

FILLERS IN DIFFERENT PROCESSING METHODS

This chapter contains a discussion of the important changes in the methods of production and in the process parameters which are required to effectively incorporate fillers. The other goal of this discussion is to evaluate the effect of filler incorporation on the properties of final products manufactured by various methods of polymer processing.

18.1 BLOW MOLDING¹⁻⁴

Two basic methods are used in this process to deliver material to the processing units. These are extrusion and injection. In the next step, the preformed material is expanded to form parison. There are many commercial variations on this basic technique some of which include continuous-extrusion-blow-molding, coextrusion-and-sequential-blow-molding, and injection-stretch-blow-molding. Both extrusion and injection molding are the subjects of later discussions below, we will concentrate here on the parison formation, its processing, and the related effects.

Two essential material related properties affect parison performance: die swell and sag. The die design and the operation parameters of the extruder or injection equipment are also very important. Die swell is the change of cross-sectional dimensions caused by the elastic recovery from deformations in the die. The sag behavior is a reaction of the material to gravitational forces. Both parameters of the parison determine its size tolerances along its length from the die exit. If the die swell is too low, the thickness of parison will be too small and the part will lack strength and toughness. If the swell is too large, resin is wasted. It is also essential that the parison have uniform thickness along its length from the die. This can be affected either by the changes in die swell vs. filling time or by sag which causes the material to flow by gravity. Figure 18.1 shows that material filled with talc performs better than unfilled material.³ Die swell is reduced and it becomes uniform with filled material. This figure also shows that a larger addition of talc (40%) produces the same effect as 20% talc. The sag of the extrudate is also improved by talc but here, a larger amount (40%) gives an even better performance than 20% talc.³ In

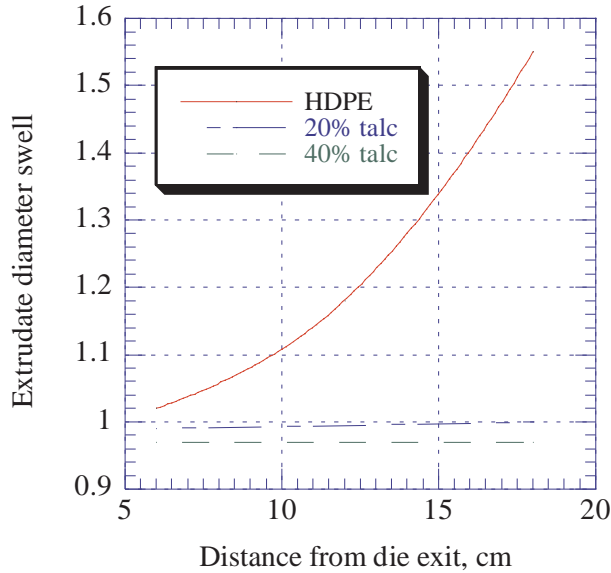


Figure 18.1. Extrudate diameter swell vs. distance from die exit. [Adapted, by permission, from Chang Ho Suh, White J L, *Polym. Engng. Sci.*, **36**, No.11, 1996, 1521-30.]

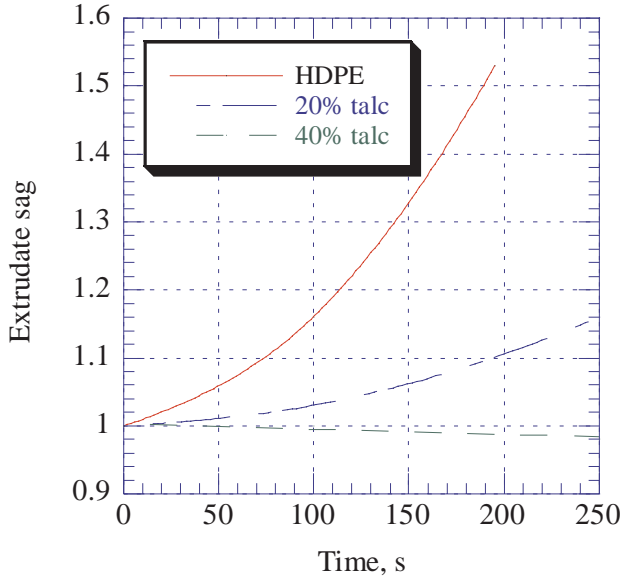


Figure 18.2. Extrudate sag vs. time. [Data from Chang Ho Suh, White J L, *Polym. Engng. Sci.*, **36**, No.11, 1996, 1521-30.]

addition to these two improvements, the material was improved because of orientation of talc particles along the wall.

Similar data come from processing of polyamide-6 with glass fibers. Diameter swell, thickness swell, and weight swell were all substantially decreased by the

addition of 12 wt% glass fiber.¹ All of these parameters are almost constant along the length of the parison from the die, giving a uniform parison.

If the parts made in the blow molding process are to be of high quality, the parison must be dimensionally stable. And fillers can play essential roles in this process as pointed out above. During the blowing and cooling stages which follow the parison formation stage, fillers also play essential roles. The blowing stage is associated with large deformations in the material. Particulate materials, especially these with elongated shapes, contribute to the material texture and rheology and allow the material to withstand more severe processing conditions. During the cooling stage, many fillers will increase the crystallization rate which reduces the cooling time.

The addition of fillers to blow molded materials does not require special equipment but frequently the process parameters must be adjusted to compensate for the changes in the rheological properties of the melt. Larger additions of fillers tend especially to introduce non-Newtonian characteristics which require careful consideration. Also, timing of processes requires adjustment to deal with the higher nucleation rate caused by the presence of filler.

18.2 CALENDERING AND HOT-MELT COATING⁵

Calendering is a popular method of rubber processing. It is also used in the production of films and in lamination of plastic film to substrates in a continuous web process. Hot-melt coating equipment is another version of calendering equipment used for production of plastic coated textile materials.

Obtaining a completely homogeneous mix and selecting the correct calender processing conditions are essential to obtaining the design performance of the filled coating. The mixing processes are discussed in a separate section later in the chapter.

A calender for processing thermoplastics has several cylinders (usually 3 or 4) which have independent drives and temperature controls. Rubber industry uses simple masticating calenders which usually have only two rolls. In the calender for processing thermoplastics, several parameters must be regulated. These include cylinder speed, the gradient of cylinders speeds between two adjacent cylinders, the gaps between the cylinders, and temperature. In the combination, these parameters affects shear rate, orientation, and stress applied to the material. Even if the material is processed without filler, polymer chains become oriented which results in reinforcement and regulation of the mechanical properties both across the width and lengthwise.

The addition of fillers, especially fibers and platelets improves properties even further, since the filler particles are also oriented. Particle orientation can be produced by relatively small materials strain (a few percent). This is demonstrated in more detail in Chapters 7 and 10. This principle is used in the rubber industry where with simple calenders, fibers are oriented preferentially in one direction. If

this material is used for production of belts then these belts have a high rigidity in one direction and flexibility in the other which increases the belt's performance and durability.

More sophisticated calenders used to coat with the thermoplastic polymers give even more control. For example, with the proper choice of conditions, metal flakes can be oriented parallel to the surface which in roofing membrane increases their ability to reflect radiation. The precision of these machines offers very broad range of possible processing conditions.

Incorporation of fillers does not require substantial adjustment in process conditions. In fact, the process is easier in the presence of fillers because the filled material usually has a lower adhesion to the cylinders of calenders which makes it easier to process. Also, cooling times are reduced because fillers increase the crystallization rate.

18.3 COMPRESSION MOLDING⁶⁻¹³

Compression molding is an example of a simple process which does not require expensive equipment but produces cheaply and in simple shapes. Unlike most other processing methods, compression molding does make materials inexpensive through the use of large quantities of fillers. Compression molding applies unidirectional forces usually perpendicular to the material's surface which may thus affect filler orientation.

Figure 18.3 shows that orientation of talc particles increases slightly with increased filler volume. The negative orientation function parameter indicates that particles are oriented parallel to the mold surface as might be expected from the application of an unidirectional force perpendicular to the surface of the mold.¹³ A study compared compression molding with two forms of extrusion and compression molding produced a higher orientation of particles than did the extrusion processes.

In compression molding, molding temperature is an important processing condition, especially in conductive blends. Figure 18.4 shows that, depending on the molding temperature, the percolation threshold of carbon black filled blend can be reduced from 0.8 vol% carbon black at 200°C to 0.2 vol% carbon black at 250°C.⁸ Fillers are not distributed equally in the components of a blend but preferentially settle in one component. If all carbon black was preferentially deposited in the polystyrene phase (45 wt% total) then the percolation threshold should be 1.6 vol% and 0.6 vol% because the percolation threshold in carbon black containing polystyrene is 3.6 vol% and 1.3 vol% at 200 and at 250°C, respectively. But data show these thresholds to be lower than predicted. This indicates that carbon black is concentrated at the interphase making it more economical to use blend of polymers in this application.

Pressure during the curing of compression molded item affects its preparation. Figure 18.5 shows that pressure and the type of the binder has an effect on the

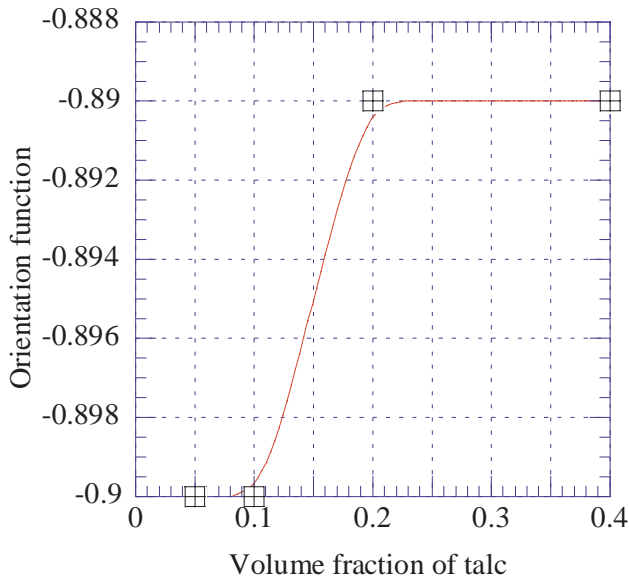


Figure 18.3. Orientation function vs. volume loading of talc in compression molded polystyrene. [Data from Kim K J, White J L, *J. of Non-Newtonian Fluid Mechanics*, **66**, Nos.2/3, 1996, 257-70.]

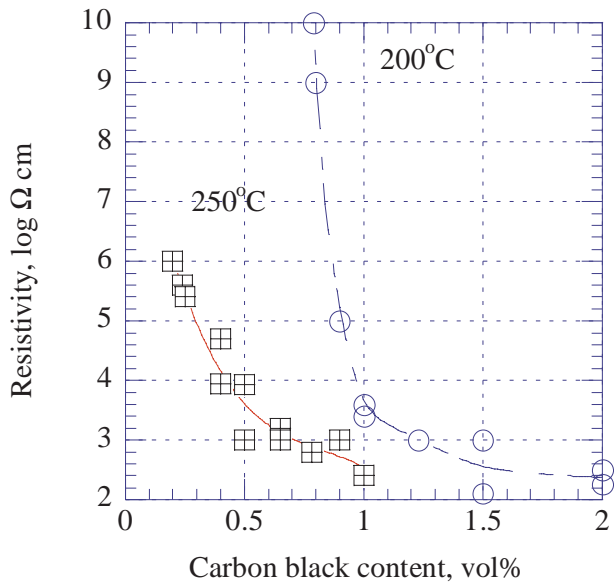


Figure 18.4. Resistivity of PS/PIB blend vs. concentration of carbon blacks. [Adapted, by permission, from Soares B G, Gubbels F, Jerome R, Teyssie P, Vanlathem E, Deltour R, *Polym. Bull.*, **35**, No.1/2, 1995, 223-8.]

resistivity of a carbon black filled composite.¹⁰ The distribution of carbon black in neoprene rubber is affected by pressure but when the same amount of carbon black is used in butyl rubber molding pressure does not influence changes in resistivity.

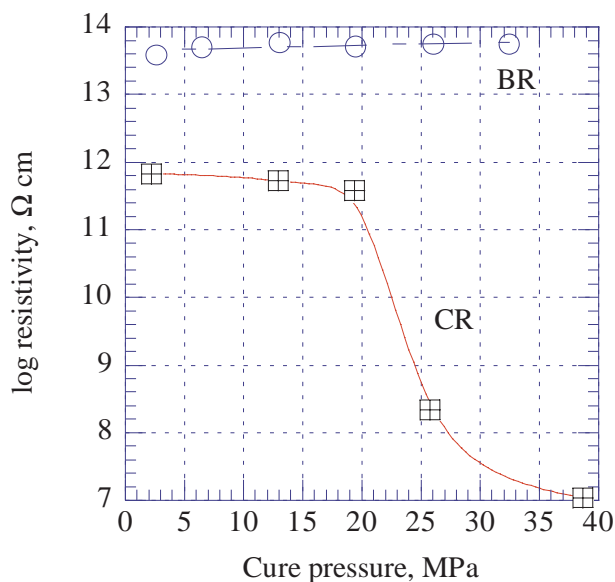


Figure 18.5. Resistivity of neoprene and butyl rubber filled with 40 phr N550 vs. pressure during the cure. [Data from Thompson C M, Allen J C, *Rubb. Chem. Technol.*, **67**, No.1, 1994, 107-18.]

These effects depend on filler concentration and its interaction with rubber. Pressure causes flow in the free rubber which has lower viscosity than rubber which has interacted with carbon black particles. As a result particles may or may not achieve a favorable distribution. If they fail to do so, the resistance is high.

A study of the cure rate⁶ of unsaturated polyester containing calcium carbonate and glass fiber indicates that calcium carbonate makes the cure more complete at a rate similar to that of neat resin. The combination of calcium carbonate and glass fiber decreases the rate of cure and lowers the extent of final cure. Small amounts (10 wt%) of talc¹¹ nucleate crystallizing polypropylene during its compression molding. This level of talc generates the maximum number of crystallization sites. Adding more has no further effect on crystallization.

18.4 DIP COATING^{5,14}

Dip coating is a process frequently used for the production of gloves. Fillers play a prominent role in dip coating formulations. The formulation must be designed to impart two opposite properties to the coating. It should have a relatively low viscosity to assist dipping process and the viscosity should rapidly increase after the form is withdrawn from the dipping tank.

Rheologically, these formulations are pseudoplastic with a significant yield value. The pseudoplastic characteristic is responsible for the performance of coating and wetting the form in the dipping tank (relatively low viscosity) and for providing a uniform coating of required thickness as form is withdrawn. The yield

value causes the material to behave as a solid immediately the form is withdrawn from the tank. If the viscosity is too high an overly thick coating results and surface uniformity may suffer. If the yield value is too low, the material moves by gravity which causes nonuniform thickness of the glove and drips at the ends of fingers. Neither is acceptable. The material should behave as a solid at the elevated temperatures of the next process steps when curing or water evaporation occurs.

Several fillers are employed in these proprietary coatings. In addition to providing the required rheological characteristics, they must contribute to a long shelf-life of the dipping mixtures and give it the stable rheological characteristics which control the performance of coating. The production output is generally too high to regulate process within the batch by adjusting the composition of the liquid mixture.

The mechanical properties of the glove are obviously important. These are strongly influenced by the orientation of filler particles. When they are oriented parallel to the length of the glove, mechanical properties are optimized. It is not desirable that particles become oriented after the glove form is withdrawn from the tank because this causes sagging and dripping problems and variations in thickness. It is important that the proper shear is applied during withdrawal to induce then necessary particle orientation and reinforcement.

18.5 DISPERSION¹⁵⁻³⁷

Dispersion is the subject of many separate monographs too extensive to be discussed in detail here. It is also a process critical to achieving the best performance of fillers. The properties imparted by fillers depend on the quality of dispersion. In most processes, the aim of dispersion is to decrease particle size and obtain a homogeneous distribution of filler particles. There are also cases in which overmixing may not be desirable. This occurs with fumed silica where overmixing causes irreversible damage to the rheological structure. Another example is in the incorporation of conductive fibers which under harsh mixing conditions are reduced to a size which can no longer give the desired performance characteristics.

Figure 18.6 shows torque vs. time during incorporation of silica in rubber.²³ Initially, the torque is increased because a solid material is being incorporated into the rubber matrix. Following the incorporation, torque decreases rapidly during the crushing phase during which time the agglomerate sizes are reduced but the solid filler has not yet come into proper contact with the matrix. The next stage, when torque increases again, is the wetting stage. During this stage the filler surface is increasingly wetted with rubber. This increases the mix viscosity because, filler interacts with the rubber, its actual concentration in the mixture increases. Now, when viscosity is high and shear rate increases the dispersion process starts causing a size reduction in the filler particles then a distribution of the dispersed particles to form a homogeneous mixture. If this figure is viewed together with Figure 18.7, it becomes clear that several important parameters lead to the attainment of a certain

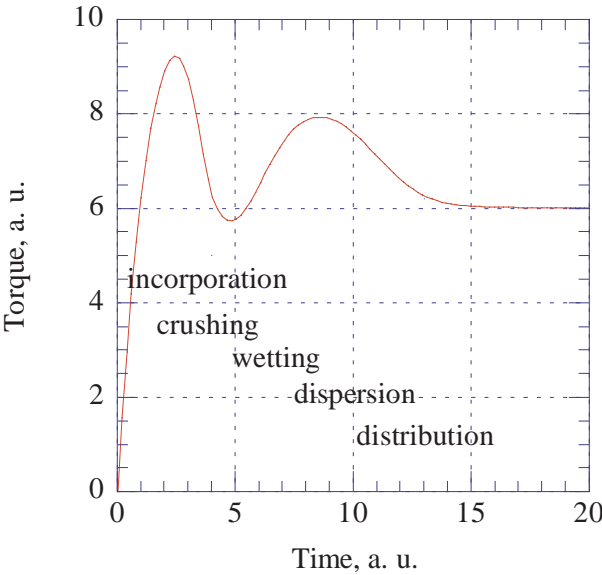


Figure 18.6. Torque vs. mixing time of silica in rubber. [Adapted, by permission, from Bomo F, Meeting of the Rubber Division, ACS, Montreal, May 5-8, 1996, paper E.]

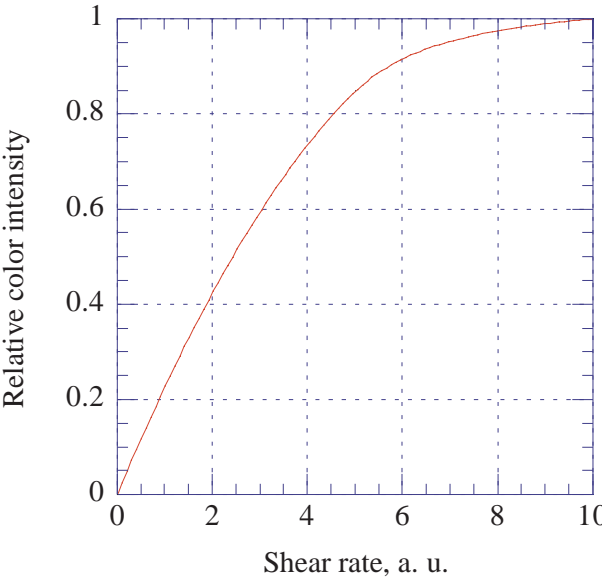


Figure 18.7. Color intensity vs. mixing time and shear rate.

maximum dispersion.¹⁷ The most critical parameters are mixing time and shear rate (torque) (Figure 18.7) but the interaction between the filler and the matrix is also a significant factor. The combination of these three parameters permits an almost unlimited number of permutations making understanding, modelling, and practical

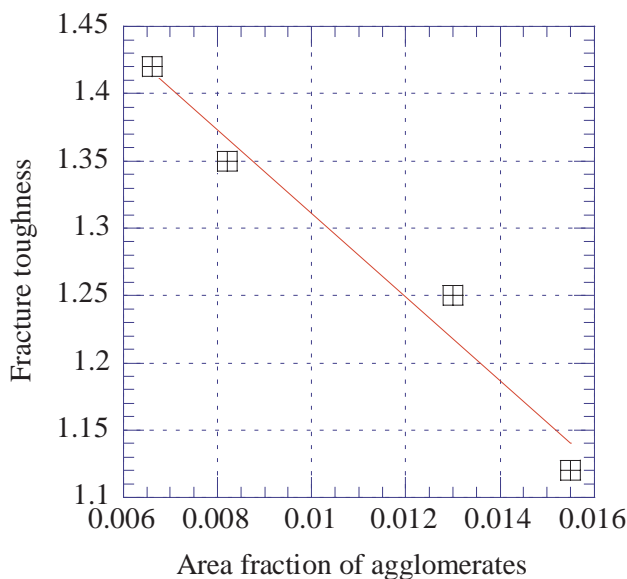


Figure 18.8. Fracture toughness vs. area fraction of agglomerates, Φ_a . [Data from Yeh Wang, Jiang-Shen Huang, *J. Appl. Polym. Sci.*, **60**, No.11, 1996, 1779-91.]

methods of dispersion so difficult that only experimentation can verify assumptions.

Figure 18.8 shows that the fracture toughness of thermoplastic material depends on the dispersion.²⁶ The degree of dispersion is characterized by the area fraction of agglomerates, Φ_a . The larger the area fraction of agglomerates, the worse is the dispersion. The graph shows that there is a substantial improvement in fracture toughness if dispersion is improved. This is never overstressed considering that we do not attain perfect dispersion but only try to limit imperfect dispersion.

18.6 EXTRUSION^{13,26,38-54}

The composition of fillers and their degree of dispersion also influence the quality of extruded materials. Extrusion, like many other processes, must disperse fillers, which are usually hydrophilic, in a matrix which is predominantly hydrophobic. This, by itself, is a difficult task. Fillers contain water which may hydrolyze some polymers (e.g., polyamide or polyesters) at the elevated temperatures of processing. Even if water does not contribute to degradative reactions, it still creates the danger of various defects on the surface and in the bulk. Being able to get the best possible dispersion can be difficult, especially with the fine particle sized fillers which contribute to high performance of extruded articles. The smaller the particles the more difficult they are to disperse because the tendency to agglomerate increases as the particle surface area increases.⁵⁴ Fillers must be incorporated into a high viscosity melt which makes the process of dispersion more difficult. In spite of

these difficulties the extrusion process must be designed for fast, cost effective production of up to several hundred kilograms per hour output from a single extruder.

Many new technologies have been developed to overcome these hurdles. Dispersion of fillers was tackled in many different ways. First, various screw and barrel designs were proposed which were capable of breaking agglomerates. These include the cavity transfer mixer and the pinned barrel. Second, a better technology of melt screening was developed using plate screen changers and continuous rotary disc filters. These filters prevent coarse particles from entering the feed stream. The dispersion and extrusion processes were optimized. It is difficult to optimize the extruder design if the extruder has to perform two functions simultaneously: mixing and dispersing of ingredients and feeding the die for maximum output and quality. Several systems were developed which separate these two functions by using extruders interconnected in series. The mixing extruder or other machine (e.g., ko-kneader) is optimized for dispersion and it feeds the melt to the production extruder. This solution eliminates the need to produce a separate granulate. It also eliminates the uncertainty about the pre-extrusion history of the granulate which affects extrusion results. This process is more efficient and outputs substantially increase.

The adverse effect of water was minimized through the use of venting systems. Traditionally, top of the barrel venting has been used. In a new Werner and Pfleiderer design, side-venting was introduced which allows for more efficient removal of water. The most modern extruders are capable to process PET containing up to 0.4% moisture. Finally, the process economics was improved by direct extrusion and development of continuous mixers which allow the material to be processed in one pass from dry powders. Unlike traditional extrusion which requires the granulate or dry blend to be formed in a separate operation, here, the ingredients are fed to the stream of molten polymer.⁵² The line is capable of automatic dosing of all ingredients including fillers and pigments, in-line coloring, and quality control.

These new developments allow materials to be produced in an economical manner into products of high quality. However, the extrusion industry continues to use the traditional technology and, therefore, many of the old problems of filler incorporation remain.

Figure 18.9 shows the effect of filler particle size on extruder throughput for PP filled with talc.⁴⁷ Several reasons account for reduction in throughput as the particle size decreases. Increasing the surface area of filler makes mixing more difficult because of agglomerate formation. Smaller particle sized talc has lower bulk density which decreases the conveying efficiency of screw. The relatively large amount of air supplied with the particles decreases the conveying efficiency and increases the time required to extract air.⁴⁷ The amount of talc added affects the ratio of throughput, Q , to the screw speed, N_s (Figure 18.10). As the concentration

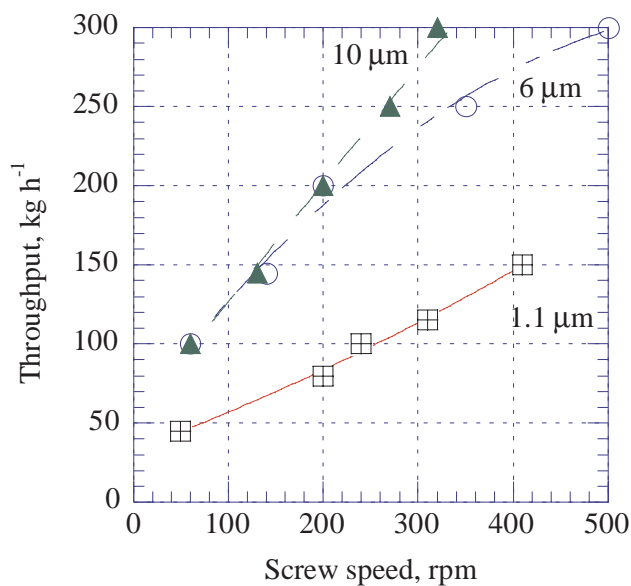


Figure 18.9. The effect of talc particle size on extruder output. [Adapted, by permission, from Ishibashi J, Kobayashi A, Yoshikawa T, Shinozaki K, Antec '96. Vol. I. Conference Proceedings, Indianapolis, 5th-10th May 1996, 386-90.]

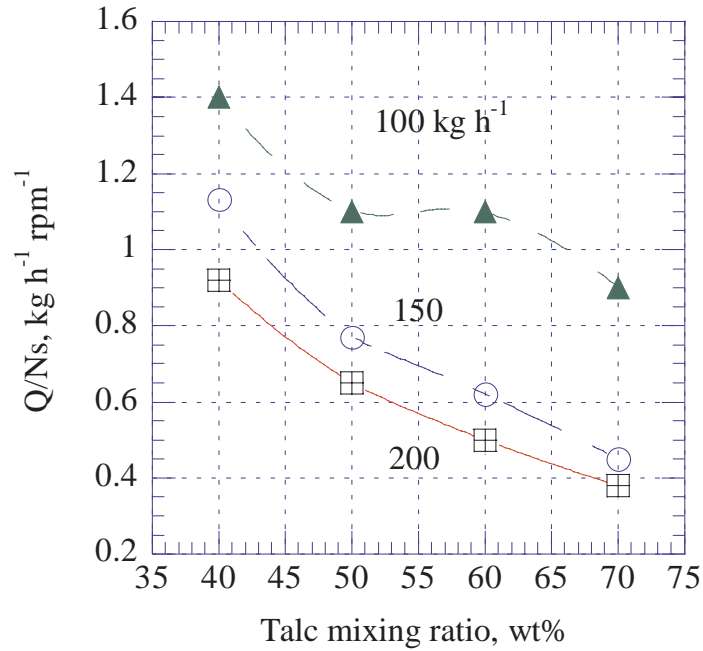


Figure 18.10. Throughput, Q/screw speed, Ns ratio vs. talc loading. [Adapted, by permission, from Ishibashi J, Kobayashi A, Yoshikawa T, Shinozaki K, Antec '96. Vol. I. Conference Proceedings, Indianapolis, 5th-10th May 1996, 386-90.]

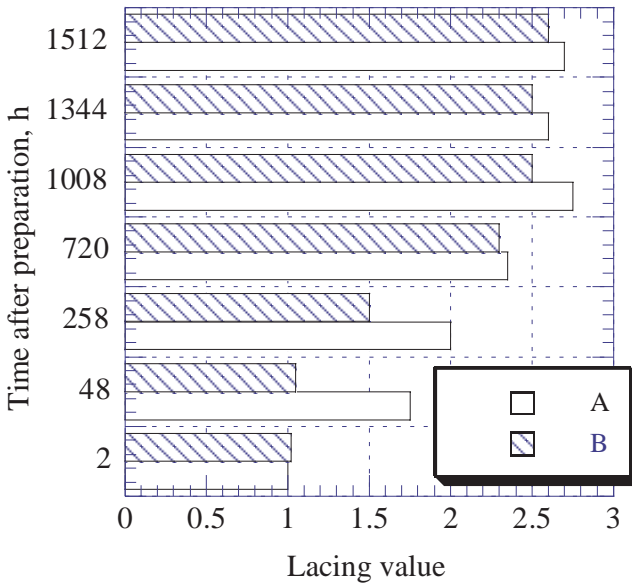


Figure 18.11. Lacing value vs. time of moisture absorption. [Adapted, by permission, from Hansen H, Polymers, Laminations & Coatings Conference, 1995, 653-8.]

of filler increases the Q/Ns ratio decreases which means that Q decreases.⁴⁷ The decrease becomes greater as the throughput increases.

Figure 18.11 characterizes the problem with moisture. The addition of titanium dioxide causes lacing in PE films. The lacing is a defect caused by the formation of series of small holes. Investigation has connected lacing to moisture in the titanium dioxide concentrate. Moisture absorption varies depending on the filler or pigment type and the time it is exposed to moisture in ambient air.

18.7 FOAMING⁵⁵⁻⁵⁷

The production of foamed products is very sensitive to changes in composition and the parameters of processing. The inclusion of fillers complicates the process and careful consideration must be given to the effects that filler incorporation has on material properties. Experimental work must be done to verify process conditions and material performance.

First, a homogeneous suspension of filler must be produced. This suspension should be sedimentation-free because it would influence foam properties. Rheological studies are used to select the appropriate dispersion agents which keep the viscosity close to the viscosity of the unfilled formulations. Complete filler wetting and network formation helps to make the stable suspensions.

From the point of view of chemistry of foaming, the reaction rate in the presence of fillers should be studied to determine if the filler slows or increases the reaction rate. Reaction rate is not only the factor determining the economy of the

process. There must be a balance between gas production, viscosity increase, and phase transition. All three must be synchronized to yield the expected results.

Fillers in these systems affect two types of nucleation: nucleation of bubble formation and nucleation of crystallization. Nucleation of bubble formation affects the density of foam. Nucleation of crystallization affects the balance of gas formation and phase transition. The timing of both processes is critical.⁵⁵

Fibers are frequently used in foam reinforcement. Due to the nature of the process, fibers are oriented as the foam rises (strain and movement) but restricted in movement by bubble wall formation (small distances between bubbles do not leave much freedom for fibers to position themselves).

Figure 13.5 shows the effect of a combination of silica and surface active agent on the formation of microporous uniform foam. This structure offers improved thermal insulation capabilities.

18.8 INJECTION MOLDING⁵⁸⁻⁸⁸

Numerous developments in injection molding machines have contributed to improvements in quality and output but have had only a limited impact on the processing of materials with fillers. But there are a few technological advancements involving fillers. Direct compounding injection molding technology is the most important. Unlike standard methods which use pre-compounded granulates, this method begins from raw materials which are metered from bulk storage facilities and compounded in a two-stage twin rotor continuous compounding mixer. The mixer performs two functions: it melts the matrix material and heats it to the required temperature while dispersing the additives. The compounded material is delivered to an accumulator injection unit which performs the injection functions. This method is a significant advance for the molding industry because it allows inventory to be reduced and a faster changeover. Shear controlled technology is another important development which has an impact on filler processing.⁶² Figure 7.3 shows the arrangements of shear units which orient fibers in the required direction. Powder injection molding technology is also related to filler processing technology. Powdery inorganic materials (metals and ceramic powders) are mixed with a sacrificial polymeric binder which allows the required shape to be pre-formed. Once shaped, the binder is removed in a manner which does not distort the initial shape and it is then subjected to a sintering process, yielding a metal or a ceramic part. In normal injection molding good mixing and dispersion are the most basic requirements. But not in the enhanced marbleizing technique which exploits ineffective mixing elements which allow parts to be produced with a marble appearance effect with excellent repeatability. New developments are reported about process aids which allow highly filled materials to be processed with less difficulty through their influence on the flow properties of the material.

The flow of material into the mold cavity affects the way in which particles are distributed in the molded object. Analysis of parts indicates that particles flow by a

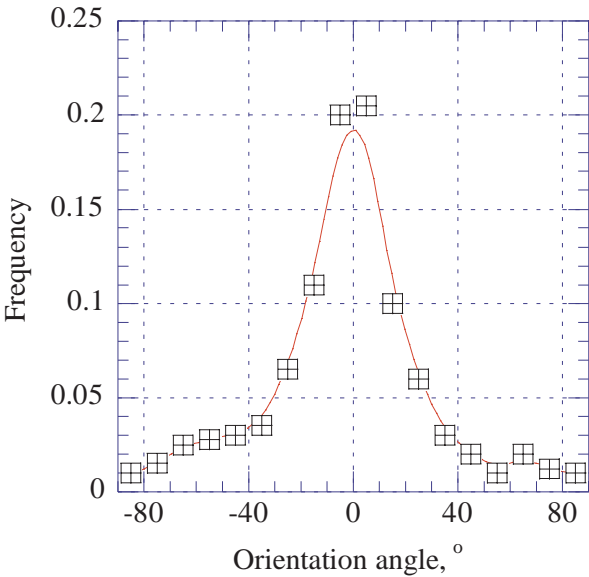


Figure 18.12. Frequency vs. orientation angle for ferromagnetic particles incorporated into a cylindrical part which was injection molded with a magnetic field applied parallel to the direction of flow. [Adapted, by permission, from Fiske T, Gokturk H S, Yazici R, Kalyon D M, *Polym. Eng. Sci.*, **37**, No.5, 1997, 826-37.]

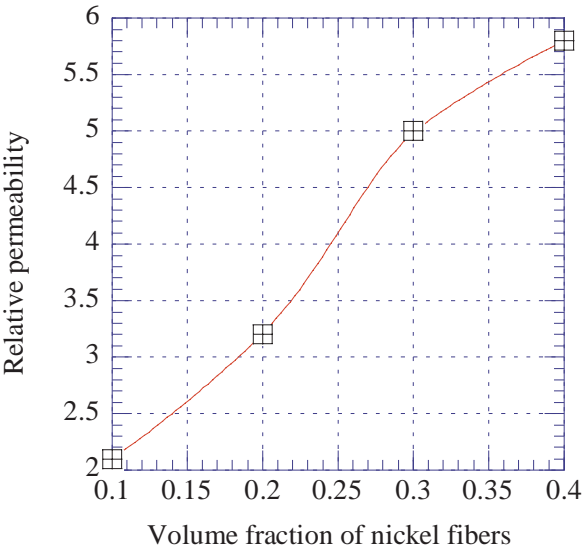


Figure 18.13. Relative permeability vs. concentration of ferromagnetic fibers in PE. [Data from Fiske T, Gokturk H S, Yazici R, Kalyon D M, *Polym. Eng. Sci.*, **37**, No.5, 1997, 826-37.]

fountain flow pattern with a high concentration of particles in the core.⁸⁶ During mold filling, the particles concentrate at the surface of the flowing material then are diverted towards the walls by back flow. Fountain flow was also detected in glass

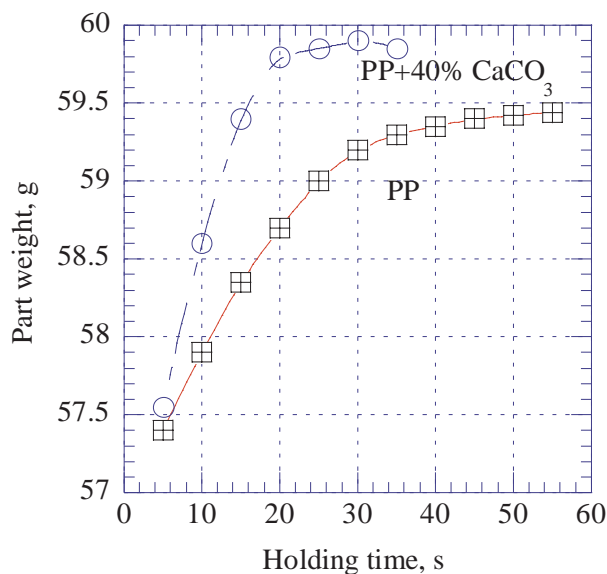


Figure 18.14. Part weight vs. holding time for neat PP and 40% calcium carbonate filled PP. [Adapted, by permission, from Mamat A, Trochu F, Sanschagrin B, *Polym. Engng. Sci.*, **35**, No.19, 1995, 1511-20.]

fiber reinforced liquid crystalline polymer.⁷⁹ The larger particles are mostly in the core whereas smaller particles spread outwards from the core.⁸¹

A magnetic field can be useful in conjunction with material flow to induce the orientation of ferromagnetic particles. Figure 18.12 shows particle orientation in injection molded cylinder with a magnetic field applied in a direction parallel to the flow.^{58,70} Particles were well oriented increasing the magnetic permeability of the part. Processing parameters such as temperature and injection rate have a minor influence on particle orientation and permeability. The quantity of fibers had the greatest effect on relative permeability (Figure 18.13).

Figure 18.14 shows that holding time affects the tolerance of part weight. Filled material requires substantially less time to reach equilibrium.⁷⁸

18.9 KNIFE COATING⁵

Knife coating is one popular technique for the coating of textile materials. Because the layers of the applied coating are usually very thin, the rheology of the coating is of primary importance. Rheological properties are controlled mostly by the choice of polymer.

In PVC coating formulation fillers play a role. Filler choice mostly depends on the way the filler affect viscosity. The filler should not absorb the plasticizers nor interfere with the pseudoplastic behavior of the paste which is determined by the resin properties and by the choice of plasticizers. Fillers must be completely dispersed, since the gaps between the coated substrate and the knife are very small. There must be no lumps. Fillers should not interfere with deaeration which is

critical for all coated layers but most critical for the foamed layer. The presence of air bubbles in the paste affects the uniformity of foam structure.

Silica fillers play a prominent role in the paste rheology of polyurethane and rubber coating mixtures. Silica fillers are also used for surface matting. In polyurethanes, the layer thickness is even thinner than is used with PVC. Dispersion is enhanced by dispersion aids. Fillers are used at relatively low concentrations in PU formulation. But in rubber coatings, large quantities of calcium carbonate are used to decrease cost. Rheology and reinforcement are adjusted with carbon black.

18.10 MIXING⁸⁹⁻¹⁰⁶

The mixing process is usually thought of as a progressive process in which two or more components are first blended together to form an inhomogeneous mixture. With additional mixing, the distribution of the components becomes more uniform and finally, more energy is put into the mixture, particles are broken down into progressively smaller and smaller entities and the mixture becomes smooth and uniform. The final stage of the process, the dispersion stage, was discussed in Section 18.5. Here, we will concentrate on the traditional rubber mixing process which has not changed dramatically in 90 years. In spite of its long term use, a full and fundamental understanding of the process is lacking.

The mixing machinery, although now built of better materials and frequently fully computerized and computer designed, is essentially the same as it was at beginning of this century when several excellent designers established the mixing technology. Two types of rotors are generally used: tangential and intermeshing. The tangential rotor first disperses then distributes the materials whereas the intermeshing rotor does it in the opposite sequence. Other differences are related to processing and include fill factor (smaller with intermeshing rotors), speed of ram and rotors (slower with intermeshing rotors), oil incorporation (slower with tangential rotor), etc.

Several mixing processes have been developed throughout the years, such as conventional mixing (rubber added first, followed by powders, plasticizers, oils, curing agents and accelerators), upside down mixing (fillers and oils mixed together before addition of polymer), single stage mixing (convenient because of one step process) and two stage mixing (lowers temperature impact and gives better dispersion). There are also processes which use variable speed mixing and most of them use ram movement. Some more recent technologies such as plate mixers take advantage of applying pressure to material to shorten the mixing time but this technology is not really new since this approach was proposed in the 1920s.

Although different rubber composition requires different equipment and processing, several general principles apply. In many mixers, especially those of older construction, fillers and oils are added in increments to facilitate dispersion. Frequently, in two stage mixing, the first stage is upside down mixing to achieve

good dispersion of fillers. This stage is followed, after cooling, by a conventional mixing cycle during which curing additives such as metal oxides are added. The uniform distribution of metal oxides is very important to guarantee uniformity of cure. Many methods are used to aid incorporation of metal oxides. One common approach is to withhold some of the liquid additives (plasticizers, oils) which may interfere with dispersion. Thermal and furnace blacks are more difficult to incorporate and are usually added first. The addition of coarser carbon black tends to help in the incorporation of finer carbon blacks. Fillers may help to disperse other additives such as plasticizers, tackifiers, or lubricants. Filler dosing during mixing can be very critical. If a mineral filler is overloaded it covers the surface of the mixing elements preventing the rubber from sticking to the mixing elements. The rubber then slips over them and no shear is applied. To overcome this, water is sprinkled over the mixture to agglomerate the filler and remove it from the surface of the mixing elements. There are many other methods used by industry to aid mixing. These have been derived from years of practical experience with various compounds, cases, and problems.

Two-roll mixing is another traditional method of mixing which relies on somewhat primitive equipment and on the skills of the operator. It has never been possible to establish standard procedure for this process and batch-to-batch results vary widely.

Problems associated with the general chemistry and physics of mixing are solved based more on practical than scientific principles. It is true that many elements of this process have been evaluated by powerful analytical techniques but knowledge of the kinetics of the process is still based on experience rather than science. The chemical and physical changes are highly complex. When heavy and powerful rotors begin to work on rubber, very high shears and temperatures are involved which contribute to the so-called mastication process. During this process, mechanical forces break bonds in the rubber resulting in free radical formation. This is a detrimental process for rubber because molecular weight decreases but also because reactive sites are formed which may react either with the rubber itself or with additives. The reactions and the numerous directions that these reactions can take are complex and random. The material properties, heat, and shear all influence the results. The process is difficult to control due to high viscosities and random local compositions which cause an inherent inhomogeneity in the system. Traditionally, heat is limited to the requirements of mastication (a state of rheological properties which allows incorporation of ingredients) but there have been suggestions that heat can be used to advantage.⁹⁰ A new method of compounding was proposed in which fillers are preheated to temperatures above 100°C. This supposedly increases the efficiency of the mixing process and shortens mixing by up to 30%. In yet another approach, mixers have been fabricated with cooled mixing elements which are designed to remove the heat of mixing and thereby reduce the rate of thermal degradation.

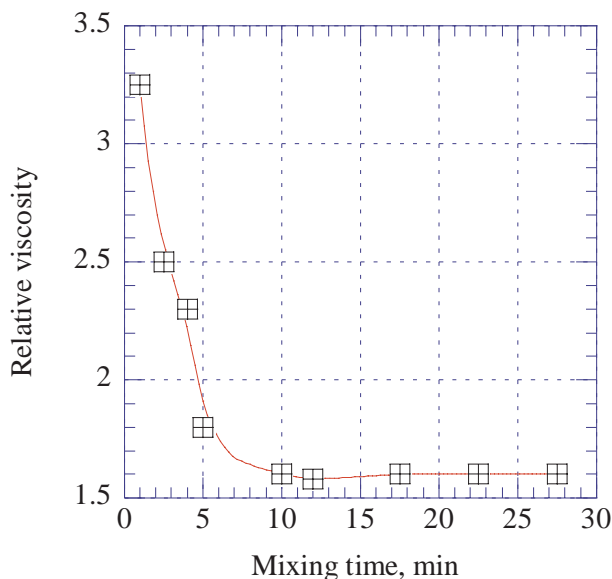


Figure 18.15. Relative viscosity of SBR rubber containing 30 phr carbon black vs. mixing time. [Adapted, by permission, from Clarke J, Freakley P K, *Rubb. Chem. Technol.*, **67**, No.4, 1994, 700-15.]

Several recent findings are reported below to illustrate new observations in the mixing technology. Figure 18.15 shows that the viscosity of SBR rubber containing 30 phr carbon black rapidly decreases at the beginning of the mixing process and then levels out.⁹¹ Viscosity levels out when agglomerates disappear. The power consumption of the mixer, depended on when oil was added relative to carbon black.⁹³ The shortest mixing time was when oil was added 0.5 min after carbon black. The power consumption had very different characteristics when oil was added together with carbon black but the overall mixing time was as short as before. If oil was added 1.5 min after the carbon black, the mixing time to plateau was substantially increased (about 70%) and the characteristic of power consumption was totally different from both previous cases. For a given set of conditions of mixing only a certain level of dispersion is achieved which cannot be improved by prolonging the mixing time.⁹⁷ An improvement in dispersion can be achieved by the choice of mixer or mixing elements or by the selection of mixing condition, or by controlling the addition of components which influence viscosity during the dispersion phase.

Figure 18.16 shows that carbon black incorporation time, BIT, is affected by the addition of ZnO and by the properties of carbon black. If no ZnO is added, the incorporation time decreases as the carbon black structure increases. The opposite is true when ZnO is present during carbon black dispersion.¹⁰⁵ The overall quality of the dispersion improves when ZnO is present and when mixing is carried out at elevated temperature Dispersion quality was assessed by optical measurements.¹⁰⁴

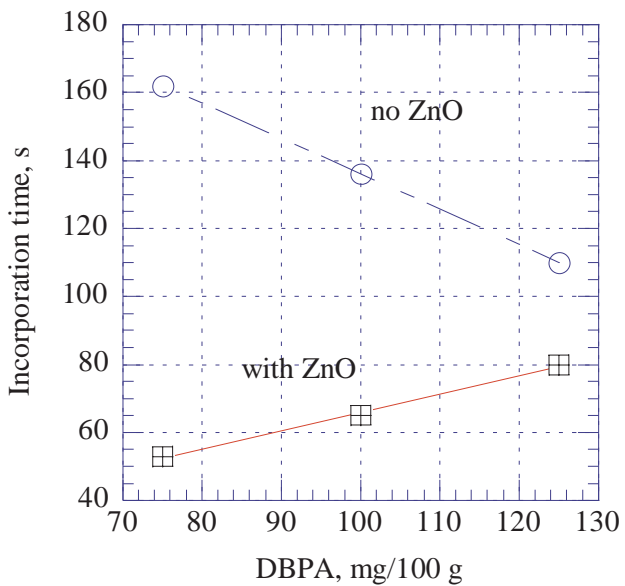


Figure 18.16. Carbon black incorporation time vs. DBPA adsorption. [Adapted, by permission, from Urabe N, Takatsugi H, Ito M, Toko H, Fukui M, *Int. Polym. Sci. Technol.*, **22**, No.5, 1995, T/68-72.]

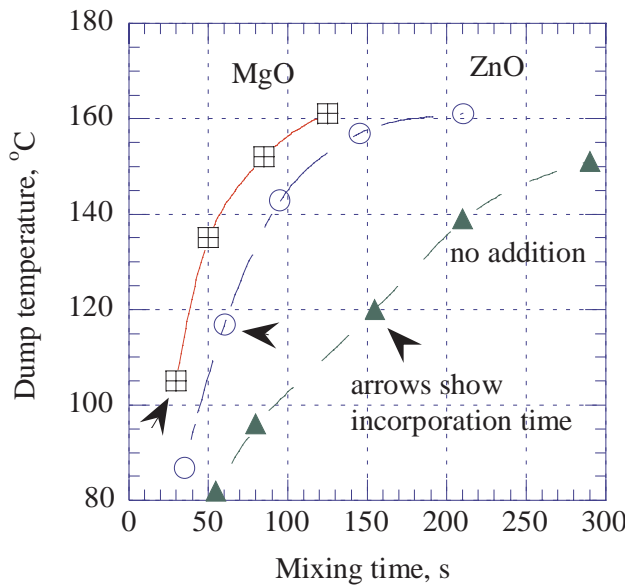


Figure 18.17. Dump temperature vs. mixing time of SBR rubber. [Adapted, by permission, from Urabe N, Takatsugi H, Ito M, Toko H, Fukui M, *Int. Polym. Sci. Technol.*, **22**, No.5, 1995, T/63-7.]

The addition of a crosslinker increases the viscosity of the mixture and the temperature of the batch increases (Figure 18.17). Magnesium oxide, used as a crosslinker, caused the temperature of the mix to rise four times faster than a mix

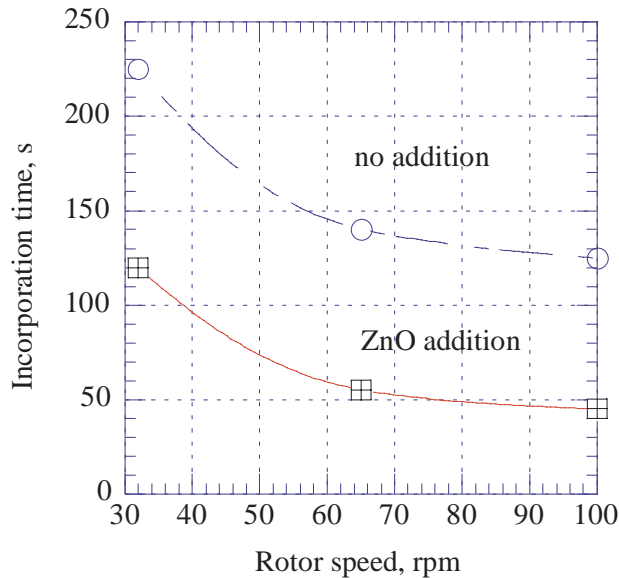


Figure 18.18. Carbon black incorporation time in SBR vs. rotor speed. [Adapted, by permission, from Urabe N, Takatsugi H, Ito M, Toko H, Nakada M, *Int. Polym. Sci. Technol.*, **23**, No.1, 1996, T/29-33.]

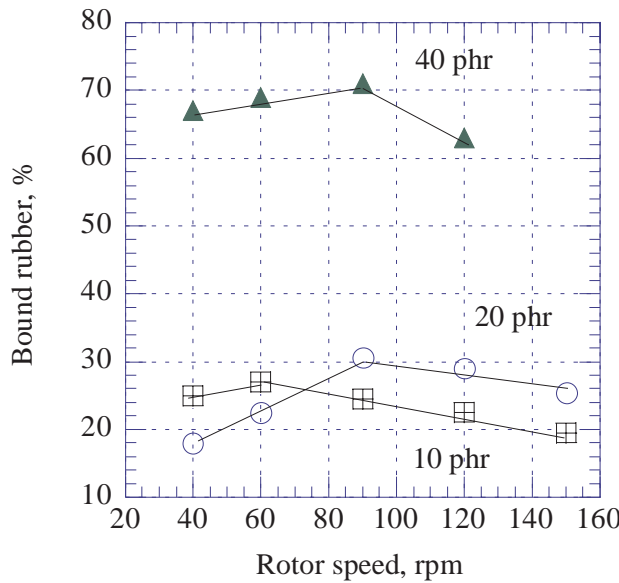


Figure 18.19. Bound rubber vs. mixer rotor speed for natural rubber filled with carbon black. [Adapted, by permission, from Mallick A, Tripathy D K, De S K, *J. Appl. Polym. Sci.*, **53**, No.11, 1994, 1477-90.]

without crosslinker.¹⁰⁴ Zinc oxide also produces a higher rate of temperature increase but its effect is less than that of magnesium oxide. In both cases the dump

temperature at the end of the mixing process was much higher than in uncrosslinked rubber batch.

The rotor speed also influences carbon black incorporation time (Figure 18.18). The characteristics of both relationships are similar but longer times are required to disperse rubber with no ZnO added.¹⁰⁵

The conditions of mixing and the filler concentration affect the bound rubber concentration (Figure 18.19).⁸⁹ For a given system, there is a certain critical rotor speed at which the bound rubber concentration reaches a maximum. A further increase in the rotor speed contributes to a decrease in the bound rubber concentration.

18.11 PULTRUSION¹⁰⁷⁻¹⁰⁸

Several types of reinforcements are used in pultrusion. These include: continuous fiber strand, roving, short fiber, and particulate fillers. Aligned fibers provide direct mechanical reinforcement. The functions of particulate fillers are several. This includes reduction of polymerization shrinkage, regulation of rheological properties, aiding in the reduction of fiber agglomeration, and fire retardancy. Many types of particulate fillers are used for these purposes, including most of the major groups of fillers. The industry custom-designs pultruded elements to the requirements of application and customer demands and these wide and varied requirements have lead to the great variety of fillers in traditional use. Because of the wide spread use of pultruded elements in construction, fire retarding properties are very important.

An analysis of the pultruded elements manufactured by the leading producers¹⁰⁷ revealed that the mass content of particulate filler was in the range of 38-50 wt%. This seemingly high range is needed to improve fire retardancy because alumina is often the filler of choice. This concentration of filler substantially reduces the mechanical strength of the element due to the fact that the mass fraction of resin in these elements is low and the resin is responsible for binding the reinforcing components. The performance of the resin depends on its penetration of the structural elements and on the resin's properties which are apparently affected by high concentrations of filler.¹⁰⁷ The particle sizes of filler are also very important. The use of large particle size filler increases fiber agglomeration during the molding process and reduces reinforcement.

Figure 18.20 shows the effect of continuous and long glass fiber concentration on the tensile properties of a pultruded element. The continuous fiber increases tensile more than does long glass fiber. Similarly, flexural modulus and impact strength increase more as the continuous fiber concentration is increased.¹⁰⁸

18.12 REACTION INJECTION MOLDING^{94,109-112}

In reaction injection molding, fillers and the reacting mass of matrix may each participate in the reactions, forming systems with a combination of features derived from the high adhesion between components. Numerous variations of this process

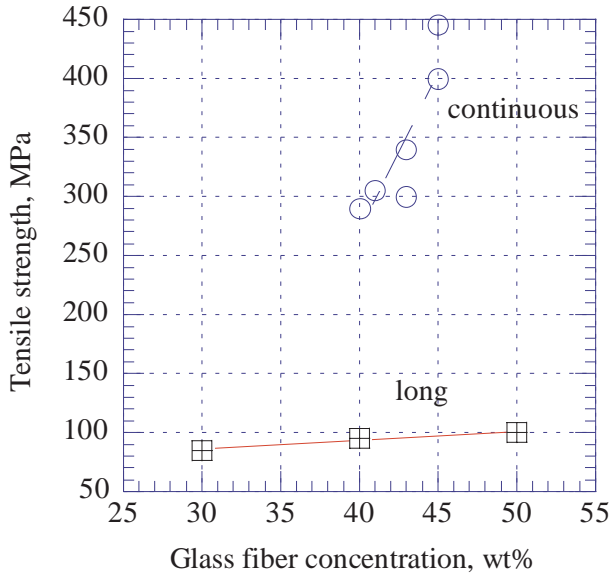


Figure 18.20. Tensile strength vs. glass fiber loading. [Adapted, by permission, from Montsinger L V, Antec '96. Volume II. Conference proceedings, Indianapolis, 5th-10th May 1996, 2546-9.]

have been developed. These include transfer molding, reaction injection molding, reactive extrusion, reinforced reaction injection molding, and structural reaction injection molding. Even pultrusion discussed in the previous section is a variation of reactive processing. All these processes have one common denominator – they use fillers to obtain the required properties. Fillers decrease warpage, reinforce, reduce thermal expansion, improve dimensional stability at elevated temperatures, and change rheology to improve flow in the mold. Since these systems are reactive, the moisture must be very well controlled. Moisture may interfere with the main curing processes (e.g., polyurethanes). This requires either special grades of fillers or filler pre-drying before incorporation.

In these applications, reinforcement by fibers is complicated by the high probability of generating anisotropic properties because of fiber orientation during the flow. Depending on the geometry and the application of the product, the anisotropy might be advantageous but in most applications efforts are made to obtain better balanced mechanical properties. This is achieved through design of dies or by the use of a micro-mixing processes as presented in Figure 9.7. Increasing the filler loading decreases the effect of micro-mixing.

A combination of reinforcement and polymer grafting gave very good results. Wood fiber was processed with polypropylene grafted with maleic anhydride. Figure 18.21 shows the result.¹⁰⁹ Tensile strength (and also Young modulus) increase with an increased concentration of wood fiber. Similar good results were

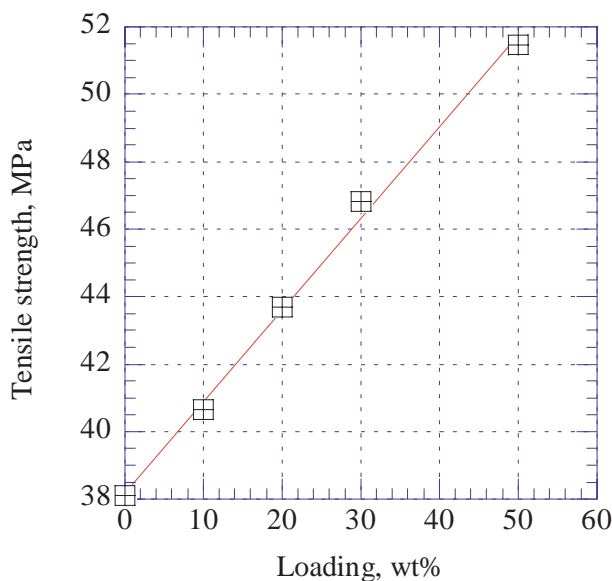


Figure 18.21. Tensile strength of wood filled maleated PP vs. wood fiber loading. [Adapted, by permission, from Collier J R, Lu M, Fahrurrozi M, Collier B J, *J. Appl. Polym. Sci.*, **61**, No.8, 1996, 1423-30.]

obtained with polyurethane reinforced with wood fibers. Good matrix/filler adhesion is important for the improvement of mechanical properties.

The use of filler may adversely affect the surface finish of some products. This is especially true, if high concentrations of filler are used (in some applications materials are filled up to 80 % of maximum packing density of filler). Work is being done to improve the properties of fillers in this application. Grades of wollastonite are available which allow parts with a high gloss to be produced.¹¹¹ Another development is in conductive RIM, ready for electrostatic painting without priming.¹¹²

18.13 ROTATIONAL MOLDING¹¹³

Fillers are not used to any extent in products made by the rotational molding process. Rotational molding is dominated by polyethylene (close to 90% volume) to which even small addition of pigments or fillers (less than 2 wt%) causes a decrease in tensile and impact properties of the products manufactured in this process. Polyethylene is vulnerable to environmental stress cracking which is made worse if fillers are present.

Resin and fillers of different density are separated by rotational forces. Even when a mixture of different particle sized resin is used, the finer particles manage to sift through the larger particles to the mold surface. If a material of higher density such as filler is added, this will, by itself, enhance the movement of heavier particles to the mold surface to cause cross-sectional inhomogeneities in the composition. This has been confirmed by studies involving incorporation of

colorants. Two methods are used in coloring: extruded masterbatching and dry blending. If dry blending is used, the mechanical properties (especially impact strength) are reduced on addition of small amount of pigments.

However, carbon black has been used with success as a filler in rotationally molded products. At concentrations of up to 2.5 wt% it improves the weathering resistance of the product. Since dimensional stability and the shape of articles would benefit from the use of fillers and fibers, it is probable that they will start to be used in the future. When this happens, fillers will be introduced in a premixed form to assure homogeneous distribution (forces normal to the surface of product cannot cause the movement of particles towards the mold surface when particles are premixed with polymer).

18.14 SHEET MOLDING¹¹⁴

Sheet molding uses three groups of fillers for different purposes: metal oxides for curing, fibers for reinforcement, particulate fillers for variety of other purposes such as improvements in mechanical properties, chemical resistance and surface appearance. The technology is very well documented.¹¹⁴

The thickening process of the mixture used for sheet molding is one of the most important production steps. It is accomplished by the use of magnesium and calcium oxides or hydroxides. Magnesium oxide is the most frequently used. The process is a two-step reaction. In the first step, magnesium oxide reacts with two carboxyl groups forming a bridge. In the second stage, molecules are aligned by hydrogen bonding through the water produced in the first step, followed by formation of complexes between magnesium and carbonyl groups. These processes increase viscosity in the first step by increasing molecular weight and through the formation of a tri-dimensional network in the second step. These process steps must be well controlled. The rheological properties that they produce are important for product quality. The process of thickening takes about a day and then the viscosity remains stable for several weeks providing the process was correct and raw materials were of good quality. Wet filler and coarse particles in fillers cause problems.

Fillers are used in these products to improve mechanical properties or impart flammability resistance. Fillers are frequently silane-treated to further improve mechanical properties. Fillers must have a low moisture (below 0.1%), a low absorption of resin, and are expected to impart thixotropic properties. There are special cases. For example, if peroxyketals are used as initiators, basic fillers have to be used because acidic fillers interfere with cure times and the shelf-life of the composition. Shape and particle size distribution must be considered in filler selection to impart the desired rheological properties. Calcium carbonate is the most popular filler but aluminum trihydrate, anhydrous calcium sulfate, and silica are also frequently used. Barite is well suited to this application, especially if acid

rain resistance is required but its more widespread use is limited because of its high specific gravity. Light weight is usually an essential requirement.

Glass fiber is used for reinforcement. The glass fiber must be properly surface sized to give the best mechanical performance and fire resistance. Good fiber wetting and low moisture content are also required.

Many defects in molded sheet can be related to fillers. Blistering may be caused by moisture but also by insufficient wetting of fibers and entrapped air pockets. Inconsistent cure and thickening is caused by the presence of moisture. Improper fiber orientation may initiate fracture cracks. Flow marks, streaks, warpage, and protruding fibers are also caused by improper fiber orientation.

18.15 THERMOFORMING¹¹⁵⁻¹¹⁸

Thermoforming is closely related to sheet molding. Compounding issues are similar to sheet formation. Fillers are added to materials for the same reasons. Again, these are reinforcement, increased dimensional stability, reaction to elevated temperature, fire proofing, and increased stiffness. The processing of a filled sheet is more complex than for unfilled resin because fillers reduce flexibility and elongation. Fiber reinforcement introduces constraints which limit the possible shapes of thermoformed material. Because of a reduced ability to change shape, only simple shapes can be manufactured from reinforced sheets without a substantial increase in the surface area. In order to process reinforced sheets to more complex shapes very large forces are required and results have not been satisfactory due to substantial surface defects.

Fibers and other non-spherical fillers change their orientation during thermoforming. Small strains are sufficient to orient fibers. Experiments have demonstrated that particles of talc orient themselves parallel to the surface of thermoformed parts.¹¹⁶ The crystallites are oriented in a direction perpendicular to the either the talc or the mold surface. This is because the mechanism of crystallite growth begins on the surface of talc and grows outwards.

18.16 WELDING AND MACHINING¹¹⁹⁻¹²⁰

Welding and machining of filled materials is known to be affected by the presence of fillers because filled materials are harder and their cutting is more difficult.¹¹⁸ The many processes used for machining and jointing plastic parts, welding is the most affected by fillers in the formulation. Fillers interact with matrix which results in the higher dimensional stability and more resistance to flow in the molten state. It is not clear if the difficulties with welding should be attributed to the presence of fillers or the failure to develop the proper welding process.

Both past and current literature does not provide many answers but there are some preliminary hypotheses. Recent papers on the subject refer to older works.^{119,120} These gave some information on welding results. In a hot-tool welding of polypropylene containing 40 wt% calcium carbonate, polypropylene containing

20 wt% short glass fibers, and poly(ether sulfone) containing 30 wt% short glass fibers, the strength of the weld relative to the material was 50-55%. Graphite fiber filled PVDF had a weld strength substantially lower than the material. But, in some instances the weld strength was higher than the tensile strength of unfilled materials. It is difficult to assess these findings because studies made on commercial materials cannot account for the influence of other components of the mixture many of which may also affect welding result. It is also difficult to determine if the conditions for welding of the filled materials were optimized.

One current paper¹¹⁹ comments on the choice of welding parameters for hot plate welding. When the results of the two studies are compared, they show that the best welding parameters for polypropylene filled with glass fibers were determined by a complex relationship between hot plate temperature, heating time, and welding pressure. Analysis of these parameters with the aid of a model determined the optimal choice of welding conditions for the filled material. Perhaps, these parameters were not optimal for neat resin. Diffusion and geometrical model for analyzing welding results was inadequate for determining optimal processing conditions.

In vibrational welding of poly(butylene terephthalate) filled with mineral filler and glass fiber, the tensile strength of unfilled polymer was compared with the weld strength.¹²⁰ For glass fiber filled polymer at all concentrations of glass fiber (15-30 wt%) and for 10 wt% mineral filler, the weld strength was close (90-95%) to the strength of unfilled polymer. Material containing 30 wt% mineral filler had only half the weld strength of neat resin. Remedies must be found in future to prevent the loss of mechanical performance in welding process which offsets results of reinforcement. This may not matter if fillers were added for other purposes than strength. This study also shows that the addition of both mineral filler and glass fibers required adjustment in the conditions of welding. In particular, either the welding time or the pressure applied to the adjoining parts had to be increased to obtain the same result as for the neat resin. More studies are clearly required.

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