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26 Functional Fillers for Plastics

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26.1 Introduction

Over the last several decades, thermoplastics have flourished, replacing traditional materials such as glass, metal, and wood. Today, they are a ubiquitous and irreplaceable part of modern day life. There are several different reasons why these materials have been so very successful. In some instances, they offer lower materials cost than the material they replace. Sometimes, they offer performance characteristics that cannot be attained using other competing materials. Finally, thermoplastics have facilitated part integration whereby several parts can be injection molded into one piece, thus reducing production time and enabling significant cost reduction through the elimination of assembly work.

As market penetration increased, people started to look for ways to reduce the cost of the plastic materials and for ways to extend the property spectrum, to allow plastics entry into new applications. Fillers were introduced and were readily accepted because they are easy to incorporate into plastics and offer myriad possibilities for product improvement and differentiation. The rather unglamorous term "filler" does not do justice to the essential role these additives play in tuning processability as well as mechanical, thermal, optical, electrical, and other key properties. Therefore, they are referred to as "functional fillers." As we shall see, these unassuming additives are a vital addition to the arsenal of the plastics formulator. Each type of filler lends a unique property set to the host polymer.

Fillers are an extremely diverse group of materials. They can be minerals, metals, ceramics, bio-based (e.g., plant matter), gases, liquids, or even other polymers. Minerals alone account for well over 4000 different distinct species. Any particulate material added to a plastic will behave like a filler. For example, anti-block, pigments, impact modifiers, nucleating agents, antioxidant crystals, and numerous other additives will affect the mechanical and other properties of polymers in the same way that filler particles do. Consequently, it is vital to understand how fillers alter properties even if no filler has been added per se.

Despite the almost limitless array of potential filler types, the numbers that have achieved wide-scale commercial adoption is far more limited (Table 26.1). A multi-billion-euro a year filler market is dominated by fewer than 10 fillers. Elastomers account for approximately 50% of filler usage followed by thermoplastics at 35% and thermosets with 15%.

Table 26.1 Fillers market in terms of volume and value

Filler	Millions of Tons	Billions of Euros
Carbon black	4.5	3.96
Natural $CaCO_3$	2.3	0.17
Precipitated $CaCO_3$	0.2	0.12
Precipitated silica	0.3	0.3
$Al(OH)_3$	0.3	0.17
Talc	0.3	0.14
Kaolin	0.2	0.03
Others	0.8	0.12
Total	8.9	5.01

Courtesy of Rothon Consultants

26.2 The Basics

There are numerous specialized texts devoted to fillers [1−3], polymers [4−6], and composites [7−14].

Before delving into the intricacies of filled polymer systems, it is prudent to begin with the following four fundamentals.

1. Filler concentration
2. Particle size and size distribution of the filler
3. Distribution and dispersion
4. Shape and aspect ratio

Note that the chemistry of the filler is not mentioned because that is secondary to the properties listed. To a large extent, the polymer does not "care" or "sense" what the chemistry of the filler is. The polymer only responds to the filler in terms of the criteria listed above. Consequently, one could add calcium carbonate, talc, mica, or glass, and the

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effect on properties would be largely the same provided that amount added, size, shape, and dispersion were equivalent.

Conversely, one could add three different grades of mica, each with a different aspect ratio and the effect on properties would be dramatically different even though the mica has the same chemistry in all the three cases.

There are exceptions to this rule, in particular when there is some specific interaction between the filler and the polymer, but for the most part, fillers and polymers are rather inert, so one should concentrate more attention on the four factors listed.

26.2.1 Filler Concentration

Usually, filler is dosed gravimetrically, that is to say the amount of filler added is measured and expressed as a weight percentage. When reporting the influence of filler on properties, it is common to plot property (*y*-axis) versus weight percentage of filler (*x*-axis). This practice is misleading, because there is no direct connection between the mass of filler added and properties. Rather, the properties all depend upon the volume percentage of filler in the polymer. Thus, one must plot results as property versus volume percentage of filler in order to gain any understanding.

Most people are astounded to learn that plotting composite density versus weight percentage of filler results in a pronounced curve (Figure 26.1). In contrast, when common properties such as density, modulus and yield strength are plotted versus the volume percentage of filler, straight lines result for commonly used filler levels.

Even when one knows that volume percentage is the appropriate parameter, it is still hard to understand conceptually why that is the case. The following example helps to clarify why it is that volume percentage is paramount. Imagine adding some very low density filler, such as air. Adding 1 wt% of air corresponds to adding 50 vol% of air filler. That means that even though only 1 wt% of filler was added, 50% of the polymer is now gone and replaced by air. It is clear that, with half of the polymer removed and replaced by voids, all the properties such as modulus, yield strength, impact resistance, and thermal conductivity will be markedly different.

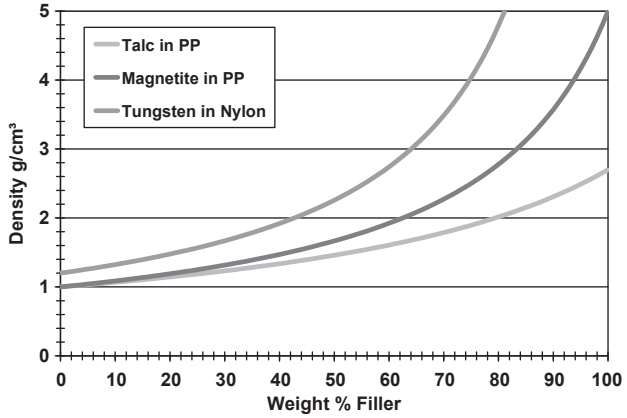

Figure 26.1 Density plotted versus weight percentage of filler.

26.2.2 Particle Size and Size Distribution

There is no one optimal particle size or size distribution. The ideal values depend upon the application and the properties desired. In general, though it is found that particles with a mean size of 1−10 microns are often well-suited as fillers. A specific example would be calcium carbonate for which a mean particle size of around 2 microns is often used in PP and PVC.

The distribution of sizes is at least as important as the mean size. Very large and very small particles both tend to be detrimental to the properties (Figure 26.2). Small particles result in high viscosity and therefore loss of processability as evidenced by poor mold filling and loss of extruder throughput. Large particles act as flaws. Stress concentrations are high around large particles and they lead to a dramatic reduction in impact resistance (especially unnotched) and elongation to break.

To complicate matters further, the very small particles are difficult to disperse and tend to agglomerate to form large particles which, as just described, are deleterious to some properties. This effect is one of the main reasons why the promise of nanoparticles has not been realized. They are so small as to be difficult or impossible to disperse so the excellent predicted properties are not seen in the real world. In addition, smaller particles are more expensive to produce, thus limiting the applications where they are cost-effective.

Usually, one attempts to correlate property changes with the size of the filler as shown on the manufacturers' datasheet. Often, no clear correlation exists because it is the size of the filler particles in the polymer that counts, not their size when they arrive in the bag. It is therefore important

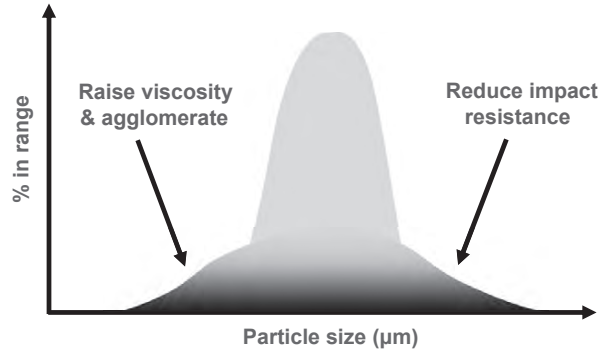

Figure 26.2 Particle size distribution and the effect on properties.

to measure the size of the filler particles in the final compounded material to ensure proper dispersion and wetting. Unfortunately, such measurements are seldom made.

26.2.3 Distribution and Dispersion

In order to obtain consistently good properties from a composite, it is vital to ensure an even concentration of filler particles throughout the material. The evenness can be viewed on different levels. Macroscopic measurements at low magnification are referred to as distribution. Microscopic measurements at higher magnification reveal the level of dispersion. Careful processing, for example extruder set-up and feeding are used to control distribution and dispersion. Use of dispersants is another way to facilitate good dispersion and is especially important when fine or nanoparticles are used. It has been shown that shear forces as found in typical extruders are not especially good for dispersing particles and elongational flow is needed instead. Therefore, new technologies have been introduced so that one can achieve elongational flow with a concomitant improvement in both dispersion and properties.

26.2.4 Particle Shape and Aspect Ratio

Different materials have a tendency to form particles of specific shape depending upon the crystal structure of the material and how it is processed. The shape is often described in terms of an "aspect ratio" which is defined as the ratio of the longest dimension to the smallest. Thus, for spherical and cubic particles the aspect ratio is one or thereabouts. For platy fillers like talc, kaolin, wollastonite, and mica, it is in the range ~5−50. For fibers and nanoclays aspect ratios of ~100−1000 are possible. A vital point to remember is that the datasheet value of aspect ratio is far less important than the aspect ratio of the filler in the final part. Compounding and subsequent steps such as injection molding can dramatically reduce the aspect ratio [9]. One should therefore measure the aspect ratio of the filler in the plastic, for example by ashing to remove the plastic and reveal the filler particles.

There is a perception that a high aspect ratio is always desirable. However, that is not true and may be misleading. Looking at the fillers market worldwide, it becomes clear that it is the low aspect ratio fillers like carbon black, silica, and calcium carbonate that dominate in terms of amount used. A look at the whole market shows that there is a place for every type of filler because each brings its own balance of properties (Table 26.1).

The effect of different fillers, with different particle shapes is outlined in Table 26.2. It is apparent that the each type of filler offers advantages and disadvantages. These pros and cons will be discussed individually.

Table 26.2 The influence of filler shape on properties

Property	Isotropic	Platy	Fibers
Modulus	↑	↑↑	↑↑↑
Yield strength	—	↑	↑↑
HDT amorphous polymer	—	—	—
HDT semi-crystalline polymer	↑	↑↑	↑↑↑
Impact resistance	↑ or ↓	↓	↑ or ↓
Elongation to break	↓	↓↓	↓↓↓
Permeability	↓	↓↓	↓

26.2.5 Mechanical Properties

Tensile testing gives rise to curves like those shown in Figure 26.3. The initial part of the curve is quasi-linear and its gradient is the modulus, i.e., the amount the polymer stretches under a small load. For short deformation times, the sample will return to its original length after the load is removed. Polymers are said to be viscoelastic meaning that they are elastic at short measurement times but for longer measurement periods the polymer slowly flows. A common material that behaves that way is Silly Putty® which, like thermoplastics, flows when you stretch it slowly but is brittle when stretched quickly. Not surprisingly, Silly Putty® is in fact a polymer.

Fillers are elastic and do not flow. Therefore, adding filler to a polymer raises its elastic response at the expense of the tendency to flow. Thus, adding filler tends to make polymers behave more like the curves shown on the left for brittle polymers and less like the curves on the right, which are for ductile polymers. So, one can expect filler addition to give rise to higher modulus, higher yield strength and lower elongation to break. This is exactly what is seen experimentally.

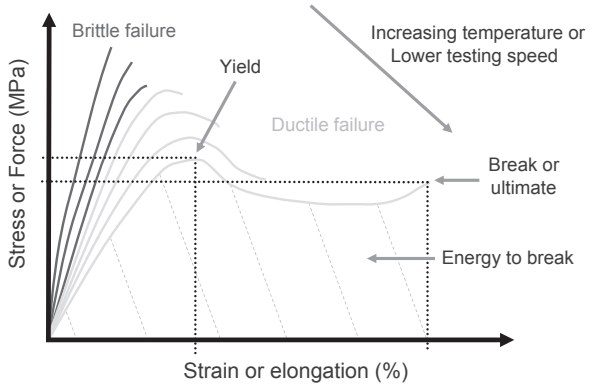

Figure 26.3 Tensile testing of polymers showing key properties.

26.2.6 Modulus

Nearly all common fillers are stiffer than, that is have higher modulus than, typical polymers. Therefore, adding filler tends to increase the tensile and flexural modulus of the polymer.

Isotropic fillers increase the modulus least but they do so equally in all three directions *x*, *y*, and *z*. As an example, adding 40 wt% calcium carbonate to PP homopolymer will increase the modulus from ~1.5 GPa to 3 GPa.

Platy fillers such as talc, clay, and mica increase the polymer modulus more strongly than do isotropic fillers such as calcium carbonate, dolomite, silica, and fly ash. The higher the aspect ratio of the filler is, the greater the increase in modulus.

Fibrous fillers such as glass fiber and carbon fiber have the highest aspect ratio and therefore are the most effective at increasing modulus. Nanoclays, although platy and not fibrous, have such high aspect ratios that they give similar increases in modulus as do glass fibers. However, nanoclays can only be used upto around 10 wt% whereas loadings of 10−60 wt% glass fiber are possible.

Modulus is not affected by the amount of adhesion between the filler and the polymer. This surprises many people who mistakenly believe that they can increase the modulus of a composite by adding a coupling agent to increase adhesion. The reason that modulus is not affected by the level of adhesion is that there is almost always significant adhesion between the filler and polymer to survive a test for modulus. The adhesion is caused by van der Waals interaction from close proximity of the filler and polymer. Additionally, as the polymer melt cools, it shrinks far more than the filler, so after cooling, there is a compressive force as the polymer clamps down around the filler particles. That ensures good contact and thus significant adhesion. Another reason why adhesion does not affect modulus is the way that modulus is measured. It is measured at very low stress and strain. In fact the strain is so low that the adhesion between filler and polymer, although relatively poor, is enough to survive the test intact. The modulus of elastomers is measured at 100% or 400% elongation, conditions which do challenge the adhesion between filler and polymer. Unsurprisingly, adhesion and therefore coupling agents do affect the modulus of elastomers.

26.2.7 Yield Strength

Yield strength is another important property that can be enhanced through the use of fillers. Similar to the trends seen for modulus, the higher the aspect ratio of the filler, the greater its ability to raise yield strength. Isotropic fillers have little or no influence on yield strength. A slight loss of yield strength may be observed when this type of filler is employed. Platy fillers enhance yield strength moderately and high aspect ratio fillers like glass fiber and nanoclay are most efficacious at elevating yield strength.

As mentioned, for the most part, fillers affect yield strength similarly to how they change modulus. However, there is an important difference too. Yield strength is affected by the level of adhesion between the filler and the polymer. Consequently, coupling agents can be successfully used to improve yield strength and also the retention of yield strength when the composite is exposed to water and/or elevated temperature. Furthermore, the surface area of the filler has an influence. High surface area fillers have more contact area to the polymer, thus adhesion and consequently yield strength are increased. The high surface area of nanoclays is one reason why they are effective at increasing yield strength. Even so, they are only about as effective as the equivalent loading of glass fiber. Furthermore, the nanoclay can only be used at low concentrations and are not cost competitive.

The effect of surface area on yield strength is often neglected. Isotropic fillers, which normally cause a slight decrease in yield strength, can actually reinforce if the particles are very fine and therefore of high surface area. Calcium carbonate can reinforce polymers when very fine or when used together with a coupling agent [11]. Once again, though the use of nano calcium carbonate limits the amount that can be added and increases the cost to the point where it makes no commercial sense. As with nanoclays, nano calcium carbonate can only be added in low concentrations below around 10 wt% because it causes a huge increase in viscosity and concomitant loss in productivity, for example the extruder throughput. In contrast, micron sized calcium carbonate is inexpensive and can be used at loadings of up to 80 wt%.

26.2.8 Heat Distortion Temperature and Vicat Temperature

The properties mentioned so far have been room temperature properties. Heat distortion temperature (HDT) and Vicat are both used to give an indication of the maximum temperature which a plastic material can withstand before unacceptably high deformation under load takes place. The effect of fillers is to increase the HDT and Vicat temperature, but because amorphous (non-crystalline) and semi-crystalline polymer respond so differently, they will be covered separately. HDT is often measured under flexural deformation and can be considered as a flexural modulus measured at elevated temperature. Thus, the effectiveness of fillers is as mentioned under the modulus section. Namely, isotropic fillers give least improvement in HDT, more anisotropic fillers such as talc, kaolin, mica, and wollastonite are better and very high aspect ratio fillers like glass fiber and nanoclay are best.

Vicat is measured by pressing a metal indenter into the polymer and measuring the temperature at which the penetration hits a pre-determined level. As Vicat is a surface measurement, one must be aware that anomalies can occur. Injection molded parts are often depleted of filler in the skin

due to movement of filler away from the surface during flow. Thus, one may see a low Vicat temperature although the bulk polymer is actually still rigid at that temperature. Also, Vicat temperature is measured in an oil bath. If the oil plasticizes the polymer then unrealistically low Vicat temperatures will be recorded. Although, as shown, use of Vicat has some caveats, it normally follows HDT quite closely.

Unlike the case of modulus, where the adhesion between filler and polymer is irrelevant, good adhesion does help HDT and Vicat. The reason is that heating reduces the compressive forces exerted on the filler by the polymer so adhesion is lessened. Furthermore, weak adhesion between filler and polymer due to van der Waals interactions is not good enough to survive heating.

26.2.9 Amorphous Polymers (e.g., PS, SAN, PMMA, COC, PC)

Adding high aspect ratio filler will bring the HDT and Vicat temperature up to just below the glass transition temperature of the polymer. No matter how much more filler is added, the HDT cannot be further boosted because the polymer phase is soft and deforms. Fillers are therefore not so effective for raising HDT and Vicat in amorphous polymers [4].

26.2.10 Semi-Crystalline Polymers (PE, PP, PA6, PA6,6, PBT, PEEK)

Adding fillers, especially anisotropic fillers like glass fibers, is very effective at boosting HDT and Vicat [4]. Even low loadings, for example 5 wt% and upward of glass fiber or nanoclay can enhance the HDT nearly up to the melting point of the polymer. It is, therefore, common to add fillers to semi-crystalline polymers to extend the limits of their operating temperature. An example is the use of glass filled nylons in under the hood car applications where the high temperatures preclude the use of unfilled nylon. Another example is nylon cooking utensils which retain their rigidity thanks to glass fiber.

26.2.11 Elongation to Break

This property is critical in some instances. For example, wire and cable insulation and jacketing need to have high elongation to break to survive sharp bends during installation. Elongation to break is very sensitive to any flaws in the polymer which includes fillers, voids, or any other inhomogeneities. The larger the particles and the higher the concentration, the lower the elongation to break will be. Some polymers are very ductile, with elongation in the hundreds of percent and they can tolerate high filler concentrations before the elongation becomes unacceptably low. For example, polyolefin cable formulations can contain 60 wt% of ATH or $Mg(OH)_2$ flame retardant and still perform acceptably. High impact polystyrene (HIPS) and ABS, however, suffer a dramatic loss of elongation to break even upon addition of very low levels of fine, well dispersed filler.

Isotropic fillers and fine fillers are least deleterious to elongation to break. Highly anisotropic and coarse fillers are worst. Dispersants help prevent agglomeration, decrease the effective particle size and thereby help maintain good elongation to break. Coupling agents normally reduce elongation to break although exceptions do exist.

26.2.12 Impact Resistance

Impact resistance is often erroneously referred to as impact strength, when, in fact, it is not a strength at all. Strength refers to a force and impact resistance is an energy. It is the energy required to break the sample in two or more pieces. Like elongation to break, impact resistance is sensitive to any particles, voids, or other inhomogeneities that act as flaws. Stresses concentrate around filler particles. The larger the particle and the more sharp the edges, the greater the stress concentration. As impact takes place, the stress concentration exceeds the strength of the polymer and failure occurs in the form of micro-cracks which then rapidly spread and eventually lead to macroscopic failure. For fillers with poor adhesion to the polymer, impact leads to dewetting and formation of a void around the filler particle. In some brittle polymer/poorly bonded filler combinations this void formation actually helps impact resistance, examples are fine, well dispersed, stearic acid coated calcium carbonate in PP homopolymer or in PVC (Figure 26.4).

Normally, addition of filler reduces impact resistance and sometimes dramatically so. Even low levels of well dispersed, stearic acid coated calcium carbonate can lead to drastic reductions in impact resistance of ABS and to a lesser extent in HIPS. ABS and HIPS are impact modified using rubber particles whereby upon impact, the rubber cavitates and helps absorb the impact energy. When filler particles are present, the stresses concentrate around them instead of the rubber particles. Cracks form around the filler and spread before the rubber particles can come into effect. This leads to an interesting interplay between the size of the filler and the size of the rubber impact modifier particles. If the filler is significantly smaller than the rubber, then the stresses concentrate around the rubber, as intended and impact resistance is good. Use of filler of similar or larger size than the impact modifier particles leads to stress concentrations preferentially around the filler, so the effect impact of the modifier is nullified. This interplay between impact modifier and other particulates is not generally known.

Failure by impact can be thought of as two distinct processes. First is crack formation which occurs at the largest flaw, which may be a filler particle, pigment particle, or agglomerate thereof. Unnotched impact resistance measures both the energy to form the crack plus the energy to grow the crack and break the sample. Unnotched impact resistance is often the most relevant because real life parts are usually not

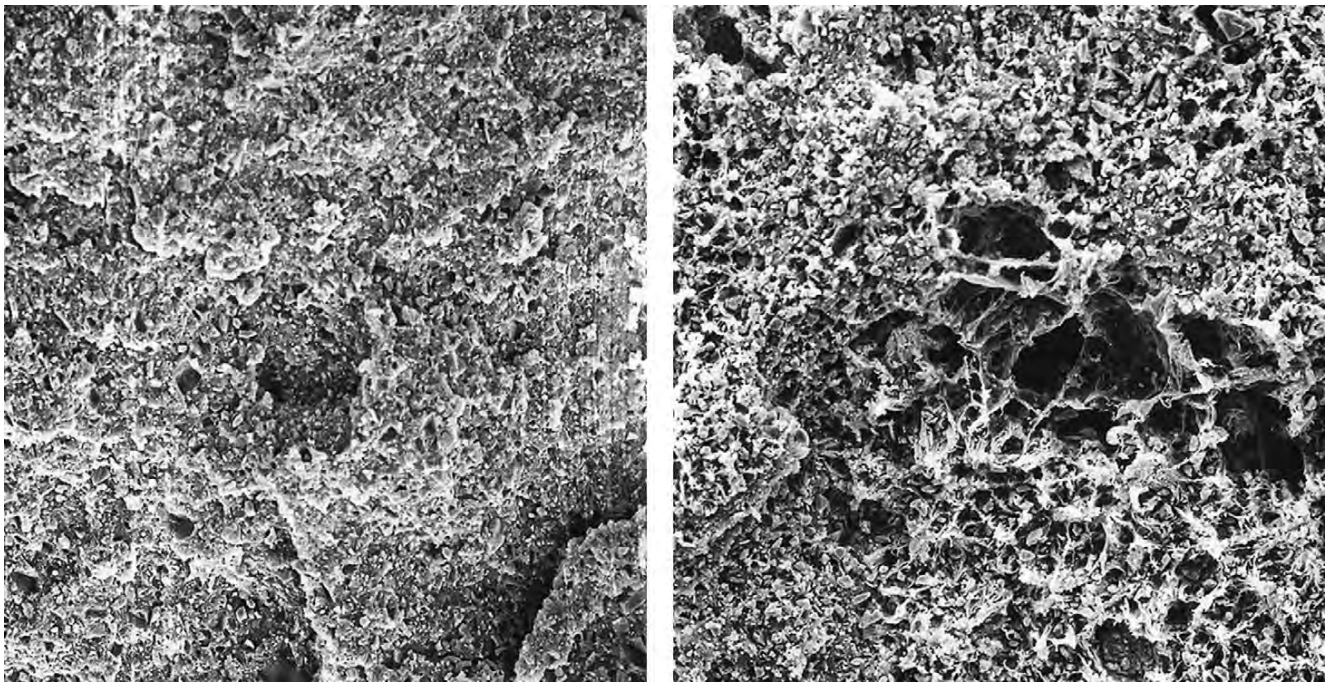

Figure 26.4 Impact fracture surface for 40 wt% of 2 micron d_{50} $CaCO_3$ in PP homopolymer non surface treated (left) and stearic acid coated (right).

notched. Unnotched impact resistance of a material may be one or two orders of magnitude higher than the notched impact resistance for the same material. Because the crack initiates at a flaw, which is often a filler particles or agglomerate, this test method is very sensitive to the filler type, amount, level of dispersion and adhesion between filler and polymer.

Notched impact resistance is performed on a sample with a large flaw introduced on purpose to ensure that the crack initiates from a predefined place, in a controlled manner. By introducing the defined flaw, one obtains experimental results with much lower scatter than those found when performing unnotched tests. This has led to the popularization of the notched test even though, as explained above, real life parts do not usually contain notches, so the results of notched testing while reproducible, are not relevant in most instances.

The ratio of the notched to the unnotched values gives an indication of how sensitive the material is to scratches or sharp features in the part design that may act like notches.

26.2.13 Creep

Creep is flow of the solid polymer over long periods. It is well known that all fillers increase the viscosity of molten polymers [14] and therefore it should be no surprise that they also increase the "viscosity," that is to say the creep resistance, of solid polymers [8,12]. The types of filler that are best at increasing viscosity and reducing creep are those that are highly anisotropic and also those that are well bonded to the polymer. Good bonding may be by virtue of high surface area like nanoparticles, or through intrinsic interaction between the polymer and the filler surface, or lastly, by use of appropriate coupling agents. Effective coupling is especially important to prevent creep at elevated temperatures and when moisture is present as those factors tend to interfere with filler to polymer adhesion.

26.3 Thermal and Electrical Properties

26.3.1 Conductivity

These two properties are covered together, because, they are related from a technical standpoint. The vast majority of polymers are excellent thermal and electrical insulators. Outstanding electrical insulation leads to extensive use in wire and cable insulation as well as numerous other applications. Although a few polymers are intrinsic conductors of electricity, for most polymers, conductivity must be induced through the use of conductive fillers. Similarly, plastics are superior thermal insulators and even more so when foamed. There are applications where plastic with exceptionally high thermal conductivity is called for. One notable example is heatsinks for laptop computers. Plastics allow complex, efficient shapes that fit within the strict confines of a laptop and when appropriate fillers are added. High thermal conductivity and performance rivaling metals is attainable.

Examples of electrically conductive fillers are carbon black, graphite (flake and fiber), and metal (copper, silver,

steel, flake, and fiber). Metallized mica or glass beads offer high electrical conductivity but at lower cost than using pure metals.

Typical mineral fillers like calcium carbonate, talc, kaolin, mica, silica, and wollastonite all have thermal conductivities an order of magnitude higher than that of polymers. However, specialty fillers are used to achieve better thermal conductivities. Examples include alumina, beryllium oxide, boron nitride (cubic and hexagonal), graphite, carbon nanotubes, metals, and the best of all, diamond.

For the most part, the properties of composites vary smoothly as more filler is added (on a volume percentage basis). The properties of the composites are more or less a weighted average of the properties of the two constituent parts. Electrical and thermal conductivity are properties that do not follow that pattern. As more filler is added, there is virtually no increase in conductivity until the point at which a continuous pathway of touching particles forms. At that point, known as the percolation threshold, the conductivity increases dramatically and by several orders of magnitude. Further addition of filler leads to a leveling off of conductivity so that the overall curve is s-shaped (Figure 26.5).

Percolation occurs at lower concentrations for smaller filler particles, for fillers that tend to agglomerate and for highly anisotropic fillers. At a given filler concentration, one can achieve higher conductivity with a low conductivity filler that has percolated compared to a high conductivity filler that has not percolated [15]. Whereas one is usually striving for optimal dispersion, in the case of conductivity, dispersion means separation of particles and therefore an absence of percolation.

As conductivity is so dependent upon filler dispersion and also filler orientation, it is very sensitive to processing conditions and in particular flow. In applications where maximum conductivity is required, the sensitivity to processing is not such a problem, one just needs to ensure that the filler concentration is above the percolation threshold with some safety margin. However, in some cases, it is desirable to hit a target intermediate conductivity on the steep part of the s-curve. For example, anti-static and RF shielding require intermediate conductivity levels. It is very challenging to reproducibly hit conductivity values on the steep part of the curve because any variation in filler concentration, orientation, or flow pattern will result in a conductivity that is out of specification by a factor of ten or more.

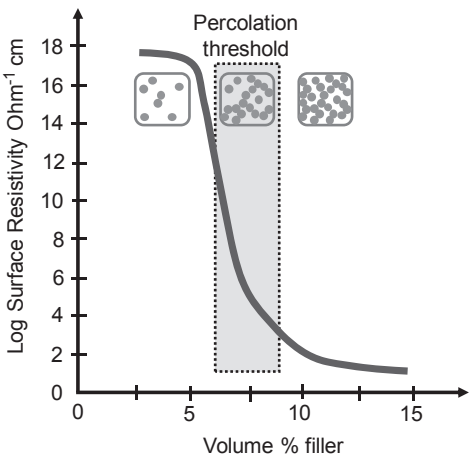

Figure 26.5 Percolation threshold.

26.3.2 Specific Heat Capacity

When processing polymers, the specific heat capacity is important because it is the amount of heat energy required to heat the polymer to melt and make a part. The reverse case is also important, namely the amount of heat that must be removed in order to solidify the part so that it can be removed and room made for the next part to be produced. Heating and cooling translates to energy costs and also productivity. Semi-crystalline polymers require more energy to heat and cool because of the specific heat of crystallization. That is, it takes extra energy to melt the crystals and then extra cooling to recrystallize them.

There is a lot of misunderstanding over the effect of fillers on specific heat capacity. In fact, some of the notable books in the field give erroneous advice in this regard. The confusion comes from a failure to take into account the units of specific heat capacity. The units for mass-specific heat capacity are J $kg^{-1}K^{-1}$ and values for mineral fillers are approximately three times greater than those for polymers. Therefore, it is often stated that minerals reduce the specific heat capacity of polymers thus aiding polymer processing. However, like all other properties, one must consider the property on a volume basis and not a weight or mass basis.

When one accounts for the density difference between polymers and mineral fillers, a factor of approximately 1:3, one arrives at the correct parameter, namely the volume-specific heat capacity with units of J L^{-1} K^{-1} which turns out to be the same for mineral fillers and polymers [8]. In fact, as a rule of thumb, all solid materials have similar volume-specific heat capacity. So, in conclusion, addition of fillers gives no advantage in terms of the energy required to heat and cool, although they do help speed of heating and cooling through their high thermal conductivity.

26.3.3 Coefficient of Thermal Expansion

Polymers have a much higher coefficient of thermal expansion (CTE) than metals or ceramics [12]. This means that when plastic parts are bonded to metals or other materials with dissimilar CTE, stresses build up at the joint leading to warpage or even failure of the joint. The CTE of fillers is approximately 10-fold lower than that of polymers so adding fillers reduces the CTE of polymers. The rule of mixtures approximates the behavior, but for high surface area, or well

bonded fillers, the effect can be more pronounced than that predicted by the linear rule of mixtures [12].

26.4 Hardness, Friction, Scratch Resistance, and Wear

26.4.1 Hardness

Most fillers are harder than polymers, so filler addition increases the hardness of polymers. The trends are similar to those for modulus and yield strength, namely that more anisotropic fillers are more effective at increasing hardness. As hardness is a surface measurement, similar to a room temperature Vicat test, the filler will only affect the hardness if it is present at or near the surface. If the filler is depleted at the surface, for example due to flow effects during injection molding, then it may have little or no effect on the measured hardness.

26.4.2 Friction

The coefficient of friction (COF) may be adjusted upward or downward by the use of fillers [16]. Addition of low COF fillers such as graphite, hexagonal boron nitride, PTFE, paraffin wax, or molybdenum disulfide will reduce the COF. Often, only a low amount of low COF filler is needed because they are soft materials that become spread out across the polymer surface during use. In contrast, safety flooring is also made by adding fillers. Large, irregular particles of tungsten carbide are added to the PVC plastisol which hardens to leave the particles protruding upward. This type of surface has a very high COF and is used worldwide, for example in buses, trains, and staircases to prevent slipping. Thus, hard irregularly shaped particles are favored for achieving high COF.

26.4.3 Scratch Resistance

Scratch resistance is an important but difficult subject for many reasons. First, in most cases, people are focused on the physical scratch and the measurement thereof, whereas the consumer usually cares only about the visibility of the scratch. Secondly, it is the various test methods which may, or may not, be appropriate depending upon how the material will be exposed to scratch conditions in use. For the most part, the focus is on passing whatever test the customer specifies, rather than on making better materials. Thirdly, scratching occurs at speeds much higher than those of standard polymer tests. This means that mechanical properties from, for example, tensile tests do not correlate at all with scratch resistance. A material may be an elastomer at low testing speeds, but at the velocity experienced during scratching, it may behave in a brittle manner. This is because polymers have a time dependent response. These factors have held back progress in the field. It should be noted that Evans and Fogel showed an excellent correlation between the scratch resistance of elastomers and the energy to break from tensile tests once the effect of scratch speed had been accounted for using the WLF equation [17].

Fillers can help reduce the dimensions of the scratch by increasing the hardness of the surface leading to less deformation and by increasing the yield strength so that the plastic recovers elastically instead of irreversibly via plastic flow. However, in many cases, fillers increase the visibility of the scratch. An example of particular note is talc filled PP copolymer for car interiors where scratching debonds the talc particles which then lay on the surface scattering light and giving rise to a highly visible white line. Instead of talc, wollastonite is used, as it stays bonded in the polymer leading to less scratch visibility.

The best approach to scratch resistance is to find or create a test that models the real application closely and develop your material using that test.

26.4.4 Wear and Abrasion

Wear is a complex subject because there are many factors at work [16]. In general wear resistance of polymers is improved, and in many cases dramatically so, by the addition of fillers. For example, PTFE has very low COF but very poor wear resistance. Addition of virtually any kind of filler has been shown to improve the wear resistance of PTFE between one and several orders of magnitude.

Wear resistance is best improved through addition of small, well bonded particles, so use of coupling agents can be beneficial. When larger, poorly bonded particles are used instead, they are pulled out of the polymer under testing and act like an abrasive at the interface. So micron sized particles help, nanoparticles are better, and very coarse particles above 50 microns are detrimental [16].

Abrasion resistance is another complex area. One of the reasons for confusion is that the various test methods do not agree well with each other. There is a perception that hard surfaces lead to the best abrasion resistance, however that does not jibe with the facts. In actuality, it is elastomeric surfaces which have excellent abrasion resistance. Look, for example, at rubber car tires and PVC flooring which is always coated with a polyurethane elastomer layer to provide wear resistance. Elastomers deform and spring back undamaged, so scratch and wear resistance is good [17].

26.5 Barrier Properties

26.5.1 Permeability

Permeation through plastics is important for many applications, especially for food packaging where the goal is to prevent oxygen and water vapor from entering and spoiling the comestibles. Polymers provide some degree of barrier

when used alone or in multi-layer structures. Addition of fillers can further improve performance. As gases and liquids can neither dissolve in, nor penetrate through, mineral fillers, such fillers impart barrier properties. For isotropic fillers, the effect is rather weak, approximating the linear rule of mixtures relative to the volume percentage of filler added. The best case is for highly anisotropic plates perfectly aligned perpendicularly to the direction of permeation. This arrangement increases the path length for diffusion, thereby slowing progress of the diffusant molecules. For conventional composites, this tortuosity effect is responsible for the barrier properties. In the case of nanocomposites, the tortuosity effect is augmented by the interphase (a layer of constricted polymer around the filler particles as described later).

It should be noted that fillers do not always improve barrier properties. If the filler is not wetted by the polymer, then the polymer-filler interface provides a pathway for easy diffusion and may even help wick liquid into the composite. This may be prevented by ensuring good wetting through careful processing or by using a surface treatment on the filler (see Chapter 25, Dispersants and coupling agents).

Fillers can also be used to intentionally increase permeability of polymers. Breathable films are prevalent in sanitary products as they allow permeation of gases but not liquids (e.g., in disposable diapers). Such films are made by compounding calcium carbonate into polypropylene. The calcium carbonate is surface treated with stearic acid to decrease adhesion between the filler and the polymer. A film of the material is made and then stretched whereupon the filler particles debond from the polymer to leave voids that permit permeation.

26.6 Optical Properties

26.6.1 Transparency/Opacity

Fillers affect the optical properties of plastics in two ways. First, because the filler and the plastic usually have different refractive indices and because the filler particles are often of similar size to the wavelength of visible light, filler addition leads to light scattering which manifests itself as opacity. In order to get high-light scattering and thus very white materials, pigments like titanium dioxide are used. Pigment grade titanium dioxide has a particle size chosen to maximize light scattering and has a very high refractive index, much greater than that of plastics, hence its ability to opacify effectively. Other more common fillers such as calcium carbonate, dolomite, and kaolin also lend opacity but to a much lesser degree because their refractive index is much closer to that of polymers. In rare instances, the refractive index of the polymer and filler are identical and in that case, the filler does not induce scattering so a transparent composite can result. One example is glass-filled PVC. In most cases, fillers have more than one refractive index due to asymmetry in their crystal structure and therefore transparency cannot be achieved because it is impossible to match the single refractive index of the polymer to the two or more refractive indices of the mineral filler.

Another point to note is that even the weak pigmentation arising from fillers limits the color palette achievable. For instance, calcium carbonate filled PP is noticeably white so it is impossible to achieve a true black, or other very dark colors, no matter how much pigment is added. Whitening from the filler also removes the possibility to achieve very vivid colors. It is not just fillers that lead to whitening of the plastic through light scattering. Impact modifiers are also particulates of different refractive index to the polymer. This is why HIPS, ABS, and ASA are white and the colors that can be achieved in those plastics are limited by the underlying whiteness. One can sometimes tune the refractive index of the polymer using miscible polymer blends (rare) or copolymerization to match the refractive index of the filler or impact modifier. This results in transparency and is how transparent ABS, known as MABS is made [17].

Nano-fillers are much smaller than the wavelengths associated with visible light (~350−780 nm) so they do not lead to scattering and can be used to make transparent materials, even when the refractive index of the filler and the plastic do not match. There are some caveats with this approach however. One is that the particles must be very well dispersed because agglomerates will act like larger particles resulting in scattering and concomitant opacity. Another aspect to be aware of is that although nanoparticles (or very large particles) may not scatter visible light, they are still scattering light of other wavelengths so the material may not be transparent to UV or IR light. This may be an advantage or a disadvantage depending upon the application. Lastly, because well dispersed nanoparticles lead to transparent materials, any coloration in the filler will be revealed. This occurs, for example, in the case of nanoclay composites where a yellow hue is often seen.

26.6.2 Color

Fillers may also impart color to the plastic. Even a filler that appears as a pure white powder may give significant color in the plastic. This is because dry filler powder scatters light intensely due to the large difference in refractive index between the filler and air. This intense scattering leads to such strong whitening that it can mask the underlying color of the filler. A quick test is to wet the filler powder with oil, preferably of similar refractive index to the target polymer, whereupon any color will be revealed. This test saves time and money compared to compounding the filler into the plastic to check color. White (colorless) fillers are preferred and carry a price premium compared to more colored grades. When the filler is to be used together with pigments to make a colored material, the consistency of filler color is more important than the degree of whiteness. If the filler were to

vary in color, then consistency of color in the final material would be very hard to achieve because the pigment formulation would need to be continuously adjusted to compensate for drift in filler color.

26.6.3 Gloss

Fillers tend to reduce the gloss of plastics; however the extent of the reduction varies widely depending upon the filler and the type of processing. High gloss is a result of light reflecting from a surface unattenuated and without scattering. Hence smooth, homogeneous surfaces lead to high gloss and rough, inhomogeneous surfaces provide low gloss. There are applications for the whole range of possible gloss values to suit the preferences of a given market. Exterior car body parts, for example, mirror housings and bumpers, are normally of high gloss to match the painted metal body panels. In contrast, interior body parts, in particular the dashboard, must be very low gloss to prevent sunlight from reflecting and dazzling the driver.

Fillers can be used to deluster or reduce gloss of a polymer surface. The best effect is seen when using larger particles that help create surface roughness and scatter light at different angles. If a high gloss surface is desired, then smaller particles, preferably surface treated with a dispersant to ensure an absence of agglomeration is a sound approach. The observed gloss is highly dependent upon the angle of measurement. Low-angle measurements are more sensitive to loss of gloss than are high-angle measurements.

The processing route employed also affects gloss to a significant extent. For example, injection molding entails high shear rate which tends to make the filler particles move away from the surface. Thus the final part will often have a skin that is depleted in filler. As there is little or no filler at the surface, gloss can remain high. The same material processed, for example by compression molding, would not display a skin depleted in filler and gloss would be commensurately lower. Water and gas assisted injection molding can lead to low gloss in the area where the gas or water bubble is grown. As the bubble grows, the polymer skin is stretched, bringing filler up from the bulk and deglossing that region while the rest of the part surface retains high gloss.

26.7 Processing

There are many processing methods used to convert polymer pellets into parts or stock shapes to be machined. The main methods include injection molding, extrusion, compression molding, and rotational molding. In order to prepare samples for testing, injection molding dominates and that can lead to measured properties being rather different than those likely to be seen in actual parts. One must be aware of these differences in order to account for them in part design.

When test bars are injection molded, the high injection speed leads to alignment of the polymer chains, and more importantly, orientation of the filler particles. The long direction of platy or fibrous fillers orients itself preferentially along the flow direction, that is to say, the longest dimension of the test bar. This means that properties like modulus and yield strength are maximized and the benefits of anisotropic fillers like talc, kaolin, mica, wollastonite, glass fiber, and nanoclay are shown to best effect. The problem is that this ideal orientation of particles rarely occurs in production parts, so the properties seen on datasheets are not achieved in reality. It also leads to the perception that anisotropic fillers are better than they really are. Even when anisotropic particles are well oriented, this can lead to warping because the part shrinks unevenly. Ironically, one solution is to change the flow pattern in the mold to intentionally disrupt the flow and prevent the filler from orientating.

Another drawback of taking datasheet values from injection molded parts is that tensile testing is only performed in one direction. Very attractive modulus and yield strength values are seen when anisotropic fillers are used, but these values are misleading because the properties in the two perpendicular directions are completely different and, in some respects, inferior [9]. Fibers will reinforce strongly only in one direction, so the modulus and yield strength in the two perpendicular directions will be only equivalent to the case where the same volume percentage of isotropic filler had been added. Platy fillers reinforce strongly in two directions but only weakly in the third. Again the modulus and yield strength in the third direction will be that expected for an isotropic filler. The opposite is seen for other properties like elongation to break. So a fiber filled composite will have high modulus and yield strength, but low elongation to break in the usual tensile test direction. However, the other two directions will show low modulus and yield strength, but high elongation to break, as expected for an isotropic filler.

Other molding techniques such as compression molding and rotational molding do not orientate the particles in any particular direction, so lower modulus and yield strength are found, but these properties are equal in all directions. This leads to parts which show little or no tendency to warp, because the material is isotropic and shrinks equally in all directions.

26.7.1 Weld Lines

Weld line refers to the place where two polymer melt fronts meet and merge (Figure 26.6). This occurs, for example, for larger parts where more than one injection port per part is used. For unfilled polymers, the polymer chains meet and they entangle easily when the melt fronts meet, so good strength is attained at the weld line. This is not the case when any type of filler or impact modifier particle is present.

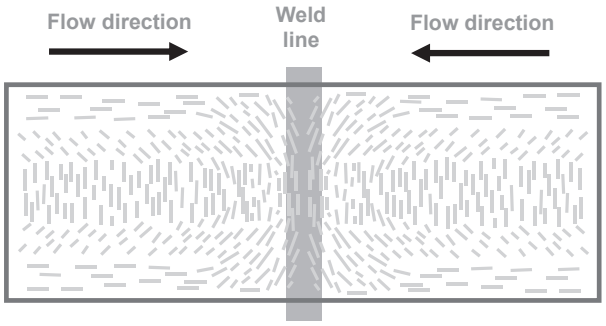

Figure 26.6 Orientation of filler particles within injection molded test bars.

Particles prevent good weld lines strength leading to a weak spot in the part where it will tend to fail under load. This is because fillers hinder optimal entanglement formation and because filler distribution at the weld line is uneven with areas of depleted and enriched filler. The results can be dramatic, in particular for anisotropic fillers with weld line elongation to break and yield strength far lower than for the rest of the part. Isotropic fillers are also deleterious to weld line strength but to a much lesser degree.

26.8 Extra Phase Effects

For the most part, when fillers are added to polymers, the polymer phase remains unchanged. That assumption is made in many of the equations used to predict composite properties. However, there are exceptions that occur and when they do, the properties of the final material deviate from the expected. When the properties found experimentally do not match theory, then look at these factors as the likely culprit.

26.8.1 Nucleation

Fillers and pigment can, in some cases, nucleate crystallization of semi-crystalline polymers including PE, PP, PA6, PA6,6, PBT, and PEEK. The effect is normally measured by differential scanning calorimetry (DSC) which detects crystallization. Nucleation results in crystals starting to form at higher temperature as the melt cools and this can be a great advantage because it can help lower injection molding cycle times, improving productivity, and saving money. Fine talc is often used to nucleate PP and nylon. Nucleating agents can have other effects too. Sometimes they lead to a different crystal phase (with different properties) and sometimes they lead to an increase in the overall level of crystallinity which will increase density, modulus, and yield strength. Nucleation also tends to give more and smaller crystallites so impact resistance may be improved and so may clarity. It should be noted that there is no satisfactory theory to predict which substances will induce nucleation so it must be determined by experiment [18].

26.8.2 Transcrystallinity

Transcrystallinity is an extreme case of nucleation whereby the polymer melt is cooled against a surface that nucleates so strongly that the spherulites immediately collide and a layer of crystals perpendicular to the nucleating surface is observed [11,19]. The effect can be seen for some types of fibrous fillers (e.g., glass, carbon, or Kevlar®) in certain polymers. A sheath of transcrystalline material forms around the fiber. Because the volume of the sheath can be greater than that of the fiber itself and its properties very different to those of the bulk polymer, the properties of the composite can be substantially altered [11].

26.8.3 Interphase

The interphase is a layer of constricted or immobilized polymer that forms on the surface of the filler particles. The influence of the interphase can be ignored for micron sized particles because their surface area is too low to cause significant amounts of interphase to form. However, nanoparticles have high surface area so that the interphase, typically 1−50 nm in thickness [10] can make up a significant volume percentage of the total composite. So, in the case of nanoparticles, the interphase can influence composite properties. In fact, many of the notable attributes of nanocomposites such as high modulus and yield strength together with low permeability are due, in part, to the contribution of the interphase.

Let us take as an example, a 5 micron particle surrounded by a 10 nm thick interphase. Calculation shows that the volume of the interphase is only approximately 1% of the particles volume. The influence of such a small amount of interphase can be neglected. However, if we take 100 nm particle, also surrounded by a 10 nm thick interphase, we find that the interphase volume is 70% of the particle volume. That is, the particle acts like it is 70% larger than it really is, so the viscosity is raised and the mechanical properties of the composites are altered because the interphase accounts for a significant volume percentage of the total material.

26.8.4 Voids/Foams

Voids may be caused by low-molecular-weight additives volatilizing during extrusion or by poor wetting of filler by the polymer melt. Such voids act as flaws where stresses concentrate, so impact resistance and elongation to break can suffer. Intentional introduction of voids, that is to say foaming, can be used to reduce weight and materials cost. It is achieved using foaming agents and the addition of filler helps nucleate formation of the bubbles leading to a fine cell structure and improved retention of mechanical properties. In particular, flexural modulus is retained to a large extent if the interior of the part is foamed, leaving a skin of unfoamed material.

26.9 Popular Fillers (Table 26.3)

A wide range of filler types enjoy commercial success providing mechanical and other benefits in a variety of polymers is shown in Table 26.3.

Table 26.3 Popular fillers and their properties

Filler	Shape	Density	Mohs Hardness	Uses
Calcite $CaCO_3$	Blocky	2.71	3.0	Mechanicals PP,PE
Talc $Mg_3(Si_4O_{10})(OH)_2$	Platy	2.7–2.8	1.0	Mechanicals PP,PE,nylons
Mica $KM(AlSi_3O_{10})(OH)_2$	Platy	2.7–2.9	2.0–2.5	Mechanicals PP,nylons
Wollastonite $CaSiO_3$	Acicular	2.9	4.5	Mechanicals PP
Kaolin Al_2O_3 $2SiO_2$ $2H_2O$	Platy		2.5–3.0	Mechanicals PE,elastomers
Dolomite $CaCO_3.MgCO_3$	Blocky	2.85	3.5	Mechanicals PP,PE
Glass fiber SiO_2	Fibrous	2.55	7	Mechanicals PP,nylons,PBT
Carbon black	Variable	2.26	2.0–2.9	Processing elastomers
Barites $BaSO_4$	Blocky	4.5	3.0–3.5	Sound
Magnetite Fe_3O_4	Blocky	5.1	5.5–6.5	Sound PP, nylons
Graphite	Platy	2.2	1–2	Conductivity lubrication
ATH $Al(OH)_3$	Platy	2.4	2.5–3.0	Flame retardant Elastomers, PE
Magnesium hydroxide $Mg(OH)_2$	Platy	2.4	2.5	Flame retardant PE,EVA,PP

within the temperature range for processing on the polymer. So, for instance ATH is not used in PP, magnesium hydroxide is used instead. Precipitated grades are common because the particle size and morphology can be tuned through the precipitation process. Brucite, a natural form of magnesium hydroxide is less expensive but is more difficult to use because of a non-ideal particle morphology and transition metal impurities. As high filler loadings are needed, dispersants are often used to help reduce viscosity and agglomeration thereby boosting processability, throughput and mechanical properties.

26.10 Specialty Fillers

26.10.1 Flame Retardant Fillers

The main two primary flame retardant fillers are aluminum hydroxide (also known as aluminum trihydrate (ATH) and magnesium hydroxide [7,8]. Both operate by decomposing upon heating to give off water which is an endothermic process, taking heat from the fire. In addition, the decomposition liberates water vapor which also helps douse the fire. Both must be used at levels of around 60 wt% in order to be effective. At such high loadings, viscosity is high and mechanical properties, specifically, elongation to break and impact resistance, drop precipitously. ATH is the preferred alternative as it is the least expensive of the two. Magnesium hydroxide is employed in cases where ATH decomposes

Nanoclay is used as a secondary flame retardant/synergist, that is in combination with ATH or magnesium hydroxide. The clay promotes char formation and helps keep the char layer intact to help prevent oxygen from reaching the underlying material. The nanoclay enables reduction in the amount of ATH or magnesium hydroxide needed to attain a given flame retardancy rating. Other nano-fillers such as hydrotalcite are also attracting attention as viable flame retardant synergists. Use of filler type flame retardants is on the rise, partly because of legislation against the once popular halogenated flame retardants.

26.10.2 Natural and Renewable Fillers

For several decades, natural fibers have been proposed as fillers for thermoplastics [9]. They provide reasonable mechanical properties and have low density compared to mineral fillers. Fibers include sisal, jute, coir, flax, and wood. Chemically they are composed of lignin and cellulose where the lignin is rather unstable toward heating and begins to decompose near 200 °C in air as determined by loss in weight via thermogravimetric analysis (TGA). Moreover, the fiber may lose its strength at 160 °C [9]. This instability limits the use of natural fibers. Other problems include high and variable water content plus the inconsistency associated with fibers from plants, which change depending upon the weather and season.

If the use of such fibers had been compelling, then they would have enjoyed commercial adoption decades ago. Instead, the present interest in them is due to a perceived environmental advantage. In fact, it can be argued that using natural and renewable fibers may actually be harmful from an environmental perspective. Whereas unfilled or mineral filled thermoplastics can be recycled numerous times without degradation of properties, natural fiber filled plastics cannot be easily recycled due to thermal degradation of the fibers during extrusion. Only life cycle analysis (LCA) can conclusively determine whether such fillers are actually good or bad for the environment.

One area where natural fillers have attained commercial success is in plastic lumber for decking which is particularly popular in the USA. By filling PE or PP with wood flour one can achieve the look of wood but without the need to maintain the product, for example by varnishing. Often such plastic lumber is optimized through use of recycled polymer and via foaming to reduce materials cost.

26.10.3 Zeolites

Zeolites, also known as molecular sieves, are inorganic substances with a nanoporous structure [13] such that molecules preferentially adsorb within the pores depending on their size and polarity. A well-known example is the use of 4 Å molecular sieves to removes traces of water from solvents. More recently, they have been used commercially to adsorb bad odors or other unwanted volatile substances from plastic films and articles.

26.10.4 Dense Fillers

Dense fillers are used when heft, weight, or sound/vibration damping is required. Heft is the perception of quality associated with products that feel substantial in the hand. Dense formulations are used in washing machine counterweights to reduce vibration. Formulations include iron slag in polypropylene or epoxy. Dense fillers include barium sulfate (density 4.5 g cm^{-3}), magnetite (density 5.0 g cm^{-3}), micaceous iron oxide (density 5.0 g cm^{-3}) and metals (density 8−20 g cm^{-3}).

26.10.5 Expandable Microspheres

These specialty fillers are comprised of a polymeric shell surrounding a core of lower molecular weight substance [7], typically a member of the alkane family. Upon heating to a temperature near the boiling point of the encapsulated substance, the particles expand dramatically due to the high vapor pressure as the boiling point is approached. By expanding such beads within a polymeric matrix, a syntactic foam is created.

26.10.6 Nano-fillers

Nanocomposites and nano-fillers are covered in a separate chapter. The fundamentals as described here for traditional microcomposites all apply but allowance has to be made for the smaller particle size, added surface area and, in the case of nanoclays, the high aspect ratio.

26.10.7 Molecular Fillers

Polyhedral oligomeric silsesquioxanes are a family of molecules that consist of a silica-like core surrounded by a shell of organic groups. Conceptually, they can be considered to be the smallest possible particle of silica, which has been surface treated either with dispersant or coupling agent depending upon the type. The term “molicle” has been coined to describe these hybrid materials [7,20] which combine the solubility of organic molecules and the rigidity of inorganic particles.

Other molecular fillers include the fullerenes such as C_{60}, C_{70} and their derivatives. Like polyhedral oligomeric silsesquioxanes however, their commercial application is severely limited by high cost.

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