high vacuum in combination with high temperature. It can be accomplished in a vented extruder, mostly of multi-screw configuration. Another system is the Vacurema manufactured by Erema, where PET flake is heated through shear and under vacuum in a specially designed reactor. On leaving the reactor, the flake is fed into an extruder with a pelletizing or a sheet line on the downstream. The LNOc recycled PET production process, from Phoenix, starts with intensive grinding resulting in very small particles with very high surface to volume ratio, enabling the removal of contaminants through de-volatizing at conditions similar to those found in a typical PET dryer. To facilitate the easy feed of the material into molding machines, the powder-like particles are compacted into pellet-size agglomerates.

Melt processing of PCR results in further lowering of IV. The IV loss can be recovered by solid stating of the material after cleaning. Buhler, a supplier of solid stating equipment, offers complete systems, including melting, re-pelletizing, crystallization, and solid stating. Additionally, Buhler has developed a system, which combines flake cleaning and solid stating in one step eliminating extrusion melt processing [32]. Other options that compete with solid stating to raise IV are chain extenders and modifiers [33].

PET can also be de-polymerized through hydrolysis, glycolysis, or methanolysis to recover DMT, PTA, and EG for use in polyester production. PET burns very cleanly and 40−45% of the energy used in making containers can be recovered (45 MJ/kg) [34]. Another environmental approach is to make PET degradable through the use of additives, which provide for the polymer break-up in land fill.

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