# 19

# Fillers in Different Products

In product development, fillers play various roles as outlined in the Chapter 1. In this chapter we will analyze

- Current changes in the market which create new opportunities
- Reasons for filler addition
- Potential improvement expected from filler addition
- Practical results of fillers use

## 19.1 ADHESIVES

Adhesives have very broad range of performance requirements. The performance spectrum ranges from pressure sensitive products where almost minimal adhesion is required, to extremely high performance adhesives with strength equivalent to that of metals. But the scope of the adhesive's performance goes well beyond adhesive strength. Flowability, force to adhere and mechanical, thermal, electrical, barrier, and optical properties as well as chemical and weather resistance and rheological behavior all must be considered in adhesive formulations. These essential parameters are discussed below from the point of view of the influence of fillers.

In the adhesive industry, the balance between tensile properties and adhesion is the most important part of the design process. Structural adhesives are expected to fail cohesively, a convincing argument to the user that the adhesive was designed for a particular substrate. Fillers frequently increase hardness and have reinforcing properties, so the choice of the filler and its concentration are often critical. In addition, adhesion may also be affected by the filler's presence either due to absorption of coupling agents, change in rheological properties (reducing mechanical adhesion), or changing moisture permeability which affects hydrolytic changes at the interphase.

Sepiolite was subjected to a thermal treatment which removes crystallization water at 500°C and constitution water at 850°C.[1] When these changes occur, they are accompanied by crystal folding which introduce substantial changes in the structure and interaction capabilities of sepiolite. Treated and untreated sepiolites were used in the preparation of a polyurethane adhesive to determine if the modification impacts the properties of the adhesive such as its interaction with polymer essential for its performance in adhesive. Figure 19.1 shows the effect of treatment

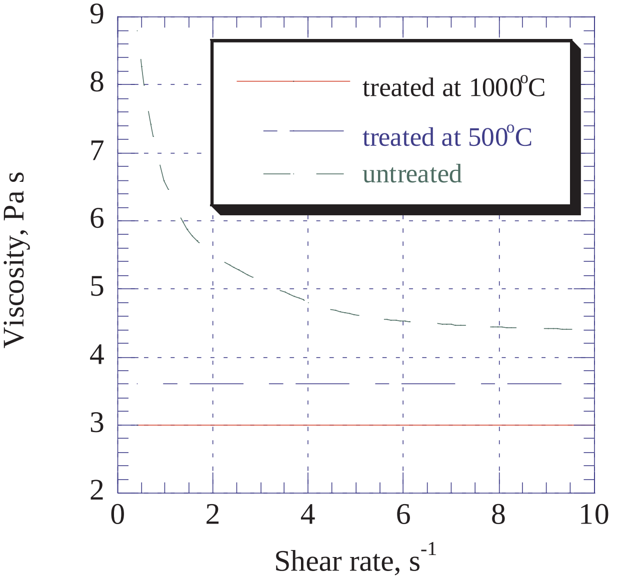


Figure 19.1. Viscosity of PU adhesive containing treated and untreated sepiolite at 10 wt%. [Data from Torro-Palau A, Fernandez-Garcia J C, Orgiles-Barcelo A C, Pastor-Blas M M, Martin-Martinez J M, *Int. J. Adhesion Adhesives*, **17**, 1997, 111-9.]

on viscosity. Treatment and its temperature had an impact on the rheological characteristics of adhesive. Sepiolites treated at 500 and 1000°C imparted Newtonian properties to the adhesive whereas non-treated sepiolite imparted non-Newtonian characteristics (pseudoplastic). Since adhesives are usually expected to have thixotropic behavior (making them easier to apply and eliminating sag after application), the treatment of sepiolite was not beneficial to the adhesive. The tensile strength of the adhesive was also reduced by the thermal treated sepiolite as was elongation. Figure 19.2 shows the effect of the treated sepiolite on green and post-cure peel strength.[1] Green strength is reduced because the treated filler does not have the ability to interact with polymer which otherwise would have formed a network which, in turn, would have contributed to viscoelastic properties of the uncured adhesive. The peel strength of the cured adhesive was improved over the unfilled polyurethane because the filler reduces tensile strength which makes the adhesive less rigid. The green strength of polyurethane adhesive containing fumed silica was increased with small amounts of filler (5-15 wt%) but decreased on a further increase of filler.[4] The peel strength of cured PU adhesive increased as silica concentration from 15 to 50 wt%.[7] These studies indicate that fillers are useful in the regulating and balancing the properties of adhesive to produce increased adhesion.

In a pressure sensitive adhesive, fillers may affect properties such as cohesion, cold flow, and peel adhesion. Most fillers increase cohesion and reduce cold flow. In some formulations, even a small addition of filler dramatically reduces peel ad-

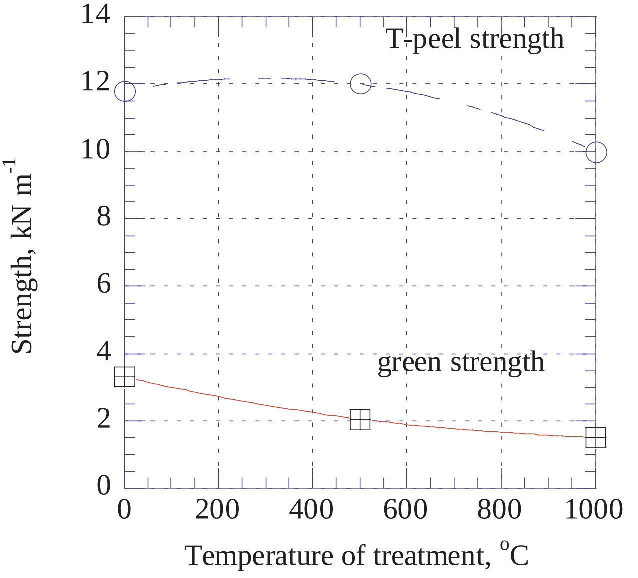


Figure 19.2. Peel and green strength of PU adhesive containing sepiolites treated at different temperatures in an adhesive for roughened rubber. [Data from Torro-Palau A, Fernandez-Garcia J C, Orgiles-Barcelo A C, Pastor-Blas M M, Martin-Martinez J M, *Int. J. Adhesion Adhesives*, **17**, 1997, 111-9.]

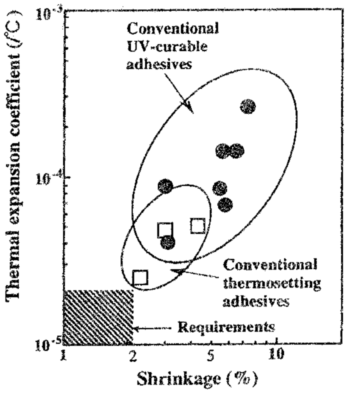


Figure 19.3. Thermal expansion coefficient of epoxy adhesive vs. shrinkage. [Adapted, by permission, from Murata N, Nishi S, Hosono S, *J. Adhesion*, **59**, Nos.1-4, 1996, 39-50.]

hesion either because of interaction with the tackifier or because filler particles at the surface reduce the area of contact between the adhesive and the substrate. Glass beads are used to regulate peel adhesion because of their ability to reduce surface contact.

Studies of UV curable adhesive show how an adhesive may be obtained which has a low thermal expansion coefficient and low shrinkage. Figure 19.3 compares adhesives with performance requirements. The product developed in this study has a shrinkage of 1.2% and a thermal expansion coefficient of less than $2\times10^{-5}/^oC$. A spherical quartz filler, surface treated with a silane, was used in this adhesive. The high degree of transparency to UV enabled the quartz to impart these excellent properties.[8]

A model was developed to analyze the conductivity of materials filled with conductive particles.[9] This model was compared with experimental data for four commercial adhesives containing silver flakes. It was discovered that the resistivity is higher in the planar direction (thin films) than in three-dimensional space. Figure 15.5 shows the effect of carbon fibers obtained from different processes on the electrical conductivity of epoxy adhesive.[2] Vapor-grown carbon fibers gave the best increase in conductivity.

## 19.2 AGRICULTURE[10-12]

Greenhouse and mulch films are the most commonly used synthetic film products in agriculture. In both technologies, fillers play an important role. In greenhouse film, calcinated clay is added at up to 10 wt% to change infrared absorption characteristics.[10] The filled film has better insulation characteristics. It transmits less infrared during the day and emits less infrared during the night which makes the temperature in the greenhouse more uniform. The same physical principle is used for laser marking. Unfilled polyethylene film is not suitable for laser marking since light is readily transmitted. In the filled film, a sufficient amount of energy is retained by the film to cause charring.

Mulch film prevents evaporation of moisture from the soil, suppresses weed growth, and prevents soil erosion. In order to perform these functions, mulch film must have a high opacity, weather stability, and proper mechanical characteristics. Carbon black is used to increase UV stability and obtain high opacity. The performance of carbon black in this application depends on the grade, amount, and dispersion. The grade is important because it determines particle size and particle chemistry. Particle size affects the absorption/reflection ratio. Smaller particles tend to absorb more light and coarser particles tend to reflect more light. The surface chemistry of carbon black affects its ability to scavenge radicals which constitutes part of the mechanism by which carbon black works as a UV stabilizer. By choosing the appropriate grade of carbon black, stabilization can be increased by a factor of 4 to 5.[11] The proper choice of grade, concentration, and dispersion method will allow the elongation of the film to be increased by up to 10 times.[11]

The concentration of carbon black is important for both UV protection and opacity (required to prevent the growth of weeds). The amount of carbon black required for a certain level of opacity depends on the film thickness. The same volume of carbon black per unit area must be maintained in the film as the film thickness is reduced in order to retain the same degree of opacity. For a 30 μm thick film this concentration varies between 4 and 9 wt% depending on the type of carbon black used.

Dispersion is also an important factor. Light reflection depends on the surface area of carbon black after dispersion. If large agglomerates are present light reflection (and UV protection and opacity) is reduced. It is a frequent practice to use fully dispersed masterbatches offered either by carbon black manufacturers or compounders to achieve good results.[12]

## 19.3 AEROSPACE

Aerospace uses a large number of plastic components, most of which contain fillers for various reasons. It is difficult to follow the development in these components due to the proprietary nature of the business. Current legislative developments are likely to cause substantial changes in this sector. FAA Regulation FAR25 restricts materials to those which will satisfy fire protection requirements. In the past, regulations allowed many materials which contained organic and inorganic flame retardants for use in aerospace applications. With the new regulations, only certain polymers qualify for the application. These are Nomex and glass fiber laminates based on phenolics and polyketones. These changes reduce the number of flame retarding fillers which can now be used.

In another, relatively new, development, a high purity thermal carbon black was used as a component of an adhesive lining used in the construction of solid-fuel rocket motors and space shuttle motors.

## 19.4 APPLIANCES[13-15]

The use of plastic materials is predicted to grow by 3.5%/year which is higher than the growth predicted for appliance sales (1.8%/year).[13] The major growth with the appliance sector is in thermoplastics (5.4-5.9%/year) followed by styrenics. There is also large change in the type of materials that are being used (replacement of one plastic by another). The largest gains are expected in polyethylene (8.8%/year), polycarbonate (8.7%/year), and polypropylene (6%/year).[13]

Electrostatic applications and fire retarding formulations have yet to become the major focus in these applications. Only in the USA and Canada is a specific fire rating a requirement. In Europe, fire is still mostly prevented by the design of the electrical circuitry rather than the plastic design. Only in some applications, close to the source of possible fire ignition are some flame retarded plastics used.

The major impact on this industry comes from two regulations: elimination of CFCs from foam production and coming requirement in the USA to reduce power consumption by 33%. These two in combination require better insulation materials and constitute the largest opportunity in this sector.

Two studies were reported on the improvement of insulating properties of foams in one case through the use of xerogels[15] and in the other through better dispersion of filler combined with a better uniformity of foam structure.[14] The theoretical calculations supported by the experiment show that decreasing the size of voids increases the k-factor or decreases thermal conductivity.[14] In filled systems, the improvement comes from absorption of radiation and low thermal conductivity of the filler. Studies on filled foam concentrated on the reduction of the radiative losses.[14] Typically, 2 wt% carbon black is added to improve the thermal properties of foam but carbon black is difficult to disperse. A special dispersing agent was developed which resulted in a more uniform structure of foam (see Figure 13.5) which obtained a sufficient decrease in thermal conductivity to fulfill the requirements of the new regulation and decreasing the power consumption by 33%.[14]

## 19.5 AUTOMOTIVE MATERIALS[16-24]

Three major initiatives affect the automotive industry now and in its future. These are fuel conservation (lighter car), ease of assembly and finishing, and post-use recycling. In addition, as always, vehicle components must be cheap, esthetic, and durable. Fillers have obviously many roles to play in fulfilling the demands of this large and powerful industry. In the area of automotive safety, fillers can contribute most to fire retardancy and elimination of static charges. However, these are not yet to priority requirements for the industry. Fire retarding of car interior is a lower priority than the engine compartment where fires may be caused by low performance of wiring and the dimensional instability of plastics. The temperature in some areas of the engine compartment has increased in recent years by about 30°C to 150°C which makes thermal stability and dimensional stability of materials a much more demanding requirement. There are no specific regulations governing the flammability of car interior.

Static electricity also causes safety concerns. Regulations to condense fuel vapors rather than releasing them to atmosphere has created new components in which fires can start. In the US market, conductive plastics such as hoses and filters are in use to minimize static electrical discharges. Either carbon black or steel fibers are used in these products. It can be expected that new parts and materials will become available in the future. Other areas which require conductive plastics include the equipment installed to monitor and control brakes, engine, environment, suspension, etc. These are electronic devices, important in their functions to the safety of car operation, which are sensitive to static charges. All the areas surrounding these devices should be designed to prevent static charges from forming and accumulating.

The major use of fillers is in parts of body and in the car interior. Here, the major goals are as outlined above. The production of lighter but mechanically strong materials is, in most cases, the major requirement. There is one exception. This is the casing for the compact disc and tape players which are required to be heavy to perform their function. In the past this element was manufactured from metals. Introduction of plastic material required that a high density filler be used to bring the density of the part above 3 g/cm$^3$. But in most cases, weight is reduced by metal replacement and reinforcement of plastic material to decrease the thickness without losing mechanical performance. Figure 19.4 shows that gains in mechanical properties of automotive TPOs can be best achieved by optimization of the mixing time. Large gains in properties were obtained when mixing time was increased to improve distribution of polymer phases and dispersion of fillers.[18] In talc concentrations from 0 to 40 wt%, there was no obvious indication that an increased filler content requires longer mixing time. It was found instead that a certain minimum mixing time is required to optimize materials properties. Filler choice and the orientation of the filler particles are the other important determinants of mechanical performance.[19,21]

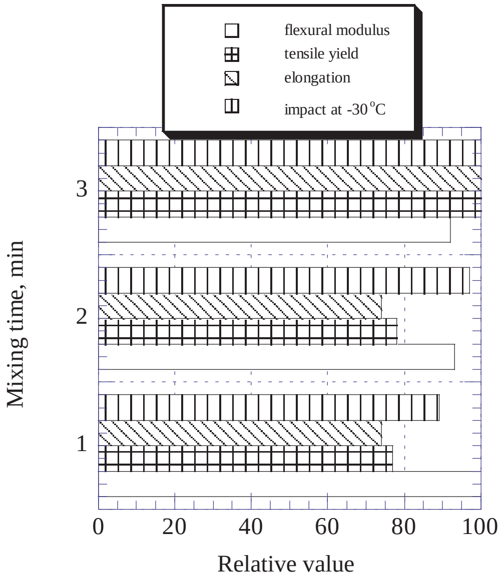


Figure 19.4. Mechanical properties of TPO vs. mixing time. [Data from Lau E, Goodman J, *J. Elastomers Plast*., **25**, No.4, 1993, 322-42.]

Surface finish of parts is another important source of economic advantage. Surface roughness depends on the orientation of glass fiber. The process was optimized using data from surface smoothness measurements.[19] A conductive RIM was developed to produce material ready for electrostatic painting without the need for further surface preparation.

The choice of plastic material for automotive parts is influenced by its potential recyclability. One recent example[16] shows that the use of recycled material gave the added benefit of an approximately 10% reduction in weight. This involved the use of recycled material in the Chrysler Neon rear spoiler. Major considerations in this respect are thermal and UV stabilities of the reprocessable material combined with low weight and mechanical protection performance characteristics.

## 19.6 BOTTLES AND CONTAINERS[25-27]

Bottles and containers do not use large quantities of fillers because of the predominant need to see the content of these packages. But this is gradually changing because of several requirements, such as protection of the contents from the effect of light, esthetic reasons (color may give the required distinction to the package), the need to use recycled materials, and to enable laser marking.

Many food products lose vitamins and undergo other compositional changes on exposure to light. Fillers or pigments with sufficiently lower light transmission may be added in small amounts to help preserve the contents. A better understanding of filler technology together with the availability of more sophisticated processing equipment enables containers to be made with filler particles oriented to give the best light barrier and improved mechanical properties.[25]

The growing use of recycled materials, especially these which contain mixed plastics requires fillers that will compatibilize these mixed polymers so that mechanical properties can be retained or improved.[26-27]

For laser marking to be effective, the energy of the laser beam must be retained in the material to cause local charring. Properly selected fillers are sufficiently opaque to absorb radiation and aid the process of marking.[10]

## 19.7 BUILDING COMPONENTS[28-30]

Several sections of this chapter discuss building materials (hoses and pipes, pavement, roofing, sealants, siding, and waterproofing). Here, we focus on wall materials and insulation in various extruded and molded profiles. Numerous polymers are used for these two applications. They include polystyrene, phenolic resin, polyvinylchloride, and polyurethanes for insulation purposes and polyvinylchloride, polyurethanes, and polyesters for wall systems and structural elements. The major methods of production include molding, extrusion, and pultrusion.

The major roles of fillers in these applications is to provide reinforcement, fire retarding properties and to lower the cost. Development work on plastic materials is ongoing and the goal is to develop technology which is inexpensive but can perform under adverse conditions. These studies have intensified recently given the increased worldwide demand for new houses. China is an extreme example. It needs 100,000,000 houses to be built in the next five years.

There is a huge market for fillers in building applications. Studies seem to indicate that the primary focus will be on local materials because low cost remains an overriding requirement. Even such a simple material as sand can be used advantageously.[30] Polyvinylchloride has improved resistance to ultraviolet light when sand is used as a filler. The type of sand is important therefore local materials must be studied for the desired applications.

Wood products such as wood fiber and flour as well as other ground natural materials (corn combs, barks, etc.) have also been tested for these applications. They are locally available, inexpensive and composed of material similar to that which is being replaced. Studies show that these materials, rather than being considered scrap, can be useful as a component of building materials.

## 19.8 BUSINESS MACHINES

This sector is a substantial consumer of plastics and fillers. The major requirements include low weight, rigidity, impact strength, aesthetic appearance, dimensional stability, high heat distortion temperature, UV resistance, and flame retardancy. Again, fillers can contribute to the performance of these products. The major polymers used are ABS, POM, PPO, and PS. Lately, new advances in PVC blends have improved the heat distortion temperature and, they too, are finding applications in this equipment. With its inherent flame resistance and good aesthetic appearance, PVC has become an important player in this market.

Several groups of fillers are very important in this sector. They include reinforcing fillers, fillers which may improve heat distortion temperature, and flame retarding additives. Recently, major improvements have been achieved in blending technology and in the incorporation of reinforcing fillers. The low weight of laptop computers is one of the results of these developments. When computer cases were first produced, the thickness of the case wall was 6 mm. Now it barely reaches 2 mm.

There are many applications for fillers in which they are required to impart conductivity to protect sensitive electronic components. Also, the paper handling components of printers, copying machines, etc. require the capability of dissipating electrostatic charges which would otherwise cause paper jams.

## 19.9 CABLES AND WIRES[31-32]

Of the polymers used in the wire and cable industry, three polymers: polyvinylchloride, polyethylene, and chlorinated polyethylene make up to 95% of the usage. Two of three contain chlorine which gives them substantial fire retarding properties. Combination of this intrinsic property with small additions of antimony oxide have provided a system which has been in use for decades. Recently, and partly as a result of the pressures from groups concerned about the environmental impact of chlorine, the emission products from these materials are being evaluated. Especially, these cables which are used in enclosed spaces are under scrutiny and tests are being conducted to evaluate the harmful effect of hydrogen chloride on people and electrical equipment. Highly corrosive gases are evaluated based on their effect on control systems during a fire.

Manufacturers of various fillers continue studies on alternative systems. Most antimony oxide used as a fire retardant can be replaced by a combination of zinc borate without the loss of other properties (in some cases improvements are reported). Another option is to use the same filler systems which are used in polyethylene insulated cables and wires. These are based on magnesium hydroxide and aluminum hydroxide. These systems perform as flame retardants but require a high filler concentration which affects jacket resistance and mechanical performance. Recently, new coated grades have been developed which can be used at up to 65 wt% without the loss of properties or productivity (extrusion rates 2,500 m/min of cable are possible).[31]

Other systems include the mixture of huntite and hydromagnesite which offers relatively good performance. Also, new grades of clay have been developed to improve the resistance of jacketing where large additions of fire retarding fillers affect the electrical insulating properties.

Resolving these issues is important although the current performance is very consistent and satisfactory the environmental and safety issues must be addressed.

There are several polymeric alternatives such as EPDM, EVA, and fluoropolymers which are used for some applications. EVA can be processed with flame retardants free of chlorine. A relatively new product – polyketone – has potential in this application in the future.

## 19.10 COATED FABRICS[33]

Fillers have not played major role in the design of coated fabrics. They have been used to regulate rheology and improve the cost/performance ratio. This is no longer a growth area, so it is unlikely that new developments in high performance fillers will be applied to coated fabrics.

However, three areas: fire retardancy, dirt pick up, and surface tack do exist as outstanding issues in this field and solutions to them exist. Perhaps future work will address these problems.

## 19.11 COATINGS AND PAINTS[34-54]

Paints and coatings are based on traditional technology and there is ample experience in formulating products throughout the industry. Still, recent developments in new fillers and resins can and do contribute to an improved technology of production and better products. Fillers are added to coatings and paints for a variety of reasons, including cost reduction, optical properties (hiding power, color, texture), surface finish (matting additives), electric properties (conductive paints), permeability to water and gases, chemical resistance, UV resistance, rheology (prevention of sag and good application properties). Mechanical properties are seldom addressed by fillers which seems unusual when compared with other products discussed in this chapter.

Still, it is important that fillers interact with the polymer (binder) for various reasons. One is the rheological characteristic of paints. Figure 19.5 shows that many processes may affect how a filler behaves in the system.[35] The simple drying of aluminum hydroxide prior to use contributes to an increased paint viscosity. It should be noted that aluminum hydroxide loses water at 220$^o$C, therefore drying at 80$^o$C may only remove the water adsorbed on the surface of particles. But this is apparently sufficient to increase the interaction with the binder since, when the partially dried filler is added, viscosity almost doubles. Similarly, treatment with 1% triethoxymethacryloylpropylsilane, MPS, contributes to an increased viscosity. This data shows that the same filler can be readily modified to give a variety of different results.

Figure 19.6 shows that interaction involves not only a chemical interaction but can also be physical in nature. Here, different acid/base interactions of different grades of titanium dioxide are involved. The choice of the type of titanium dioxide results in a different thickness in the layer of adsorbed binder. This layer increases the sizes of particles and changes the amount of fillers contributing to the maximum packing density. The calculation of maximum packing density is complicated by

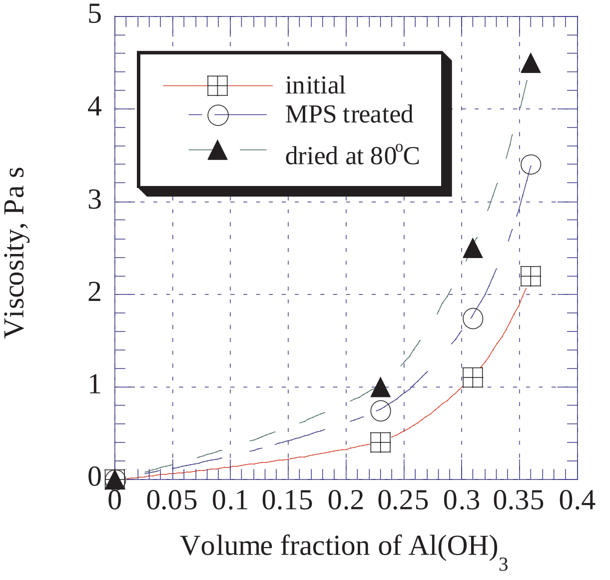


Figure 19.5. Viscosity of polyester coating vs. volume fraction of $Al(OH)_3$ subjected to various treatments. [Adapted, by permission, from Balard H, Papirer E, *Prog. Org. Coatings*, **22**, No.1-4, 1993, 1-17.]

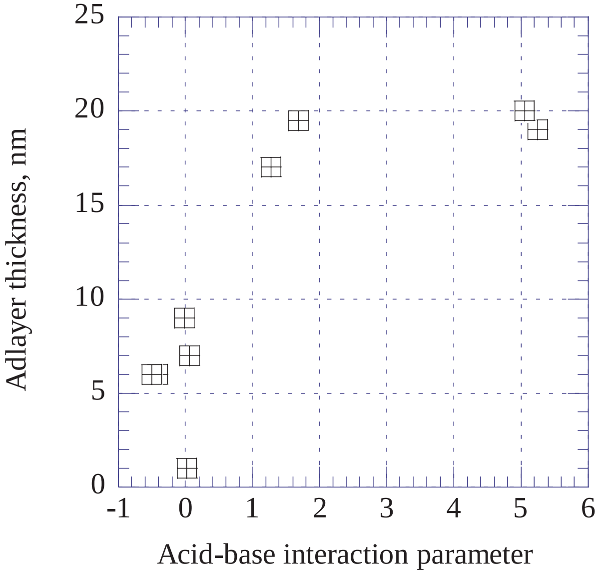


Figure 19.6. The thickness of a layer of adsorbed chlorinated polyethylene on a surface of titanium dioxide vs. the acid/base parameter of the titanium dioxide grade. [Adapted, by permission, from Hedgus C R, Kamel I L, J. Coatings Technol., 65, No.821, June 1993, 49-61.]

the fact that the thickness of the layer is not constant for a given filler but depends on the concentration of filler (Figure 19.7).[36]

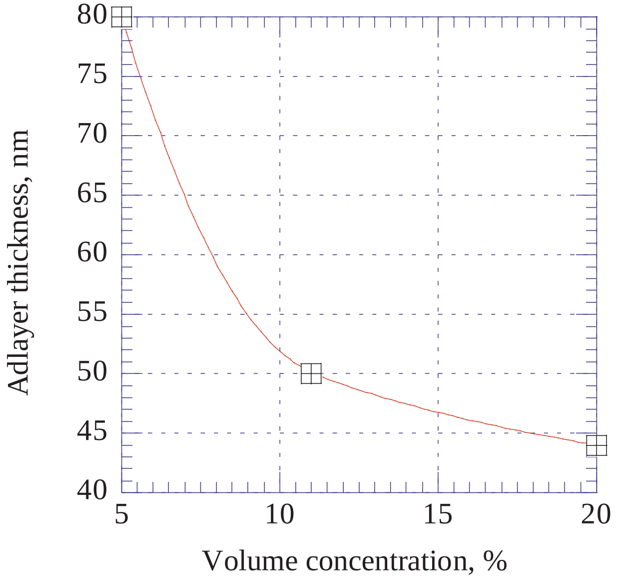


Figure 19.7. The thickness of a layer of adsorbed PVC on titanium dioxide vs. its concentration. [Data from Hedgus C R, Kamel I L, *J. Coatings Technol.*, **65**, No.821, June 1993, 49-61.]

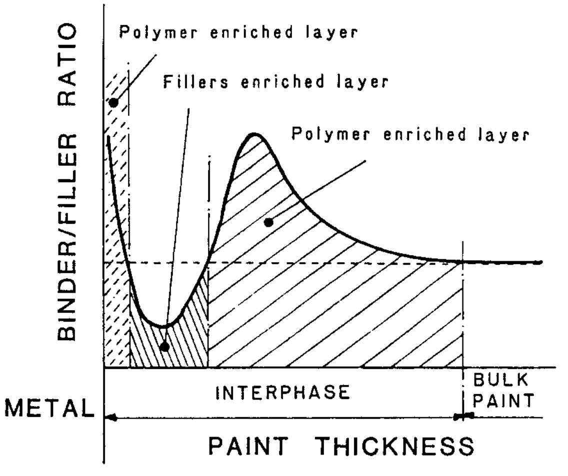


Figure 19.8. Paint/metal interphase model. [Adapted, by permission, from Roche A A, Dole P, Bouzziri M, *J. Adhesion Sci. Technol.*, **8**, No.6, 1994, 587-609.]

The amount of titanium dioxide and its type affects the permeability of the coating. With increased permeability, the corrosion protection of a steel substrate is decreased. The pigment level was increased from 6.4 to 28 vol% and produced a corresponding reduction in corrosion resistance.[37] In this study, the type and quantity of titanium dioxide did not have an effect on the adhesion of the coating to the substrate.[37] Figure 19.8 provides the reason for this lack of effect on adhesion. In this study, a set of coatings was analyzed for their adhesion to metal substrates.[41] Figure 19.8 complements the information given in Figure 7.16 which shows a distribution of filler particles across a cross-section of paint. The layer which is responsible for adhesion is depleted of filler.

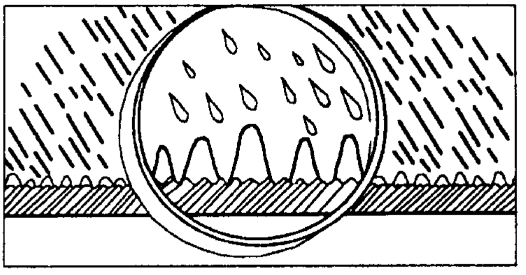

Figure 19.9. Surface spraying with white-hot stainless steel fibers. [Adapted, by permission, from Knowles J, *Polym. Paint Col. J.*, **185**, No.4366, 1995, 26-7.]

Figures 19.9 and 19.10 show two unusual applications of fillers in coatings. Figure 19.9 shows a schematic diagram of the surface of metal (e.g., a pan) on which white-hot particles of stainless steel fibers are sprayed to prepare the surface for a nonstick coating. In the past, these coatings were known to have a limited durability. Durability could be increased by a change to the surface through welding the fibers to the surface. These fibers increase the mechanical adhesion and the durability of coating.[45] The goal of the study illustrated in Figure 19.10 was to determine if ground glass from bottles can be recycled as a paint filler.[50] The paint obtained had a refractive index close to that of both the binder and the ground glass. As long as ground glass was added in quantities below the critical pigment volume, the paint was fully transparent. Above this concentration the paint became opaque.[50]

A primary objective in paints (and paper) formulation is to obtain opacity in the most economical way. In paints, this leads to the search for fillers which may replace some titanium dioxide while still retaining the required degree of opacity.

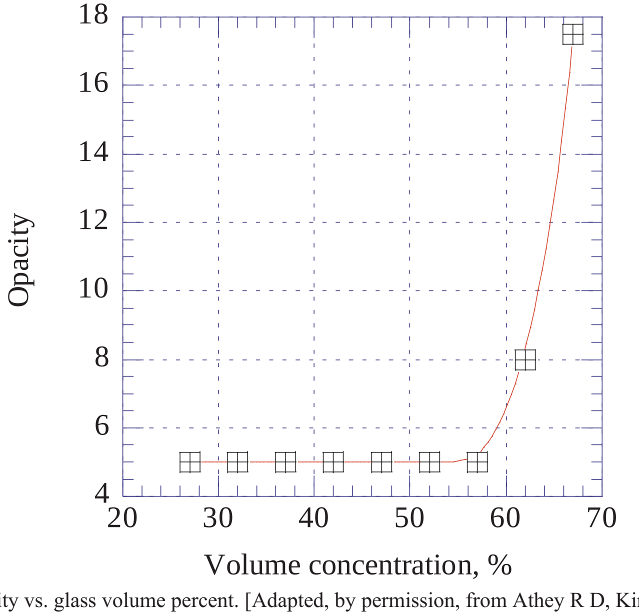


Figure 19.10. Opacity vs. glass volume percent. [Adapted, by permission, from Athey R D, Kirkland T, Lindblom G, Swoboda J, *Eur. Coatings J.*, No.11, 1995, 793-8.]

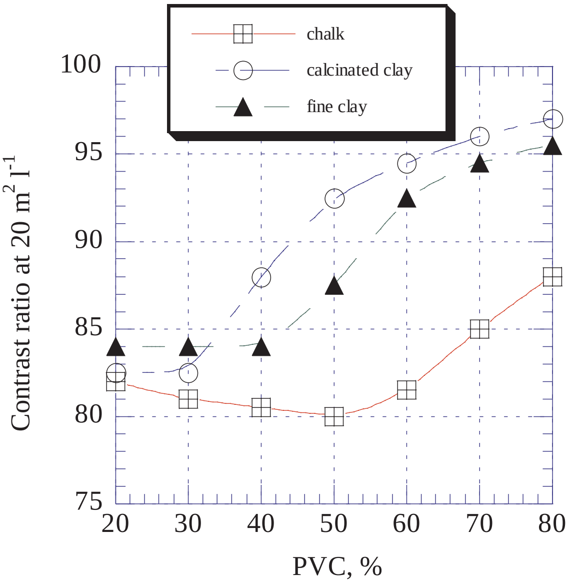


Figure 19.11. Contrast ratio vs. percentage PVC. *Courtesy of ECC International, St Austell, UK* in McGuffog R M, **Clays as Extenders in Decorative Paints**. *ECC International*.

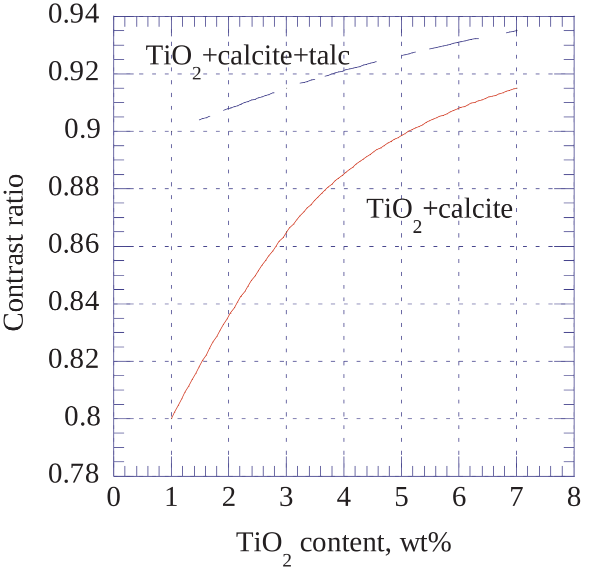


Figure 19.12. Contrast ratio vs. titanium dioxide concentration. 10 wt% calcite (out of 40 wt%) was replaced by talc. *Courtesy of Luzenac, Toulouse, France.*

Figure 19.11 shows one of the candidate products for such replacement.[53] Calcinated clay is used as an extender in paints. Chalk has very limited effect on opacity.

Figure 19.12 shows that the replacement of calcite by the same amount of talc improves opacity and allows a reduction in amount of titanium dioxide.[54]

These works show that there is an interest in finding partial replacements for titanium dioxide which is the major material cost component of paints.

## 19.12 COSMETICS AND PHARMACEUTICAL PRODUCTS[55-56]

Fillers are used by the pharmaceutical industry for three main functions: as colorants, disintegrants, and glidants. Each application demands special properties, as discussed below. Pharmaceutical grade fillers differ from those used by other industries in that they must comply with a high purity standard. The purity of material for pharmaceutical use is not only defined in terms of chemical composition but microbiological contamination is strictly limited.

The pharmaceutical industry uses organic dyes and lakes and inorganic pigments as common colorants. Red, yellow, and black iron oxides, titanium dioxide, calcium carbonate and talc are typical examples of inorganic pigments used in tablet production in order to provide the user with distinctive colors for different products. Inorganic pigments used by the pharmaceutical industry are analyzed for particulate properties (particle size, specific surface area, etc.), refractive index, stability of with respect to heat, UV degradation, and effect of pH. Trace elements are analyzed. These include arsenic, lead, antimony, cadmium, chromium, mercury, copper, zinc, barium, and iron.

The term disintegrant is applied to a substance added to a tablet formulation for the purpose of causing the tablet to break apart in an aqueous environment. Starch is the most commonly used disintegrant but several other materials are also used including inorganic fillers, namely, kaolin and bentonite. These fillers are usually added in concentrations in a range from 5 to 15%. The filler should work in conjunction with the tablet binder and withstand physical forces of compression. A typical disintegrant should, on contact with water, swell, hydrate, change volume or position, or react chemically to produce disruptive changes in the tablet. Kaolin and bentonite swell in contact with water. Their major disadvantage is their off-white color.

Glidants are substances added to cohesive powders in order to improve their flow properties by reducing interparticle friction. The effect produced by glidants depends on their chemical composition, which should be able to form permanent or temporary bonds with cohesive powder. Properties of glidants depend on physical factors such as grain size and shape, moisture content, hygroscopicity, etc. Talc and silica type fillers are typical examples of glidants. These materials, when added to the powdery composition, promote free-flow in the hopper and complete filling of tablet molds.

Theories developed in the study of metal powder compression have been adapted to the compacting of pharmaceutical powders.[55] A mathematical model is used to explain the reasons for defect formation during powder compression because of sticking and capping.[56]

In the cosmetics industry, finely dispersed fillers, are used as abrasives (toothpaste, scrub cosmetics), for their light reflecting properties (sunscreen lotions), for their dehydrating and astringent effect (kaolin in face masks), for their cooling effect (zinc oxide in sunburn lotion), and as cosmetic color additives and extenders (makeup). The many different applications require an extensive range of filler properties.

Within this sector, dentifrice is the most important market for fillers. Traditionally, dentifrice abrasives included dicalcium phosphate dihydrate, calcium carbonate, and insoluble sodium metaphosphate.[21,22] But now, aluminum trihydrate and hydrated silica are the most important fillers in toothpastes. Aluminum trihydrate is used extensively in the European market, whereas hydrated silica dominates the American market. Fillers for toothpaste production are required to have a carefully controlled grain size distribution. It is this property which controls the abrasiveness and the rheology of the toothpaste. Oil absorption depends on grain size distribution and consequently the rheology of the paste is related to the oil absorption of the filler. The abrasiveness of silica is also related to its oil absorption. Since oil absorption increases as grain size distribution decreases, it is not surprising that abrasive RDA (radioactive dentin abrasion) decreases when grain size decreases, with oil absorption increasing. Commercially available pharmaceutical grades of aluminum hydroxide are compatible with humectants, flavoring compounds, detergents, and enzymes. Aluminum hydroxide is also used by pharmaceutical industry (as well as plastics industry) as an antiacid.

Scrub cosmetics use abrasives to remove old horny cells, to massage, to smooth the skin surface, and to remove dirt from skin pores. Natural scrubbing agents are obtained from plant shells, seeds, and oils, and from animal shells and fats. Several inorganic materials are also in use, such as aluminum oxide, silica, kaolin, talc, calcium carbonate, and zirconium dioxide. An inorganic scrub agent should be carefully analyzed for grain size distribution, grain shape and the presence of crystalline forms. Some materials used in scrub agents have a high hardness, and, if they are present in the form of abrasive particles, may cause severe skin damage. Iron oxides, titanium dioxide, and mica are the most frequently used color additives for cosmetics. Zinc oxide and titanium dioxide, in addition to their use as colorants, play the role of UV absorbers, protecting skin from radiation. Talc, kaolin, iron oxides, titanium dioxide, and fumed silica are popular colorants, extenders, and rheology modifiers. Talc is commonly used in formulations where softness and slip are required. A caution: if talc penetrates a wound it may cause talcum granulomae; therefore, in products which may come into contact with wounds, talc should be replaced by aluminum hydrosilicate.

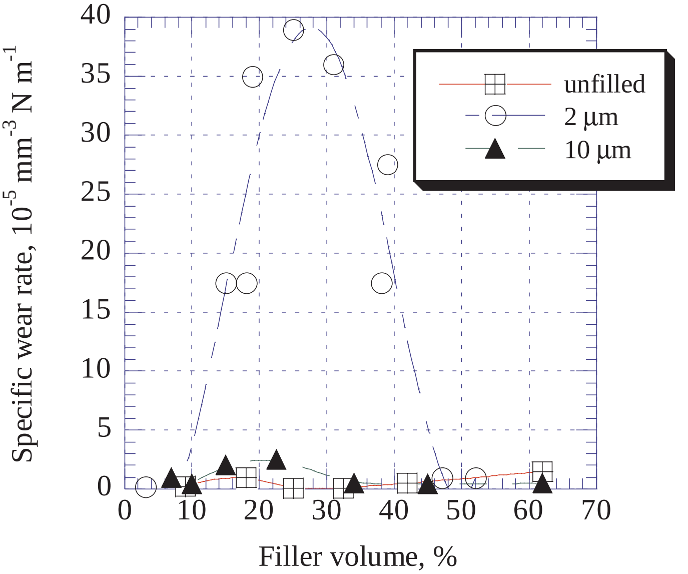


Figure 19.13. Specific wear rate of dental composites vs. filler volume. [Adapted, by permission, from Friedrich K, *J. Mat. Sci. Mat. In Med.*, **4**, No.3, 1993, 266-72.]

## 19.13 DENTAL RESTORATIVE COMPOSITES[57-61]

Adhesion, filler/matrix adhesion, dimensional stability, reinforcement, and wear resistance are the most important concerns in the development of dental composites.[57-61] These requirements are shared with composites used for many other purposes. So much as the methods of testing, mathematical models, methods of interpretation, and remedies developed in other applications may be applied to dental composites.

Figure 19.13 shows that wear rate depends on the concentration of filler and its particle size.[58] During the last decade, the particle size of fillers dropped from 8-30 µm to 0.7-3.6 µm in the present restorative composites.[60] This has increased surface smoothness and decreased plaque retention in unpolished surfaces. The wear rate of the composites increases when fillers are added and small particle size fillers cause more rapid increase of wear rate at a certain range of concentrations. Outside this range, composites have wear rate similar to the unfilled matrix.

The most frequently used fillers are glass powder, lithium aminosilicate, and glass-ceramic. Figure 19.14 shows that properties of dental composites are enhanced by the use of silanes. Treatment with silane also improves water resistance.[61]

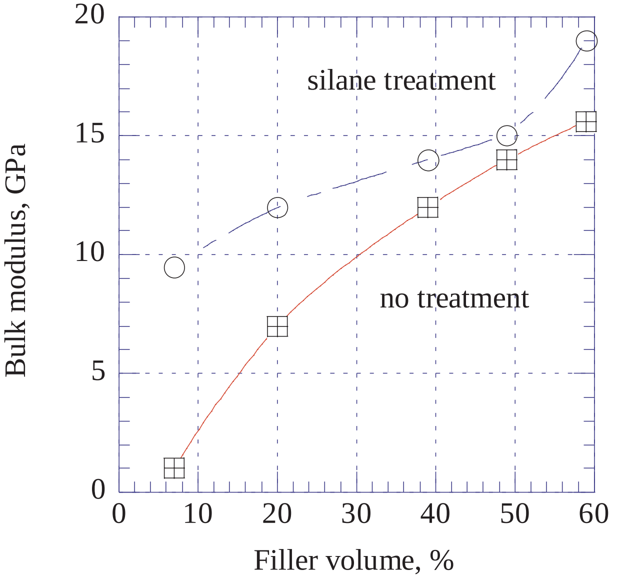


Figure 19.14. Bulk modulus of dental composite vs. filler concentration. [Adapted, by permission, from Jones D W, Rizkalla A S, *J. Biomedical Materials Research (Applied Biomaterials)*, **33**, No.2, 1996, 89-100.]

## 19.14 ELECTRICAL AND ELECTRONIC MATERIALS[62-70]

An extremely large number of products contain components which must meet stringent requirements. Such diversity prevents us from going beyond a general discussion. In the US and Canada products need the Underwriters Laboratories approvals and, in most cases, a V-0 rating is required. When brominated fire retardants were banned in Germany, some polymers such as polyester were affected. This generated a search for alternative fire retardants and different polymers (e.g., polyamide) for fire retardant applications. The opportunity for fire retarding fillers will continue to expand since in other countries (US, Japan, European countries) brominated flame retardants may also be restricted.

Various industries make efforts to introduce static control to work place, products and packaging. As many as 10% of the failures of electronic equipment are related to static electricity. To control static electricity in the work place, many products should be conductive (coatings, mats, bench tops, etc.). Packaging has been developed using conductive fillers. This creates new opportunities for manufacturers of products and fillers.

Electrically insulating and thermally conductive qualities are important in computer chips fabrication. One approach taken is based on boron nitride fillers which offers these two properties. There is also a need to develop materials which are thermally conductive but electrically insulating in high humidity conditions. Polyurethane composites filled with aluminum oxide or carbon fiber can be used for this application. Figure 19.15 shows the effect of the amount of filler on thermal

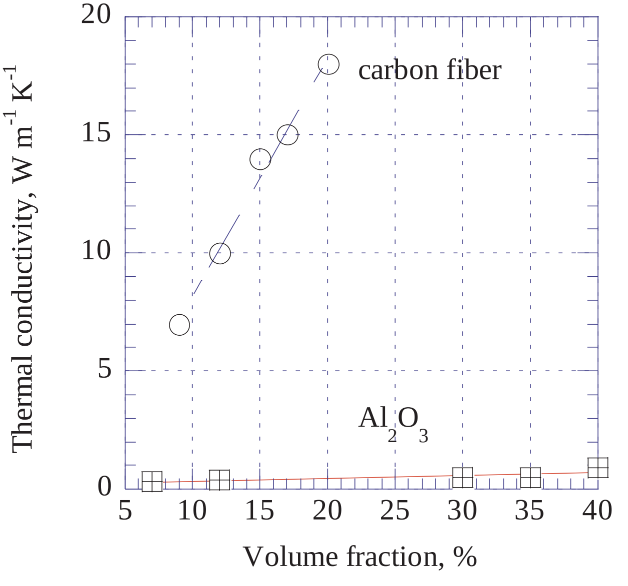


Figure 19.15. Thermal conductivity of PU vs. filler concentration. [Data from Lu X, Xu G, *J. Appl. Polym. Sci*., **65**, 1997, 2733-8.]

conductivity. A carbon fiber filled material was found to be more resistant to changing humidity.[63]

Z-axis adhesives are a unique class of new products. These adhesives contain conductive particles, which due to their orientation, conduct electricity across their thickness but are non-conductive along their length and width. Several circuit lines can be connected through the same strip of Z-axis adhesive with no current flow between circuit lines.

## 19.15 ELECTROMAGNETIC INTERFERENCE SHIELDING[71-75]

EMI shielding prevents distortion of television, radio, aircraft control signals. Electromagnetic waves have an undesirable effect on people, animals and plants. Because of these interferences, sales of goods which may emit EMI is prohibited. EMI can be controlled by the use of plastic filled with conductive particles, conductive paints, metallization, use of inherently conductive polymers, conductive films, fabrics, and metal shields. Many solutions can thus be offered by fillers. There is a great number of different fillers used in these applications. These include carbon black, carbon fibers, graphite, metal powders, flakes, and fibers, and particles coated with metals. Depending on the type of filler used for EMI shielding, concentrations from 3 to over 40 wt% are required to obtain effective EMI shielding. EMI shielding efficiency is not only dependent on the type and conductivity of material used but it also depends on the particle size shape, its surface finish, its compatibil-

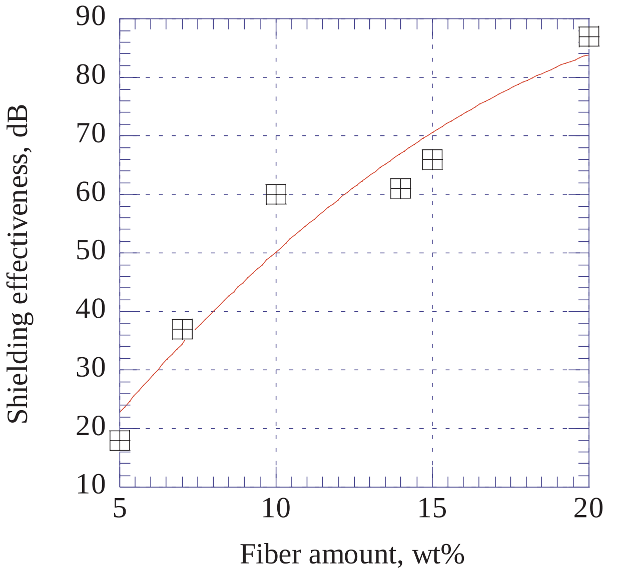


Figure 19.16. Shielding effectiveness vs. concentration of nickel fiber in PC. [Data from Rosenow M W K, Bell J A E, Antec '97. Conference proceedings, Toronto, April 1997, 1492-8.]

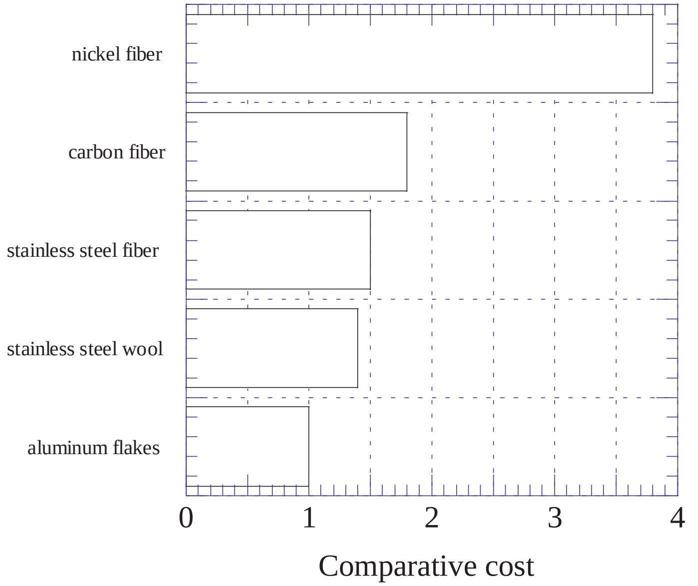


Figure 19.17. Comparative cost of metal filled PES composites. *Courtesy of Transmet Corporation, Columbus, USA.*

ity with matrix, its distribution in matrix, and the incorporation technology used. Shielding effectiveness should be 50 dB.

Figure 19.16 shows how nickel fiber changes EMI shielding effectiveness in polycarbonate. Less than 10 wt% fiber is needed to reach the target value.[71] Figure 15.2 shows that shielding effectiveness depends on the method of incorporation and that the length of fibers can be changed by the process of incorporation.[73]

Figure 19.17 shows comparative cost data which indicate that aluminum flakes and stainless steel fibers are the most cost effective.[76] Carbon black and graphite can, in principle be used in this application, but require a large loading and offer only limited protection. If metal fillers are used, consideration must be given to their oxidation potential and chemical resistance. Surface chemical changes may drastically reduce their performance. Metallization is also an efficient method of producing a conductive material. This was discussed in a recent monograph.[77]

## 19.16 FIBERS[78-79]

Microporous fiber have been produced using the following method.[78] Polypropylene is filled with 25 wt% calcium carbonate. After extrusion, the fiber is stretched at 150°C and calcium carbonate is dissolved by an acid treatment. Pore sizes from 0.01 to 0.02 μm are obtained depending on the type of acid treatment and the stretching ratio. Crystallinity decreases as the stretching ratio decreases and the fiber diameter increases after acid treatment because of shrinkage.

Choosing carbon black as a filler for fibers has many implications. Figure 19.18 shows the effect of carbon black loading on viscosity in PET.[79] Viscosity depends on the type of carbon black. A reduction of 50% viscosity can be attained at the same carbon black concentration simply by change to another grade of carbon black. Moisture absorption, which affects the drying time, can be substantially reduced (by about 50%) by the selection of the appropriate carbon black.[79] Fiber color and tone are affected by the carbon black type and by the method of its dispersion.

## 19.17 FILM[80-85]

Fillers provide films with conductive properties, influence their surface properties, affect their permeability, mechanical and optical properties, and affect their durability against environmental exposure. Various technologies are used to produce conductive films. These include lamination to metal foils (in-plant, using pressure sensitive adhesives), surface coating, and addition of conductive materials. Conductive films are widely used in packaging to limit static electricity.

China clays and calcium carbonates can be used to impart anti-blocking properties to films produced from polyester, and cellulose acetate. Figure 19.19 shows the effect of coated ground calcium carbonate. Even such a small addition as 10 wt% has a substantial effect on blocking. Many other properties such as impact strength, modulus of elasticity, and opacity are improved.[83]

The permeability of HDPE film containing variable quantities of talc is given in Figure 19.20. Talc in smaller quantities reduces oxygen permeability.[79] Talc has

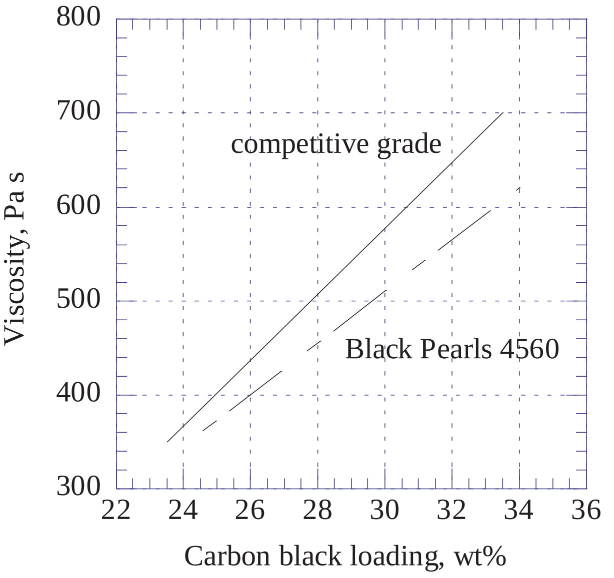


Figure 19.18. Viscosity of PET vs. concentration of carbon black. *Courtesy of Cabot Corporation, Billerica, USA.*

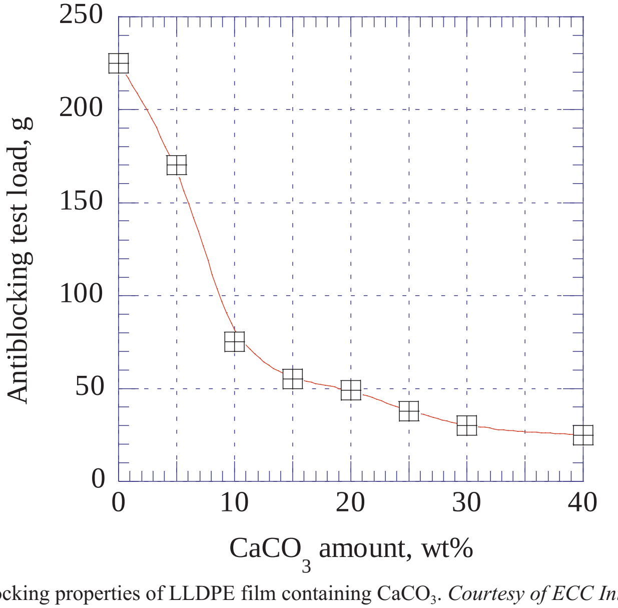


Figure 19.19. Antiblocking properties of LLDPE film containing $CaCO_3$. *Courtesy of ECC International, St Austell, UK* in Johnson S L, Ahsan T, Polymers, Laminations & Coatings Conference, TAPPI Press, Atlanta, 1997.

a flow-induced planar orientation which affects gas permeability. The addition of large amounts reduces permeability but decreases mechanical properties.

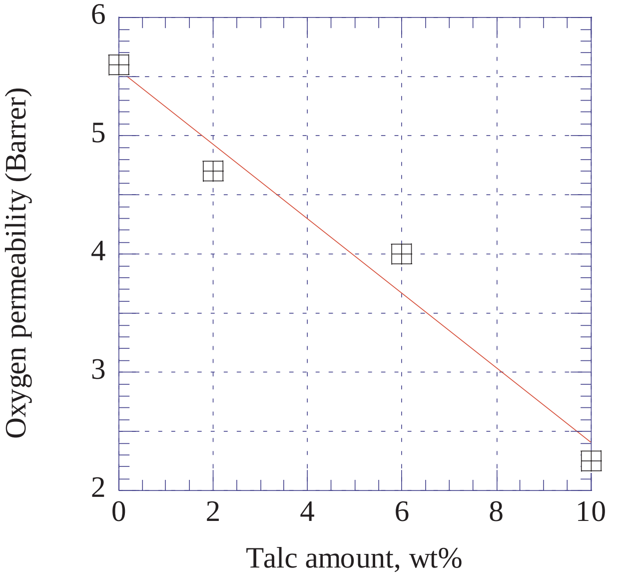


Figure 19.20. Effect of talc on oxygen permeability of HDPE film. [Data from Gill T S, Xanthos M, *J. Vinyl and Additive Technol.*, **2**, No.3, 1996, 248-52.]

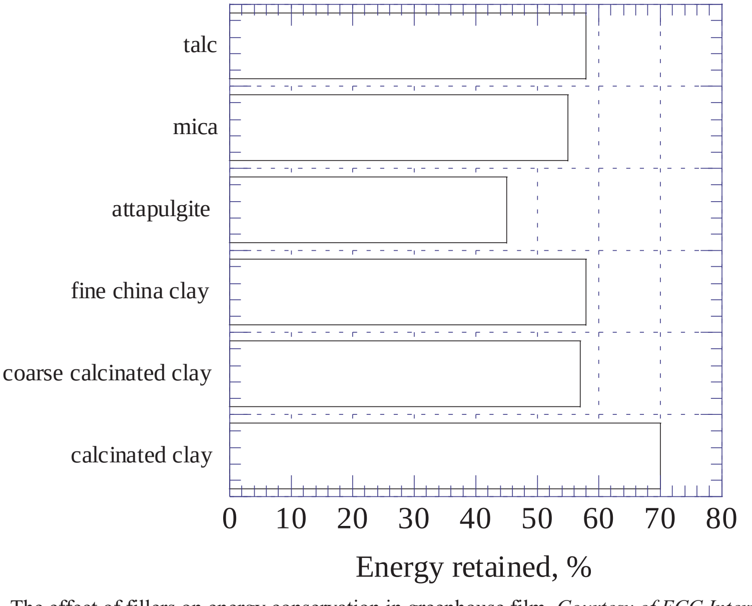


Figure 19.21. The effect of fillers on energy conservation in greenhouse film. *Courtesy of ECC International, St Austell, UK* in Hancock M, *Plasticulture*, **79**, 4, 1988.

As mentioned earlier (section 19.2), the addition of filler reduces the transmission of infrared energy through a greenhouse film. Figure 19.21 shows the effect of various fillers in energy conservation applications.[84] Calcinated clay gives the best results. The reformulation of greenhouse film to include a filler resulted in an increase in crop growth rate and in energy savings.

Fillers improve mechanical properties of films. Calcium carbonate coated with stearic acid improved the impact strength of polyethylene bag films.[80,81] Production output was increased and printability of the film was improved.[81]

Films containing filler may have a substantially improved UV stability due to the addition of carbon black. It is also possible to produce films which will be biodegradable by the combined action of UV degradation and biodegradation.[85] It was confirmed that china clay increases the degradation rate of polyolefins by consuming stabilizers and thus reducing polymer stability.[85]

## 19.18 FOAM[86-91]

Fillers affect foams in several ways: they induce nucleation of gas bubbles and polymer crystallization, they destabilize liquid foam, they interfere with rate of chemical reactions and gas generation processes, they influence the viscosity of liquid premixes, they improve mechanical properties of foam, and foam durability. Care must be used in the selection of fillers for foams. They are used only sparingly in spite of the potential gains in foam performance which might be expected.

A major problem for the foam industry is the recycling of used foam which has now been addressed by the use of pulverized foam as a filler in foam production.[86,89,90] Up to 30 phr of pulverized foam can be added with a positive effect on foam properties. A combination of pulverized foam and carbon black gave good results.[89]

Novel PVC foams are produced with wood fibers.[91] Untreated and silane treated wood fibers were used. It was determined that by the selection of plasticizer level, foaming time, foaming temperature, and silane treatment of wood fiber, the foam of expected properties can be obtained.

## 19.19 FOOD AND FEED[92-93]

There are two main reasons why substances classified as fillers are used in agriculture: feed supplementation and application of pesticides in granular form. The nutritional applications usually involve calcium carbonate, iron salts, and zinc oxide as feed supplements with the required levels of these three metal salts.

Fillers are used in food products in the following functions: colorants, viscosity regulators, nutrients, bleaching agents, and anticaking agents. Some foods include titanium dioxide and alumina or its lakes as food colorants. Calcium sulfate is used as a part of the bleaching system in flour production. Fillers which have high sorptive capacities, like bentonite, are used as viscosity regulators or agents preventing sedimentation of other solids.

Calcium carbonate, calcium sulfate, kaolin, talc, magnesium carbonate, and zinc oxide are frequently used as nutrient supplements or food diluents. Calcium silicate and fumed silica are used as anticaking agents. They are added in concentrations of up to 2% to materials which are hygroscopic. The surface coatings of such material and their ability to absorb moisture make it possible for these materials to transform the hygroscopic materials to free-flowing powders. The type and concentration of fumed silica affects the material's free-flowing properties and the durability of the induced effect. Silane-coated fumed silica performs better because it is hydrophobic.

## 19.20 FRICTION MATERIALS[94]

Asbestos-free fiber-reinforced brake linings are being improved through a continuous development effort. A review of problems and achievements was recently published.[94] Two types of fillers are used in brake pads: particulate fillers and reinforcing fibers. Low cost materials are used as particulate fillers, such as calcium carbonate and barite. Their role is to decrease cost without detracting from the performance of the product.

Fibers are responsible for strength, thermal stability, and frictional properties. 1,200 fibers have been tested to-date for this application. The major groups include aramid, glass, carbon, steel, and cellulose fibers. Each fiber has its own set of problems in the application. This may be price, low melting point, low friction characteristics, corrosion, abrasion of metal elements, low strength, etc. Studies in this field affect the automotive, land transportation, military, and aerospace industries and are being maintained at a high level to further improve the properties of brake materials.

## 19.21 GEOSYNTHETICS[95-96]

Geosynthetics include three groups of products: geotextiles, geogrids, and geomembranes. All materials are required to have UV protection (although the geomembranes are usually covered in application; part of the membrane is exposed and degradation may occur during installation).

Carbon black is the usual UV stabilizer in these products. Weathering studies are reported elsewhere.[97] Several other fillers are employed including titanium dioxide, calcium carbonate, and clay. Clays are used in large volumes in secondary liners where bentonites are used as the absorption media.

## 19.22 HOSES AND PIPES[98-99]

Mechanical performance (tensile, flexural, impact, bursting pressure, and compressive strength), resistance to heat, thermal expansion coefficient, heat distortion temperature, maximum working temperature, burning class, UV stability, and working stress are the most important parameters characterizing performance requirements of pipes and hoses and are used as selection criteria. Fillers can help to fulfill these requirements, but are underutilized. Fillers seem mainly to be used to lower cost.

Carbon black is very frequently used as an UV stabilizer. Pipes which are not normally exposed under their working conditions do need UV stabilization because during storage and transportation pipes are damaged by sun light. The most important parameter of pipe performance – bursting pressure – is severely reduced by the presence of cracks on the pipe surface induced by UV degradation.

For some applications a low thermal expansion coefficient is required and pipes are produced with glass fiber reinforcement which also increases the heat deflection temperature.

Electrically conductive pipes are less well known. These pipes are used to prevent electrostatic hazards in oil tanker applications.[99] The pipe for this purpose was developed using glass fiber for reinforcement and carbon fiber to obtain conductivity. There are also methods of production of such pipe where aluminized glass fiber is mixed with reinforcing glass fiber.

## 19.23 MAGNETIC DEVICES[100-101]

Polymer magnets, although common today, are a quite recent development. The first patent application was filed in France in 1955. Since that time, many ferromagnetic fillers have found their way to market. Plastics magnets do not match the performance of metal magnets but their properties are being systematically improved.

Barium ferrites do not affect the mechanical properties of natural rubber and hence are useful in magnetic applications. Cure rates are increased considerably but ferrites may cause reversion problem.[100] The magnetic properties increase almost linearly with the amount of ferrite added.

A magnetic filler in the form of fiber was added to HDPE and injection molded test products were made.[101] Anisotropic composites were manufactured to induce flow orientation of the fibers. The increased orientation contributed to the generation of a higher permeability magnet. The orientation can be affected by changing the die diameter.

Magnetizable particles were used in the separation of biochemical compounds. Magnetizable particles of iron oxide are produced on different supports capable of absorbing various biological substances which are then removed from suspension by a magnetic field (see more about this application in Chapter 2).

## 19.24 MEDICAL APPLICATIONS[102-110]

The medical sector is the fourth largest consumer of plastics after the packaging, construction, and automotive sectors. It has a relatively high growth rate (8%/year). The growth is in part due to our longer life expectancy but also by new technological advances in medicine.

As is evident from the conducted studies, the majority of problems within this sector are very typical of the plastic industry in general. These include the need to improve reinforcement, durability, fatigue resistance, adhesion, reduce water absorption, etc. In addition to these problems are some issues which are only related specifically to medical applications such as toxicity and biocompatibility. These issues make this research an exclusive field in which the publication of findings is found only in industry specific journals. The medical plastics industry would benefit from greater integration with the mainstream development of plastic materials. It is quite usual to find that although many new materials are available, but only a few are used by medical plastics. The area of prosthesis and dental applications seems dominated by polymethylmethacrylate. The use of fillers is mostly limited to hydroxyapatite and glass. Distressingly studies report numerous fatal failures due to the lack of adhesion between the bone substrate and the implant due to unsatisfactory properties of "Plexiglas" related cements.

Reading these studies one gets a feeling that interdisciplinary effort could be dramatically improved in many strategic ways. However, some pioneering studies are also conducted. One involves the crystallization of inorganic materials in the presence of simulated or specific body fluids. This process affects the structure of the crystal which develops a surface structure similar to that of bone. In this way it becomes more acceptable (or more difficult to recognize as artificial) to living tissues.

Most material studies reported in medical journals are of interest to those involved in mainstream plastic applications. Some medical plastics must perform under constant water immersion. It was reported that absorption of 1% water reduces the fatigue life of PMMA by a factor of four, since bone cement can only be replaced by a surgical operation such a performance is clearly unacceptable.[104] The use of silane to treat the hydroxyapatite filler in this material reduced water uptake. The water uptake increased with increased concentration of hydroxyapatite. In applications, such as dental fillings, increased water uptake is considered helpful since it compensates for the loss of volume due to shrinkage of the filling during curing.

Silanes were also used to treat hydroxyapatite in biodegradable composites which are used for the temporary joining of fractured bones. This material is intended to be gradually replaced by biologically generated material so that a second operation may be avoided. The major problem is that such cements rapidly lose their integrity. Again, a silane coating with suitable functional groups can be used to improve water resistance without affecting the process of gradual biological replacement.[109]

In hard tissue replacement, polyurethane filled with hydroxyapatite is used. The composite must have high strength and stiffness and excellent creep and fatigue resistance. The material in the study met these requirements when hydroxyapatite was pretreated with hexamethylene diisocyanate. The treatment improved the adhesion between the matrix and the filler.[108]

The durability of cemented joint replacements depends on the properties of PMMA bone cement. A titanium fiber was used to reinforce the cement. Before the cement was applied it was centrifuged to remove entrapped air which would cause voids in the connection. The treatment also improved the ductility of the cement. Similar processes are used in many plastic industries to improve elastic properties.

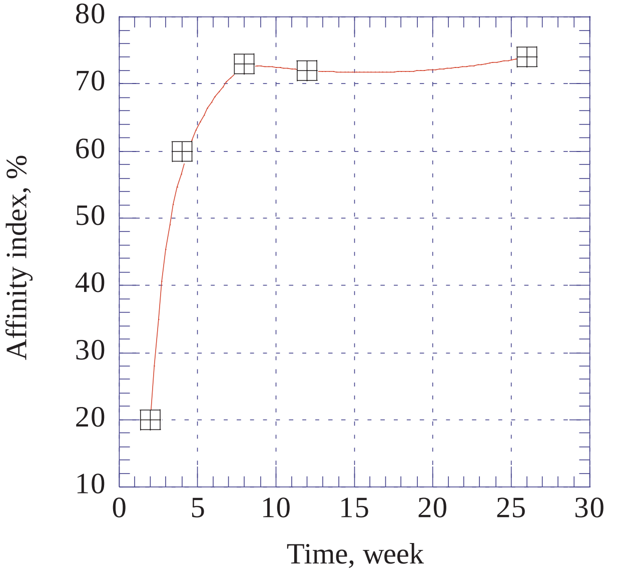


Figure 19.22. Affinity index of bone cement containing 70 wt% glass powder vs. time. [Adapted, by permission, from Tamura J, Kawanabe K, Yamamuro T, Nakamura T, Kokubo T, Yoshihara S, Shibuya T, *J. Biomed. Mat. Res*., **29**, No.5, 1995, 551-9.]

Figure 15.23 shows that an increased amount of glass filler increases the affinity index of bioactive bone cement. Because fillers are relatively inert they have the potential to improve biocompatibility of artificially produced materials. Figure 19.22 shows that the affinity index increases with time.[106] This suggests that there is an ion exchange between the glass filler and the organism which modifies implant to become more compatible with the surrounding tissue. It was also determined in this study that an increased amounts of filler increased not only the biocompatibility but also the mechanical performance of the composite. Silane treatment was also apart of this study but it is yet to be determined if it will affect the ion exchange process which allows the compatibility to develop.

Fillers are essential in plastics which must be sterilized. Glass fiber in particular is used to withstand sterilization and retain mechanical properties.

Most medical plastics must be kept scrupulously clean and are handled only in a clean room environment. Static charge built up on these parts will attract contaminants therefore it is critical that static charges be dissipated. Fillers perform this function because fillers, unlike organic antistatics, have no tendency to migrate and contaminate the surroundings.

Medical plastics present a large opportunity for filled products but much more work is needed. A review of the literature indicates that efforts are concentrated on materials used for replacement of body tissues. Much less attention is being paid to items produced for everyday use such as packaging, hoses, syringes, etc. which can benefit substantially from incorporation of fillers.

## 19.25 MEMBRANES[111-112]

Two types of membranes may contains fillers: hydrophobic membranes (usually polydimethoxysiloxane filled with zoelites) and heterogeneous ion-exchange membranes which may contain various surface modified inorganic materials.

One important requirement of membranes is that the filler and the matrix must be in good contact which accounts for the widespread use of silane modified materials. An example of such an improvement is reported in work done on silicate used in various polymeric matrices.[112]

Both phases (the matrix and the filler) must be homogeneously distributed and the sizes of particles must be uniform and well controlled. Layered fillers such as montmorillonite are finding growing applications many of which involve the use of nanocomposite technology. One example of intercalation process to produce membrane resulted in the development of nanocomposite with controlled ion mobility.[111]

## 19.26 NOISE DAMPING[113]

Noise pollution can be reduced by controlling the dampening characteristics of a material. The dampening material converts the energy of vibration to heat rather than emitting it to air.[113] Incorporation of fillers gives such characteristics.

Figure 19.23 shows the effect of filler type on vibration dampening. Mica was the most effective filler in this group because of its platelet structure. Figure 19.24 shows the effect of concentration of mica on dampening properties. The dampening characteristic is improved with higher filler. Overloading with filler spoils the effect (dampening properties of material are reduced if the filler concentration is increased beyond a certain level).

## 19.27 OPTICAL DEVICES[114-115]

Fillers are usually considered to be opaque materials but they can play an important role in high technology optical devices. This is possible due to the use of very small particles of controlled size obtained through application of nanocomposite technology.

Optical switches for optical computing devices and hard transparent coatings are two examples of materials which contain such fillers. Very precise mixing technology is required since uniformity of dispersion is critical if acceptable optical properties are to be obtained. Particles must be evenly distributed in the matrix and should have the capability to amplify light by having nonlinear optical properties. Optical scattering should be avoided, particle size and refractive index strongly influence scattering. If particles are smaller than 25 nm, the refractive index mismatch does not matter. If larger particles are used, the difference between the refractive indices of the matrix and the particles should be very small. For example, for particles of 100 nm, the refractive index mismatch must be less than 0.02.[114]

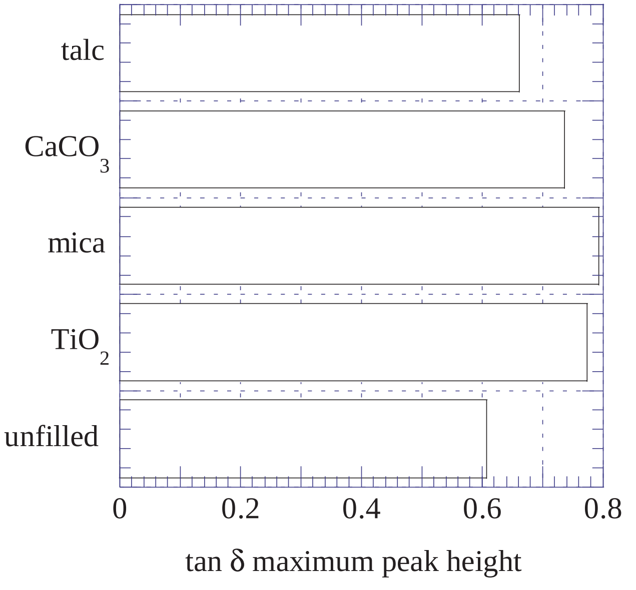


Figure 19.23. The effect of filler type on noise dampening properties of IPN. [Data from Li Shucai, Peng Weijang, Lu Xiuping, *Int. J. Polym. Mat*., **29**, Nos.1-2, 1995, 37-42.]

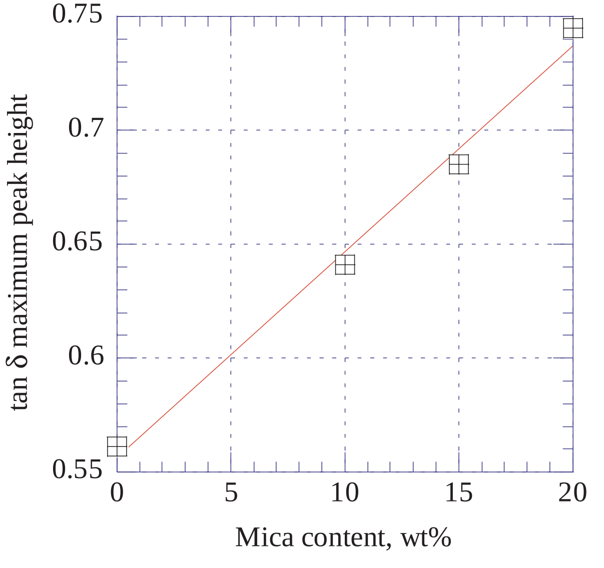


Figure 19.24. The effect of mica concentration on noise dampening properties of IPN. [Data from Li Shucai, Peng Weijang, Lu Xiuping, *Int. J. Polym. Mat*., **29**, Nos.1-2, 1995, 37-42.]

Several particulate materials are used in these applications, such as CdS, CdSe, silica, $V_2O_5$.

Figure 8.41 shows a reactions scheme by which a nanocomposite was prepared from boehmite.[115] This composite is being commercially used in a hard transparent coating for scratch-resistant glasses.

## 19.28 PAPER[116-120]

The major reason to coat paper with filler-containing mixtures is to improve printability. The secondary requirements include: brightness, opacity, gloss, ink receptivity, and flame resistance. Pigment or filler is the major component of a paper coating. It occupies 70 to 90% of the total dry weight. Pigment selection is based primarily on the expected characteristics of the paper, on the mixing and handling equipment available, on the method of coating, and, perhaps, most importantly on price-performance criteria. Several general principles are considered in filler choice. Fillers can be classified as general purpose fillers used at loading levels greater than 10% of paper weight or specialty fillers used at loading levels less than 10 wt% and more often at less than 5 wt%. The particle size of the general purpose fillers is in a range from 0.5 to 10 μm, whereas specialty fillers (silica, $TiO_2$, etc.) have particles ranging into the tens of nanometers. All fillers have hydrophilic properties, with exception of talc, which is slightly hydrophobic. The ζ-potential of fillers is important to prevent coagulation. A ζ-potential higher than 20 mV is sufficient to prevent flocculation. Interactions between fillers and the other components of paper and the effect of such interactions on paper properties is discussed in detail elsewhere.[120]

A filler in the paper industry is a material which is mixed with fiber to manufacture uncoated stock. If this filler helps to reduce amount of fiber used, it may be called an extender. The particulate used for the coating of paper is called a pigment by the paper industry. Materials of the same chemistry can be used as fillers or pigments but they will frequently have different specification for each application. Based on this, titanium dioxide is a filler if processed together with fiber and a pigment if used to coat paper.

Aluminum trihydrate, barium sulfate, calcium carbonate, clay, amorphous silica, talc, titanium dioxide, and zinc oxide are the major pigments/fillers used by the paper industry. Aluminum trihydrate is mostly used at a level equivalent to 10-20% of the total fillers. It is compatible with other fillers. Aluminum trihydrate improves brightness, opacity, the receptivity of gloss inks, surface smoothness, and flame resistance, it is truly a universal pigment. Used in excessive amounts, it affects the high-shear rheological properties of the coating. Aluminum trihydrate needs more binder than titanium dioxide or clay. Barium sulfate (blanc fixe) is used mostly in photographic paper.

Calcium carbonate is one of the most commonly used fillers in the paper industry. In most cases, it is used in a range from 5 to 50% of the total pigment, but in some processes, at above 70%. Brightening, ink receptivity, and surface smoothness are improved by calcium carbonate. Calcium carbonate is easy to disperse,

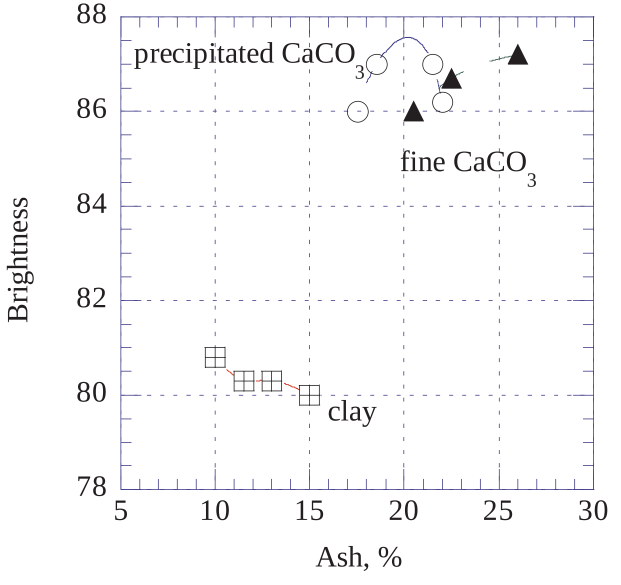


Figure 19.25. Paper brightness vs. ash content. [Data from Anderson T C, Yunko A L, *Pulp Paper*, **53**, 1983, 82.]

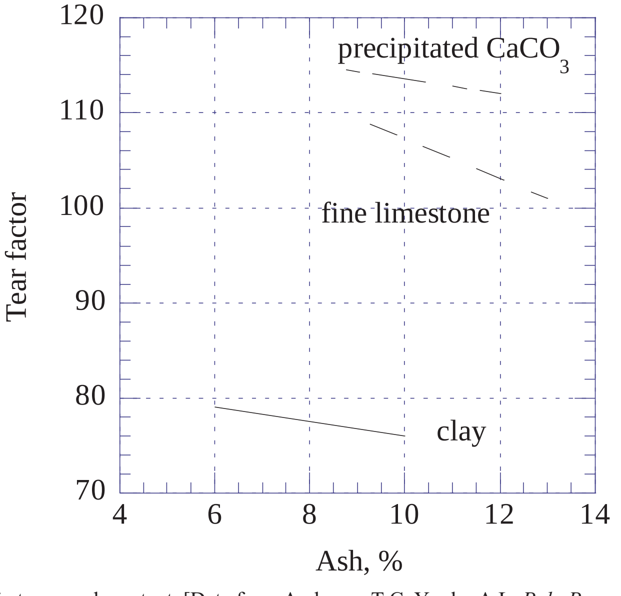


Figure 19.26. Tear factor vs. ash content. [Data from Anderson T C, Yunko A L, *Pulp Paper*, **53**, 1983, 82.]

does not have a tendency to form agglomerates and dispersions containing it are easily stabilized by inorganic dispersants, usually polyphosphate compounds. Calcium carbonate fillers are most beneficial in an alkaline paper process because they

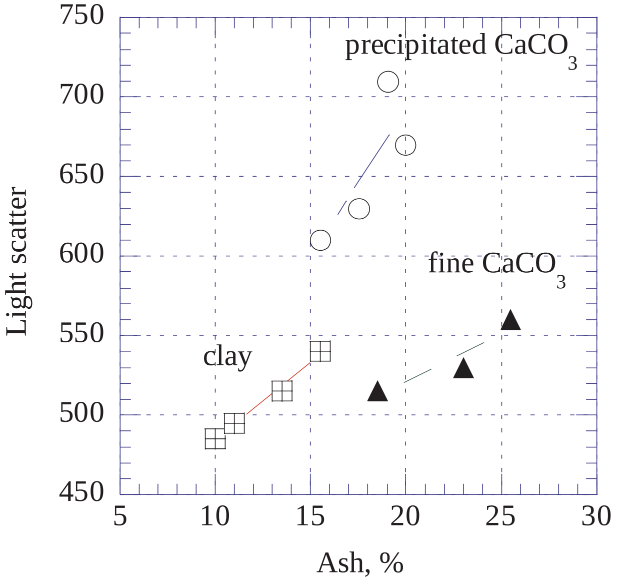


Figure 19.27. Sheet light scatter vs. ash content. [Data from Anderson T C, Yunko A L, *Pulp Paper*, **53**, 1983, 82.]

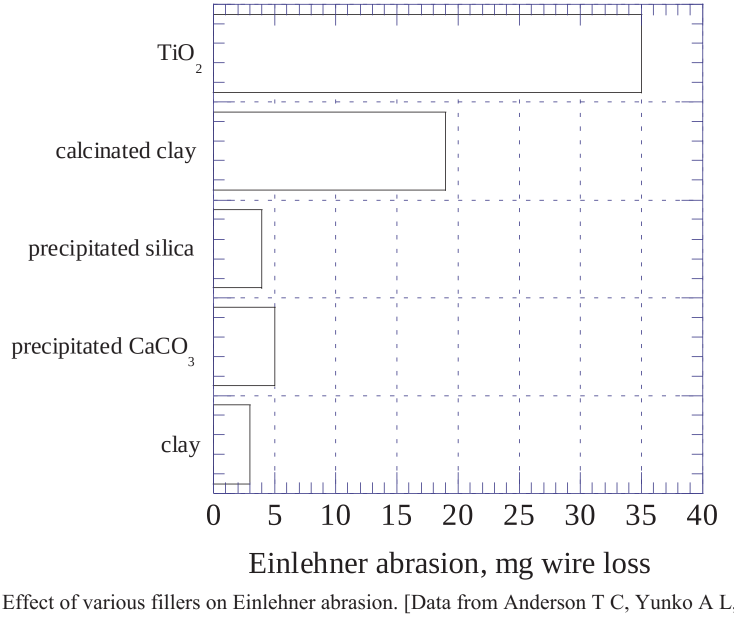


Figure 19.28. Effect of various fillers on Einlehner abrasion. [Data from Anderson T C, Yunko A L, *Pulp Paper*, **53**, 1983, 82.]

provide pH buffering in the required range. There is an ever increasing demand for acid-free paper so the future of calcium carbonate in this application is assured. Figures 19.25 to 19.28 review the results of comparative studies of various pigments on paper properties.[121] Filler fineness does not affect paper brightness, but all other quality factors are related to filler grain size. Pigment distribution in the paper layers as related to brightness and opacity, and the application of retention aids, is discussed in detail elsewhere.[120]

Amorphous silica has become increasingly important in paper technology. It cannot be used alone because it affects coating rheology and adhesive demand. But used in combinations with other fillers, it improves the brightness, opacity, and ink receptivity of paper. Similarly, talc is used as a 10 to 40% replacement for other fillers to improve paper surface smoothness and ink receptivity. Talc is also used in place of clay if clay is not locally available.

Clays and titanium dioxide are the most heavily used fillers and pigments by the paper industry. Clay is easy to disperse because of the hydrophilic character of its surface. It improves brightness, opacity, gloss, ink receptivity, and surface smoothness. It is therefore the universal filler/pigment in paper manufacturing. There are, however, complexities. Fine particle clays decrease gloss but increase surface smoothness. Ink receptivity is generally low with clays, but it also depends on clay particle size and on the calendering process. Excessive adhesive reduces gloss and surface smoothness. It is difficult to achieve all the required properties with a single filler but clay comes close. The technology of clay preparation is exceptionally important because air incorporation into a paper coating affects the brightness and opacity of paper.

Titanium dioxide, with its high refractive index, provides brightness and opacity, which is why it is used in paper manufacturing. Titanium dioxide also contributes to surface smoothness. The rutile form is more opaque than the anatase. Zinc oxide is popular in document duplication papers because of its photoconductivity. Recently, a hollow-sphere polymer pigment has become a useful new material in the paper industry to decrease paper weight.

Chemical composition, particle size, particle shape, specific gravity, surface area, refractive index, brightness, absorptivity, and wettability are the most important criteria used in selecting a filler for the paper industry. For further reading, a recent monograph on the use of fillers in paper industry is an excellent source of practical information.[120]

## 19.29 RADIATION SHIELDS[122]

Filled polymers play a role in primary and secondary protection against γ-radiation. The photons interact with matter by photoelectric absorption and Rayleigh scattering. For primary partitions which separate an unshielded source from its surroundings, lead bricks or concrete blocks are used. For the secondary partitions which protect personnel from radiation, a protective shield or vest can be made by incorporating metal particles or lead oxide in rubber or plastic. Such shields are used by physicians and dentists or their patients to limit exposure to x-rays. The radiation

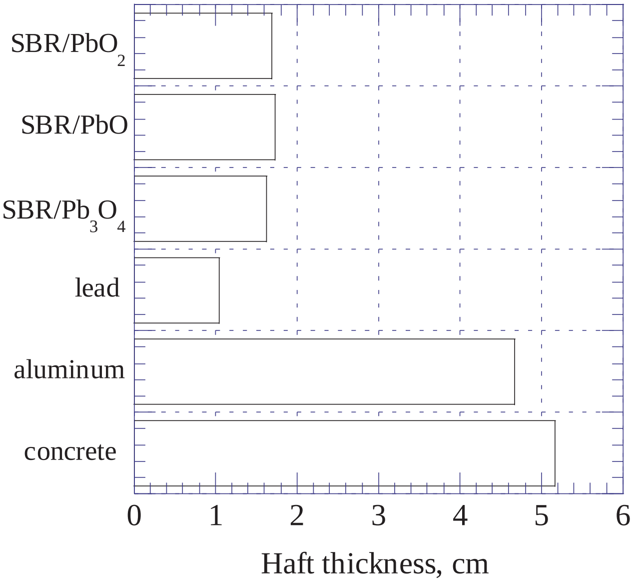


Figure 19.29. Half thickness for $^{60}Co$ γ-radiation in different materials. [Adapted, by permission, from Abdel-Aziz M M, Gwaily S E, *Polym. Degradat. Stabil.*, **55**, 1997, 269-74.]

shielding is inferior to high density metals but complex shapes available can shield the body effectively.

Figure 19.29 shows the comparative shielding efficiency data for various materials. Rubber filled with lead oxides comes very close in performance to lead and is superior to concrete and aluminum. Exposure of these shields to radiation causes degradation of mechanical properties (hardness, in particular, is increased) but it does not affect shielding efficiency.

## 19.30 RAIL TRANSPORTATION[123]

Polyester composites have been used in subway coaches in the UK.[123] After the King's Cross fire in the London underground a new regulation was introduced dealing with the interior use of plastics which could only be met by phenolics. Polyester parts manufacturers searched for alternatives and, with the cooperation of companies manufacturing additives, they developed a system which surpassed phenolic resins in fire rating. This system contains aluminum hydroxide and an additive to help its incorporation. A large amount (350 phr) of aluminum hydroxide is used. Such a large amount normally increases viscosity and makes production of composites difficult but an additive was found which lowers the viscosity of the composition to below that of the viscosity of the unfilled resin.[123] This system has excellent performance. In addition to its fire retardancy, it has a very low smoke emission and low toxicity.

During the project on the Channel Tunnel, British and French authorities were cooperating on the project and standards of both countries were used with only some differences in the methods of testing. The system described above passed both standards. The German regulations are not as demanding as those of the British and French. An interior plastic panel for passenger rail cars was made 25% lighter by the addition of glass microspheres and it employed the same fire retardancy strategy as described above. This product can pass the German standard but it does not pass French and British regulations.

A primary requirement for plastic composites used in rail car applications is fire and smoke retardancy.

## 19.31 ROOFING

During the last decade many new roofing materials were introduced which are applied in the form of weldable membranes, liquid curable materials, self-adhesive products, and torchable materials. These materials are produced from numerous polymers such as, PVC, chlorinated polyethylene, chlorosulfonated polyethylene, EPDM, acrylics, bitumen, polymer-reinforced bitumen and several other materials. It is beyond the scope of this book to analyze compositional changes in these materials. We will provide a brief overview.

The current market requires a roof which can perform 20 years. Many products are available to do this and more. However, it is becoming more common for warranties only being provided for a 5 year term. Among fillers, only carbon black is important in extending roof durability and it is used widely. Roof durability is related to the plastic behavior of many roofing materials. Efforts have been made to provide better reinforcement to prevent plastic flow and improve dimensional stability.

The second requirement is to conserve energy. This is a factor in summer since winter insulation is done by other means. Many reflective pigments are in use with special emphasis on metal flakes which are becoming increasingly popular either as an additive to the roofing material or as a component of the roof surface coating.

The third requirement is weld durability. Fillers do not appear to be involved in this process but concerns remain that inorganic powder may affect weldability.

## 19.32 TELECOMMUNICATION

Components of switches, relays, and connectors use glass fiber reinforced semicrystalline polymers, such as PA, PPS, PBT, and PET. The following requirements are important in these applications: dimensional stability and precision, low moisture absorption, strength, resistance to creep, electrical insulating properties, and resistance to high working temperatures (~85$^o$C).

Electric insulating properties should be retained at elevated temperatures and in changing relative humidity. The choice of composition is important since the material should not absorb moisture which may corrode metal elements. Usually polyamides 610 and 612 are used since they absorb considerably less moisture than polyamide 6 and 66.

The equipment is designed to operate without failure for more than 20 years. In its design, the flow properties of plastic components are important since a degree of high precision must be maintained in the molded part because metal contacts are frequently very close (less than 1 mm apart). Good flow in the mold is required because some sections are very thin. In the more demanding applications, PPS is used.

## 19.33 TIRES[124-132]

For many decades carbon black has enjoyed a practical monopoly as a filler in the tire industry. It retains this position today, the tire industry consumes 70% of carbon black production. A major breakthrough for non-black fillers came in the early 1970s when a winter tire containing silica in its treading compound was introduced. This resulted in numerous problems with rubber compound processing. The tire compound had different flow and molding characteristics. The development initiated friendly competition (friendly because the major producers of carbon black are also major manufacturers of precipitated silica) which continues to bring improvements to tire performance.

Figure 19.30 shows end use opportunities for non-black fillers.[124] The tire elements show highlights of various opportunities for white fillers. Figure 19.30 omits to show that silica can be used to advantage in treading compound. This is discussed below.

Table 19.1 shows the design criteria for the elements of tire.

**Table 19.1 design requirements of tire elements. Data from Ref. 127.**

| Tire section | Important design criteria |
|---|---|
| White side wall | processability, cure rate, hardness, stress-strain properties, adhesion to adjoining components, resistance to tear, cut/crack propagation resistance, resistance to ozone, oxygen and UV, retention of white color on exposure to environment, low cost |
| Black side wall | resistance to weathering, abrasion, ozone, tear, radial and circumferential cracking, fatigue resistance, protection of adjoining elements of tire |
| Wire coats | good adhesion to brass coated steel wire and to adjoining rubber compounds, tear, fatigue, and age resistance |
| Inner liner | formulated to ensure retention of compressed air in tubeless tire, good air retention, moisture impermeability, flex fatigue resistance, durability |
| Carcass ply coat | promote reinforcement by coating parallel cords |
| Tread | wear resistance, abrasion resistance, traction, speed stability, protection to casing, rolling resistance, ice skid resistance, durability |

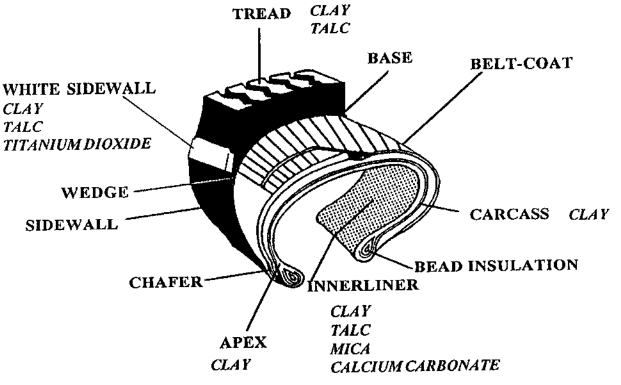


Figure 19.30. Tire cross-section. [Adapted, by permission, from Evans L R, Meeting of the Rubber Division, ACS, Montreal, May 5-8, 1996, paper D.]

The fillers listed in Figure 19.30 are in commercial use performing various functions discussed in detail elsewhere in reference to various tire applications.[124,127]

It was known for a long that the use of silica in tire treads gives better wet and ice skid resistance and better rolling resistance which are important factors in safety and lower consumption of fuel. Real changes in the market occurred recently when reinforcement by silica was improved by the introduction of a new silane. This silane is bistriethoxysilylpropyl tetrasulfone (Si-69). Introduction of this reinforcement removed the barrier of low abrasion resistance and reduced cost of use of silica in comparison with carbon black. The present cost increase due to the use of silica is estimated at $4.75/tire.[128] Part of this cost is raw material ($1) and rest is the cost of additional equipment and processing.[128] But the improvement in tire properties and the possibility of producing "green tire" are offsetting the additional cost and manufacturers are introducing this new technology. One such manufacturer is Michelin.

The technology is still not problem-free. Carbon black is a conductive filler therefore it does not cause an accumulation of static electricity formed because of frictional contact with the road. In a silica reinforced tire, static charge is a problem. Remedial actions have already been taken by the introduction of neoalkoxy zirconates and titanates which are capable of dissipating electrostatic charges. The future of the tire is not yet clear but it is expected that silica's share of this market will be 150,000 tons. This will be supplied to make full silica and silica/carbon black tires.

The carbon black industry is also working on new grades which will offer rolling resistant tires. Two types of carbon black have been tested: super-active carbon blacks and inversion blacks.[132] Both types give promising results.

The reduction of air permeability and the promise of lower cost has increased interest in thermal black use in liners. It is expected that 27,000 tons of thermal black will be needed for this application.[130] The use of thermal black is expected to lower the cost of the liner by 20%.

In the retreading market, new silicas are expected to improve properties of retreaded tires which are currently inferior to new tires.[131] Tread wear resistance and rolling resistance are substantially lower with retreaded tires.

## 19.34 SEALANTS[133-134]

The performance expected from a sealant and the polymer used in its production determine the type of fillers used. From the point of view of performance, sealants can be divided into these having plastic behavior and these with elastomeric behavior. Sealants which have plastic behavior are low-cost and low-performance products which are being gradually eliminated from the market. These sealants use inexpensive fillers to lower cost and regulate non-sag properties. Typical fillers used in these products are calcium carbonate and some fibrous materials which are used as replacement for asbestos which was very popular in the past. This combination of fibrous and spherical particles provided a useful tool to the sealant formulator to regulate non-sag properties which are very important in sealants. Fibers have also been used to reinforce these products because the properties of polymers were poor.

In elastomeric sealants, which now dominate the market, the type of polymer and the application determine filler choice. If the polymer requires reinforcement, reinforcing fillers must be used. Polymers such as silicones and acrylics must be reinforced by fillers. On the other hand, polyurethanes have an excess of tensile strength and in most construction applications this tensile strength has to be decreased by a factor of three to fifteen depending on specific elastomer used. This decrease in tensile properties has to be done carefully to retain good elongation and adhesion to substrates. This requires a combination of fillers and plasticizers which retain all of the other properties required for sealant performance such as rheological characteristics, UV stability, and surface properties which prevent dirt pickup. There are exceptions such as polyurethane automotive sealants which do require reinforcement to give adequate performance.

The mechanism of cure has an important influence on the filler choice. In reactive systems such as polyurethanes, water present in formulation adversely affects sealant stability (shelf-life) which imposes the additional selection criterion of water content. If water is present in the filler it must be removed by additional operations either by an expensive drying process or through the use of chemical moisture scavengers which is also an expensive approach.

Silicone sealant manufacture makes use of fumed silica to regulate rheological properties and reinforce the polymer which, without filler, has too low a tensile and elongation. Precipitated silicas are also used. The use of precipitated silica is regional. The lowest consumption is in Western Europe, followed by USA and the largest is in Japan.[133] Fumed silica may contain a large amount of water depending on the grade. Water in silicone sealants is usually not as critical as it is in polyurethanes because the silicone crosslinker acts as moisture scavenger. Still, control of water input is an important cost and quality factor. In addition to silica, calcium carbonate and titanium dioxide are used in silicone sealants. Silicon polymer is relatively durable on exposure to UV therefore carbon black is used more as a pigment than as a UV stabilizer although, there are grades of silicone sealants which rapidly lose elongation on exposure to UV.

Acrylic sealants have been gaining market share due to their price/performance ratio, high UV durability, and low toxicity. Fillers are used in acrylic sealants for the same reasons as they are used in silicone sealants. Fumed silica is reinforcing filler and plays a role in the rheological system. In addition to fumed silica, zinc oxide is used as crosslinker, calcium carbonate as general purpose filler, and titanium dioxide as a pigment. Acrylic sealants have low tolerance for fillers and high loadings of fillers degrade their properties.

In polyurethane sealants, fillers are used for several purposes. These include rheological control, cost reduction, reinforcement, moisture scavenging, reduction of surface tack, and UV protection. The major requirement is that fillers contain a low level of moisture. A typical specification for fillers is 0.03% moisture which is achieved by filler selection, drying, or moisture scavenging. For cost reduction and rheology regulation, calcium carbonate is the most commonly used filler but many other fillers have been used in these applications. Calcium sulfate, molecular sieves, and some other fillers may be used as moisture scavengers. At high levels, most fillers reduce surface tack and give green strength. However, at these high levels, elongation and fatigue resistance may be adversely affected. The UV protection of sealants is complex. Carbon black provides protection but it also adsorbs UV stabilizers (HALS) therefore use of carbon black is detrimental in most colors. Large quantities of carbon black are used in special applications such as windshield adhesives and sealants. Such high loadings create very high viscosities. The solution lies in the selection of carbon black with appropriate concentration of reactive groups on their surface.

## 19.35 SIDING[135-136]

Vinyl siding is a large consumer of PVC. The most important properties are impact strength and the stability of the color and the material to UV exposure. Relatively low filler content was traditionally used to prevent loss of impact strength and other mechanical properties. Recent findings show that the incorporation of chlorinated polyethylene as an impact modifier allows the amount of calcium carbonate to be increased without affecting tensile strength and elongation and with an increase in impact strength (Figure 19.31).

Titanium dioxide can be used as primary or secondary UV stabilizer in the formulations. Excellent UV stability can be obtained with a high loadings of titanium dioxide.

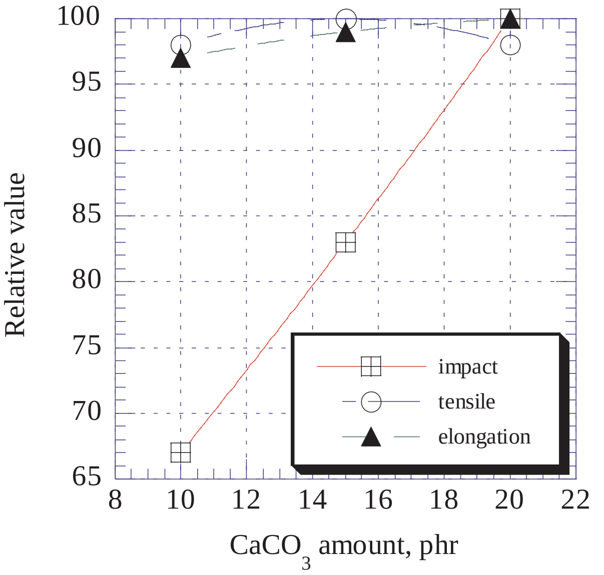


Figure 19.31 Tensile strength, elongation and impact strength of PVC containing 20 phr CPE vs. calcium carbonate content. [Data from Ventresca D A, Berard M T, Antec '97. Conference proceedings, Toronto, April 1997, 3574-9.]

## 19.36 SPORTS EQUIPMENT

Tensile and flexural strength, flexibility, compression strength, abrasion and scratch resistance, coefficient of friction, dimensional tolerance and stability were all improved by incorporating fillers. In sporting goods, such equipment as tennis racquets, skis, ski bindings, skates, etc. were all improved by fillers. High performance fibers such as carbon fiber, aramid , and glass fiber made these advances possible.

## 19.37 WATERPROOFING

Waterproofing has not changed in the last decades as much as other fields. Thus, most significant technological advances has been the introduction of polymer modified membranes. Poor biological resistance of most materials is the factor which has caused delay in its introduction. Bitumen and coal tar are low cost materials which perform well in below grade application because of their low moisture permeability and their excellent biological resistance. Consequently, it is difficult to find cost effective replacements. These traditional products use only a limited amount of fillers because of their adverse effect on mechanical properties. Carbon black is the most widely used additive for regulating rheological properties and reinforcement. Current regulations limiting the use of coal tar and concerns over the toxicity of asphalt may change the situation and force manufacturers to look for less toxic alternative solutions.

By contrast, in above grade applications, where waterproofing coatings are exposed to UV and other degrading environments, many significant changes have occurred. Here, new elastomeric materials have been introduced because crack bridging in a broad range of temperatures is required. These coatings include textured (stucco) and colored acrylic coatings which make the coated substrate waterproof, durable, provide aesthetic values, and low dirt pick up. These new coatings use fumed silica as a rheological additive and for reinforcement, small amounts of calcium carbonate to improve rheological properties and large amounts (textured coatings) of silica sand. Silica sand for this application should have low content of iron to prevent formation of streaks from the iron and its rusts. A variety of glass beads are used for decorative purposes either to develop a certain texture or to impart color.

## 19.38 WINDOWS[137]

A complete window is composed of a frame, gaskets, the insulated glass assembly, seals, and sealants all of which contain fillers. The plastic window market in Europe differs from the North American market. The major difference is in the extruded frame profile and sealing technology. Extruded frame profiles in Germany and other European countries are up to twice as thick as the North American profile. This determines the selection of plastics materials. Also the sealing technology is different. In Germany, polysulfide sealants are used extensively but they are not popular in North America where many other sealing systems are used to increase productivity. PVC containing approximately 10 wt% filler/pigment made up of calcium carbonate and titanium dioxide (about 40% consists of titanium dioxide) is typically the plastic of choice, worldwide. Titanium dioxide plays the additional role of a UV stabilizer. A small number of window frames are produced from glass fiber composite.

The market for composite window materials is expanding because new production facilities are starting up throughout the word in countries which have not traditionally used this type of window. Even in countries where plastic windows are common only about 50% of windows are of this type. They enjoy about 80% of the replacement market but a smaller percentage of the new construction market.

New developments in recycling will reduce consumption of fillers. A technology was developed that recycles the complete window.[137] An automatic line grinds the entire window, then separates the glass, PVC, the metal and the elastomeric seals. PVC is even separated by color and returned for reprocessing. The use of coextrusion permits the use of 80% recycled material. Only the face of the profile is manufactured from a new compound. This technology will not substantially reduce growth because growth is still driven by new markets but eventually demand for new compound should be reduced.

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