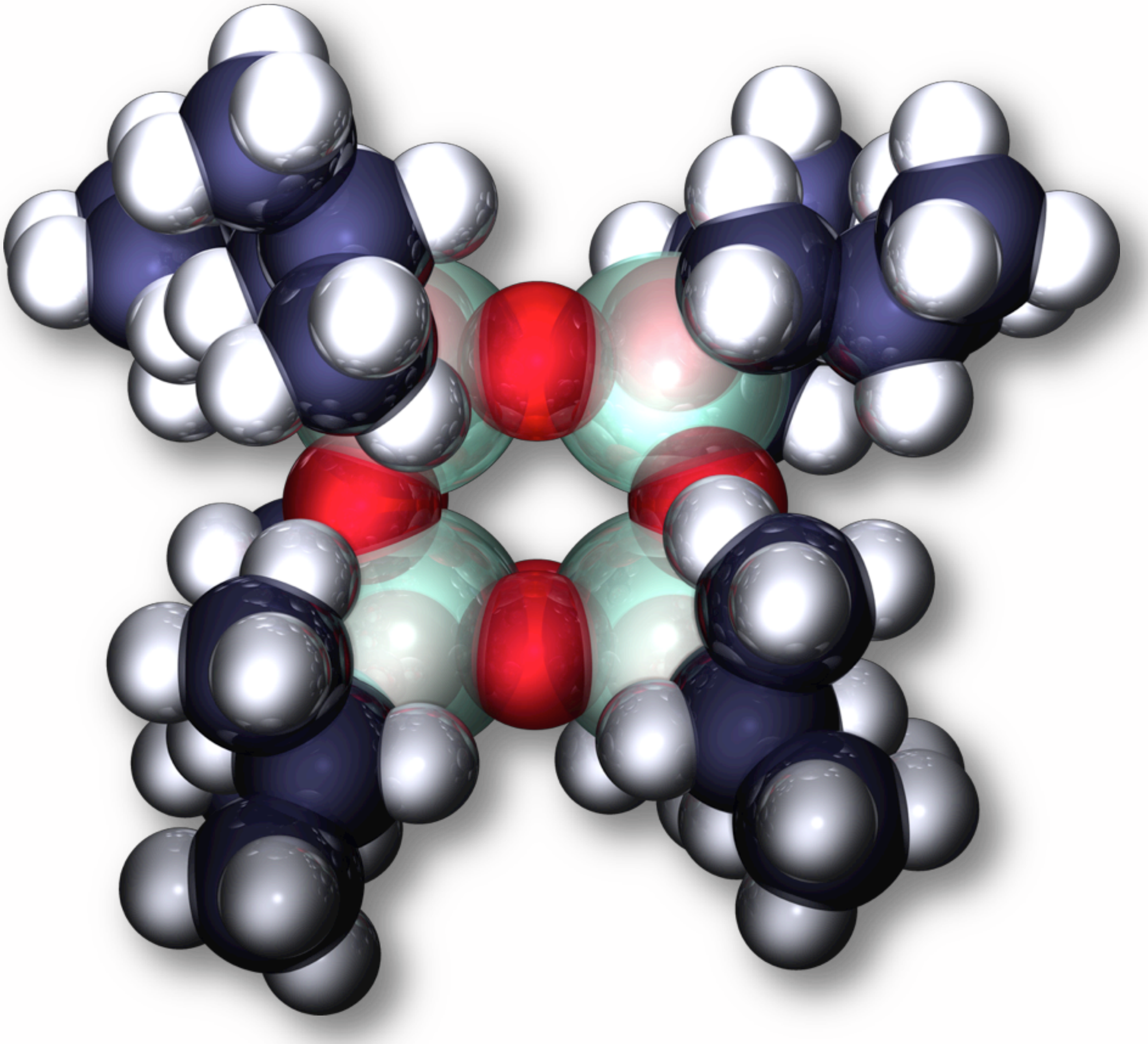

FILLERS & FILLED PLASTICS

KIRK-OTHMER ENCYCLOPEDIA OF CHEMICAL TECHNOLOGY

Short Biography

Chris DeArmitt PhD FRSC
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Chris is considered one of the top plastic materials experts and problem solvers in the World, which is why companies like HP, Apple, Exxon, P&G, Eaton, Total and Disney come to him for help.

A deep understanding of materials, combined with high creativity, allow him to quickly solve even the toughest problems. As one example, he solved a serious production problem that had plagued BASF for 30 years and cost them millions. Chris has also received 6 open innovation cash prizes placing him among the top 0.01% of innovators.

In 2016 he published the book Innovation Abyss which reveals the true reasons for innovation failure and the proven path to success. In 2018 he was featured on CBS 60 Minutes with Scott Pelley as an expert witness in a class-action lawsuit related to Marlex mesh plastic implants. He helped thousands of women get settlements.

Chris has a multitude of granted patents as well as numerous articles, book chapters, encyclopedia chapters and conference presentations to his name. He is a keynote speaker on plastics and innovation related topics.

If you need a breakthrough solution, some training, or want to know how to make innovation work, contact Chris today!

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Fillers & Filled Plastics

ABSTRACT

Functional fillers are used to enhance the intrinsic properties of plastics and to impart entirely new effects. Addition of a filler changes many properties at once, so successful formulation depends on an understanding of structure-property relationships in order to maximize the desirable effects and minimize any detrimental changes.

This chapter gives guidance on the selection of ingredients, i.e. polymers, fillers and surface treatments as well as aspects related to their processing and influence on the performance of the final part. The reader will gain a firm grasp of the topic as well as suggestions for further reading. Some myths and misunderstandings are explained and new insights into filled plastics are revealed.

Keywords: Plastic, filler, composite, functional filler, mineral

Introduction

Plastics have improved our lives immeasurably. They enable our electronic devices, give us memory-foam beds to sleep on and so much more. They also make our cars and planes lighter and insulate our homes. Life cycle analysis shows that plastics are usually greener[1,2,3,4] than steel, glass and even natural materials such as cotton or paper. So, as well as being irreplaceable, they are often the most responsible choice.

Part of what makes plastics so useful is their versatility. From humble beginnings, just a handful of decades ago, a plethora of plastic materials have been created to meet an array of demands from toothbrushes to fighter planes. However, even plastics have limitations and that is where additives come in. Stabilizers, pigments, lubricants, impact modifiers, functional fillers and reinforcements are used to craft formulations that extend what is possible with unmodified plastic materials.

Here is a list of some properties we can alter using fillers:

Modulus	Strength	HDT/Vicat	Creep	ESCR
Gloss	Impact	Abrasion	Flow	Warpage
Crystallization	Flame retardance	Barrier	Opacity	Electricals
Magnetics	X-ray absorption	Density	Adhesion	Degradability
Brittleness	Shrinkage	Lubricity	Processability	Hardness

Table 1 Properties that can be altered using fillers

Clearly, there is a wide array of options, but there are caveats. For example, if we add a filler to increase stiffness, we find that all of the other properties in the table change as well, even though that was not the intent. To be able to make successful plastic formulations, it is essential to understand the structure-property relationships at play. In this chapter we will describe each filler, its unique properties and how they can be used to improve the performance of polymeric materials.

Any particle added will act as a filler, which makes it doubly important to understand how fillers affect plastics. As an example, ABS plastic is always pigmented, and the pigment particles affect the ABS just as an equivalently sized filler would. Other examples of particulate additives that mimic fillers are antimicrobials, nucleating agents and catalyst residues. Even if you are not working with fillers, it is still valuable to understand how particles affect polymers.

For the reader who wants to learn more, some very good books are available by Roger Rothon[5], Marino Xanthos[6] and Jancar[7] as well as the older books by Katz and Milewski[8,9]. The Handbook of Fillers[10] and Functional Fillers[11] by Wypych are also very insightful. There is also a particularly good review by Fu[12] et al.

Some books and articles tell you about the theoretical side of composites but provide little true understanding about the materials and how to formulate them. This chapter is written from the point of view of someone who has spent a career creating materials for the Fortune 100, so you will learn what makes commercial materials work.

The first point to make is that all properties of a composite depend on the volume fraction (or volume %) of each constituent. Almost every graph you will see will be plotted as property versus weight % filler and that is misleading because properties do not depend on the weight of filler added. When performing an experiment, a certain weight of filler is added to a certain weight of polymer, so it is understandable that people talk about weight. However, plotting properties versus weight % filler leads to curves, which leads to people devising equations to fit those curves, which then leads to headaches and confusion.

As a simple example, let us consider composite density. One would think that if we mix equal amounts of filler and polymer, we would end up with a composite with a density that is the average of the two. What happens when we try that?

> 500g polymer with density 1.00 $\mathrm{gcm^{-3}}$ + 500g filler with density 3.00 $\mathrm{gcm^{-3}}$
> Predicted density of the composite is $(0.5\mathrm{x}1.00 + 0.5\mathrm{x}3.00)/2 = 2.00$ $\mathrm{gcm^{-3}}$

What value do we actually find when we measure density of that composite? The answer is that the density is 1.50 $\mathrm{gcm^{-3}}$ and not 2.00 $\mathrm{gcm^{-3}}$.

So, what went wrong? We made the mistake of using weight percentages instead of volume percentages. If you want to calculate densities from weight percentages, then Equation 1 will allow you to do that. It correctly predicts the density in the example.

$$\rho_c = \frac{\rho_f\ x\ \rho_p}{\rho_p m_f + \rho_f x(1 - m_f)}$$

$$\rho_c = density\ of\ the\ composite, \rho_f = density\ of\ the\ filler, \rho_p = density\ of\ the\ polymer$$
$$m_f = weight\ fraction\ of\ filler\ (between\ 0\ and\ 1)$$

Equation 1 Calculating density of a composite based on the weight % of filler

In Figure 1 we see some curves of density versus weight percentage of filler. We have just said that all properties actually depend on the volume percentage of filler. If we replotted density against volume percentage on the x axis, then would get straight lines instead. Straight lines are easy to understand, do not require complex equations to fit them, plus they make interpolation and extrapolation easier.

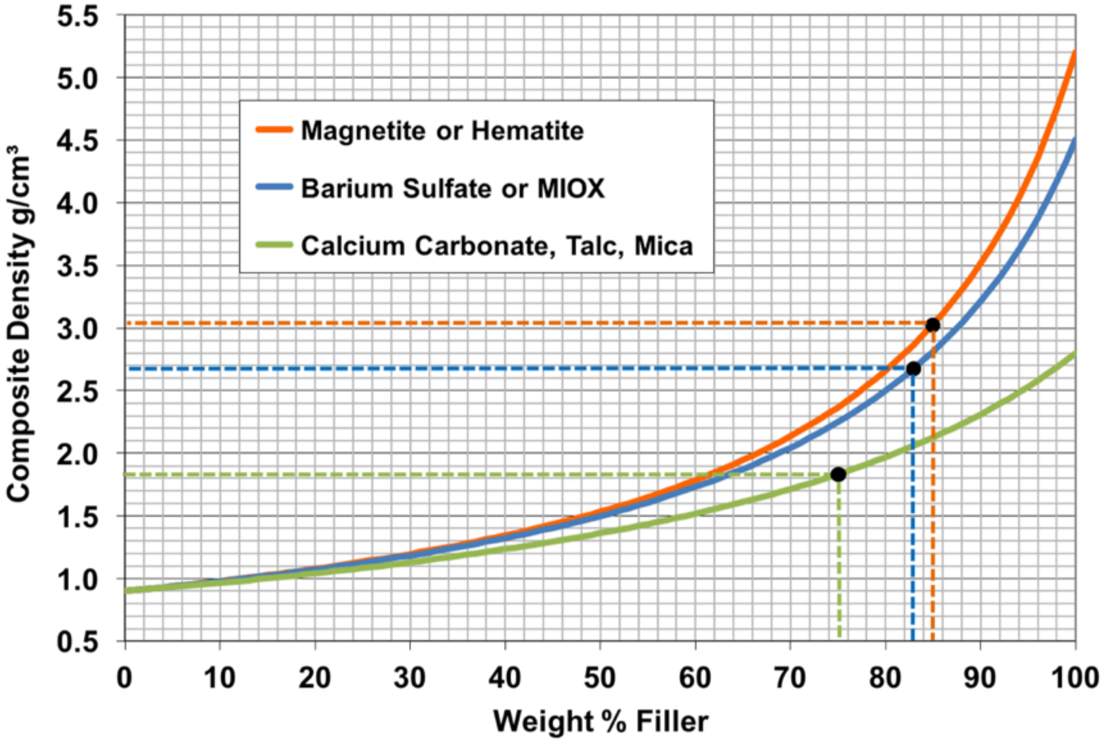


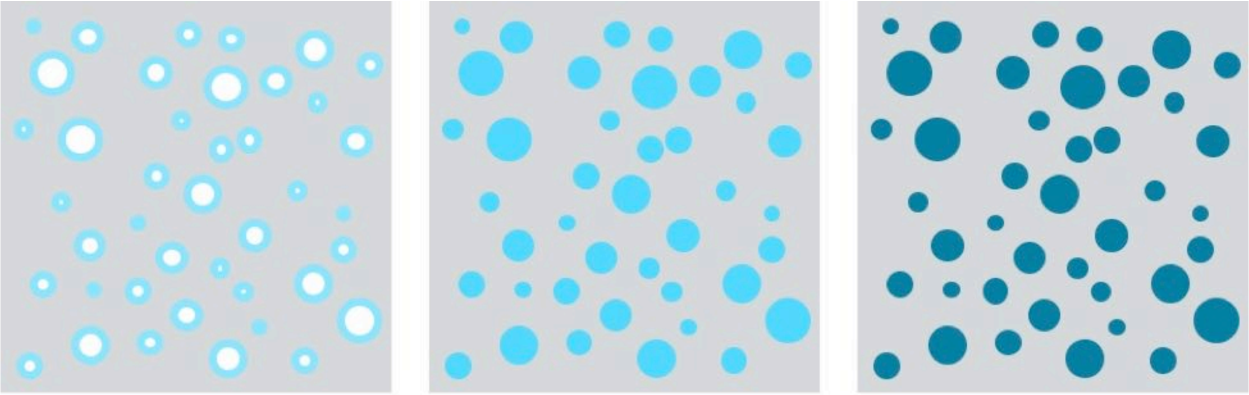
Figure 1 Density as a function of weight % filler leads to curved lines (black dots are 50 volume % filler)

Many of the most important mechanical and thermal properties of composites vary linearly with the volume percentage of each phase.

Price also depends on the volume % of each ingredient. People think that fillers are added to reduce cost, but usually that is not the case. If a plastic costs $1/lb and a filler costs $0.40/lb, then the filler is actually adding cost to the composite because typical fillers are about three times more dense than plastics. To replace one pound of plastic one needs to buy three pounds of mineral filler to occupy the same amount of volume. This vital point is often overlooked by scientists but not by people in Purchasing who appreciate the importance of volume on raw materials costs. Compounding in the filler also adds significant cost.

Another way to conceptualize the importance of volume percentage is depicted in Figure 2. Each composite shown has the same volume fraction of filler and the same size particles dispersed identically. Although the filler types are chemically different, and the weight percentage of filler varies greatly, we would expect each of these composites to show almost identical mechanical properties.

The chemistry of the particles is, to a first approximation, immaterial because the forces experienced by the polymer only depend on the size, shape, distribution and concentration of particulate filler. We will look at each of those in the following section.



Hollow glass - 25 Volume %
Filler - 19 Weight %
Density - 0.93 gcm^{-3}

Calcium carbonate - 25 Volume %
Filler - 47 Weight %
Density - 1.43 gcm^{-3}

Tungsten - 25 Volume %
Filler - 87 Weight %
Density - 5.58 gcm^{-3}

Figure 2 Equal size and volume fraction of filler lead to equivalent mechanical properties

When discussing properties, we will assume good dispersion of the particles, as depicted above, unless stated otherwise.

Filler properties

There is no ideal polymer, nor ideal filler. Composites are about compromises and making the best trade-offs requires a firm grasp of the properties of the starting materials and how the ingredients interact with each other[13]. One can however, list some generally desirable properties of functional fillers.

- Low cost
- Readily available, preferably world-wide
- Safe
- Pure
- Chemically unreactive / inert
- Stiffer and stronger than the polymer
- Non-abrasive
- Colorless (appears white in powder form)

Following from that, it may come as no surprise that the most popular mineral fillers are calcium carbonate, talc, kaolin, mica and glass. There are many types of specialty filler available, but these common types are a good starting point for understanding structure-property relationships and because they are so important from an economic standpoint. They are the go-to additives in many cases. Before looking at each in turn, it must first be said that it is misleading, almost to the point of being meaningless, to describe a filler by its chemistry because in most cases, the chemistry has no effect on the composite. So, what is important? The main properties of a functional filler that matter for mechanical properties are:

- Particle size distribution
- Particle shape
- Surface area

Therefore, we will consider each briefly.

Particle size distribution

When people talk about particle size, they normally focus on the average particle size, known as the D_{50}, which is commonly specified on datasheets from the filler suppliers. Ironically, it has almost nothing to do with the properties of a composite. Instead it turns out that the smallest and largest particles in the distribution dominate properties (Figure 3). The D_{98} gives an indication about the size of the largest particles. Those acts as flaws in the polymer, weakening it and providing a place for a crack to start and grow. In laypersons terms, think of felling a tree. To fell a tree, you put sharp notch in it, to provide a weak spot, so it becomes easier to make the tree fall. Filler particles act in much the same way and the larger the particles, the worse the problem. As a rule of thumb, for common thermoplastics, even a few particles over about 20-40 microns start to seriously affect the impact resistance and elongation to break of a composite. Coarser particles also lead to poor surface finish, i.e. low gloss. That may be useful if you want a matt surface but usually, it is not desirable.

The D_{10} relates to the smallest particles in the distribution curve. Small particles are better in theory and that is one reason for all the talk about nanocomposites. In practice however, very fine particles cause problems. They tend to stick together, causing large agglomerates that act just like larger particles and ruin impact resistance, elongation to break and gloss. Small particles also lead to high viscosity because of their greater surface area increased interparticle interaction. That lowers productivity and limits how much filler you can add before the material becomes unprocessable.

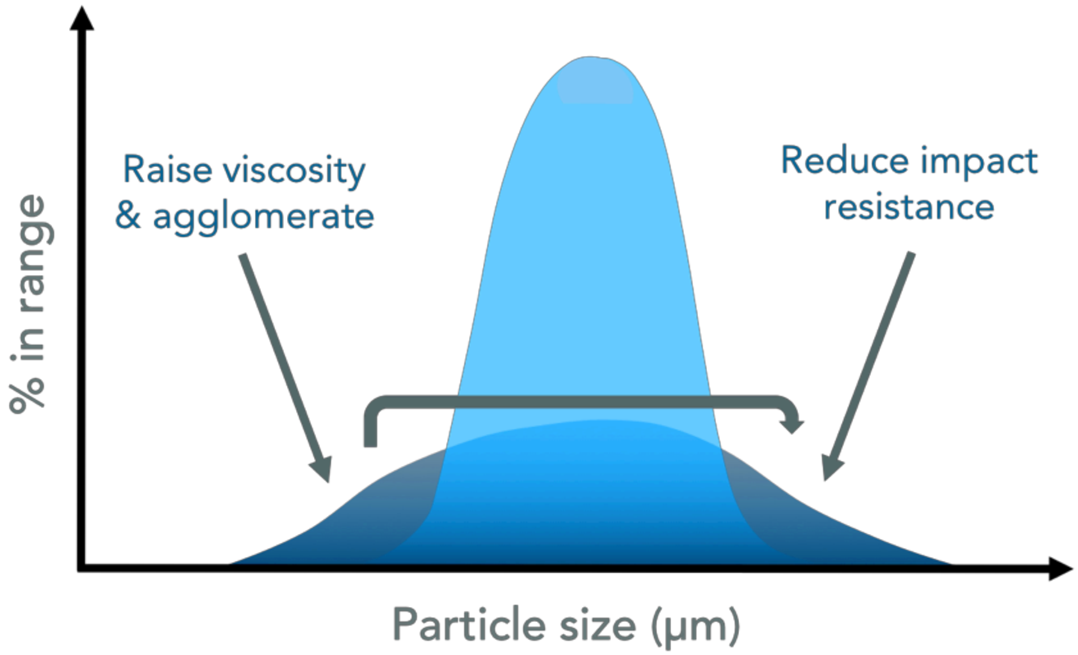


Figure 3 Particle size distribution effects (small particles can agglomerate for form large particles)

Particle shape

Particles can have many shapes, but for simplicity, we can put them in three groups.

Round or cubic particles - where calcium carbonate (calcite) or glass spheres are typical examples. That shape of particle increases stiffness somewhat, usually decreases strength slightly and has least detrimental effect on impact resistance and elongation to break. A further advantage is that properties are altered equally in all three directions (x, y & z) so there is no tendency for warpage.

Needle shaped particle and fibers - typified by wollastonite and glass fiber, can reinforce plastics if the aspect ratio is high enough and if they are well bonded to the surrounding polymer. The aspect ratio simply means the largest dimension of the particle divided by the smallest dimension. So, for a needle 10 microns long and 1 micron wide, the aspect ratio is 10:1. Higher aspect ratio means better reinforcement. What does reinforcement mean exactly? It is a term used a lot, but rarely does anyone say what it means. The best definition I have seen is that a reinforcement increases both stiffness and strength simultaneously.

Platy particles - for example talc and mica, can also reinforce and the higher the aspect ratio, the more effective they are. They reinforce along both of the long dimensions of the plate, whereas a fiber only reinforces along its one long dimension. So, in that sense, plates are more effective than fibers of equivalent aspect ratio. Plates also have the benefit of giving barrier properties, that is gasses and liquids cannot easily penetrate through plastics filled with high aspect ratio platy fillers. In recent years, high aspect ratio talc and mica have gained traction due to high reinforcement effectiveness. Platy fillers also lead to more isotropic shrinkage, i.e. less warpage, compared to fibers and are often added to fiber filled composites to alleviate high warpage.

Aspect ratio - fillers with high aspect ratio provide reinforcement but usually low impact resistance and elongation to break. This implies that fibers and plates act as flaws. To have high aspect ratio, you need to have one (for fibers) or two (for plates) long dimension(s). The long dimension is likely to be over the 20-40 micron limit where stress concentrations are high, facilitating crack initiation and failure.

There is one more important point to make about aspect ratio. The aspect ratio that matters is not only the one from the datasheet, which describes the as-supplied powder. What matters most, is the aspect ratio of the particles inside the final composite material because that is what affects mechanical properties, barrier performance and so on. It is therefore vital to ensure the particles are not broken down, decreasing aspect ratio, during handling and compounding. The more aspect ratio that can be preserved, the better the final properties.

Although talc is usually described as a platy filler, the aspect ratio can vary widely between grades. Some grades have such low aspect ratio that they provide no reinforcement. The same is true for mica. A poor-quality grade will not reinforce well, whereas a very high aspect ratio wet-ground type can provide reinforcement rivalling chopped glass fiber. It is difficult to compare aspect ratio values from different suppliers because reported values vary widely depending on measurement method.

Surface area

Surface area is relatively easy to measure using BET or dye adsorption. As the surface of a filler particle is what interacts with other particles and with the surrounding polymer, the more surface there is, the more such interaction we can expect. So, what does that mean in practical terms? High surface area means more tendency for agglomeration, creating higher viscosity and more work is needed to keep the particles separated. On the other hand, high surface area means more contact with the polymer, giving improved adhesion between the two. As an everyday example, we often sand a surface before applying glue because sanding increases the surface area and thereby improves adhesion. The same principle applies to composites. Increased adhesion between filler and polymer primarily affects the tensile and flexural strength. Strength increases because, when there is good adhesion, the forces acting on the polymer can be transferred to the filler particles. When adhesion is poor, then the filler particles debond and cannot bear a load, so the strength of the composite suffers. Surprisingly, good adhesion is not always desirable.

In a later section, we look at dispersants and coupling agents, which are surface treatments used to modify the adhesion between the polymer and filler particles.

Common functional fillers

There are many different fillers and each one has a unique property set. This section gives an introduction to the more common fillers, reinforcements and specialty fillers, as well as their properties and applications. DeArmitt and Rothon have published about the selection and use of fillers in polymer composites[14].

Filler	2017 Volume (tonnes)	Value (Million USD)
Carbon black	18,000,000	18,000
Precipitated silica	1,400,000	1,400
Fumed silica	110,000	600
Crystalline silica	300,000	<200
Precipitated calcium carbonate	275,000	165
Ground calcium carbonate	12,000,000	2,500
Talc	1,000,000	600
Kaolin	1,750,000	800
Calcined kaolin	175,000	<200
Wollastonite	150,000	<200
Barium sulfate	350,000	250
Natural fibers	350,000	NA
Others	250,000	NA
Total	**30,885,000**	**>2,750**

Table 2 Global fillers for plastics market data for 2017 - Courtesy of Rothon Consultants

Calcium Carbonate – $CaCO_3$

Calcium carbonate is a soft, inexpensive filler, that is readily available world-wide[15]. High purity calcium carbonate is colorless but appears white in powder form due to light scattering. Different particle sizes are available, as are surface treatments. For many applications, it is the obvious choice, particularly in the less expensive polymers like PE, PP and PVC where it can improve stiffness, retain strength and improve impact resistance while lowering materials costs. Ground calcium carbonate is used predominantly but finer, submicron precipitated grades are available. A book devoted entirely to calcium carbonate goes into great detail[16].

Talc – $Mg_3Si_4O_{10}(OH)_2$

Talc is a very soft mineral that is colorless when pure and appears white in powder form[17]. The particles are generally platy, so talc does reinforce if the aspect ratio is high enough. It is used extensively for applications needing good mechanicals combined with low cost and low weight. The newer high aspect ratio (HAR) talc grades are in demand for automotive applications. Talc is also a good nucleating agent, helping polymers like PP, nylon and PLA to crystallize faster, which speeds part production.

Kaolinite – $Al_2Si_2O_5(OH)_4$

Kaolinite clay is a member of the Kaolin family of aluminosilicates. It is a soft white or tan powder and the particles are platy in shape[18]. It is similar to talc as it can reinforce when the aspect ratio is high enough. Kaolinite is widely available, inert and inexpensive.

Wollastonite – $CaSiO_3$

Wollastonite appears as a white powder with moderate hardness (Mohs 4.5) compared to other common fillers[19]. The hardness makes it good for scratch resistance particularly in PP for automotive use. It is the most common fibrous mineral reinforcement and has replaced asbestos since its demise. It is not as effective as the best reinforcements because the aspect ratio tends to be lower than for HAR talc or mica. Unlike other silicates, wollastonite does not have good resistance to acids and bases and can dissolve, which is useful in certain niches.

Glass beads – SiO_2

Glass beads may be solid or hollow[20] and are used to reduce warpage, particularly in glass fiber filled polymers. They promote good flow and smooth surface finish and are therefore particularly popular in the engineering polymers like nylon and PBT or thermosets like phenolic resins and epoxies. Hollow types are used when density reduction is sought but more expensive, high crush strength types are required to survive extrusion and molding pressures.

Fumed and precipitated silica – SiO_2

These are isotropic fillers with small size and high surface area. They are widely used in elastomers where they improve many properties including modulus, strength, elongation to break and tear strength[21]. The single most important application is in car tires where the use of surface treated precipitated silica has brought about reductions in rolling resistance leading to better fuel efficiency. Fumed silica is finer than precipitated silica and can be considered a nano-material. It is more effective at lower loading levels. For example, for equal viscosity, one must add approximately twice as much precipitated silica to match the performance of fumed silica. Even so, precipitated silica works out to be the less expensive of the two options.

Carbon black

Carbon black is used in many of the same applications as silica, except that it offers a black pigment effect, UV blocking and electrical conductivity on top of the reinforcement. Most carbon blacks are nano-materials and their performance as a reinforcement is attributed to the very high surface area and propensity to form a structure, whereby adjacent particles interact. Different production methods lead to various particle sizes, degree of structure and surface reactivity. A recent overview by Spahr and Rothon[22] provides a great deal of information.

Common reinforcements

Mica muscovite – $KAl_2(Si_3AlO_{10})(OH)_2$ and phlogopite – $KMg_3(AlSi_3O_{10})(OH)_2$

Muscovite is the most common form of mica and is white, or off white. Phlogopite is darker, typically tan in color but has much high temperature stability (900°C versus 600°C). Both types behave similarly in polymers, assuming comparable particle size and aspect ratio. They can be highly reinforcing when carefully milled to give platelets with aspect ratios of 80 or 100:1. Sound damping and good electrical properties are other desirable attributes. When comparing equivalent grades of the two micas in terms of PSD and aspect ratio, it is found that the phlogopite performs best in thermoplastics because it retains its aspect ratio better when compounded. See works by Zilles[23] and Xanthos[24] for more detail.

Glass fiber

There are difference glass types, but E glass is most commonly used in polymers. As with all other fillers, the degree of reinforcement depends on the aspect ratio. In the case of glass fiber, high aspect ratio chopped glass or even continuous fibers, can be used, leading to very effective reinforcement. Surface treatments are commonly employed to protect the fibers and to improve adhesion to the polymer under harsh conditions such as high humidity or elevated temperature. Glass fibers are hard, so special care must be taken to protect the processing equipment from wear and the glass fibers from breakage. Therefore, hardened steel machinery is normally chosen.

Filler Type	Density (gcm^{-3})	Mohs hardness	Refractive index	Mean Size (microns)	Aspect Ratio
Calcium carbonate	2.7	3-4	1.48,1.65,1.70	0.02-30	1-3 Blocky
Talc	2.7-2.8	1	1.55,1.57,1.58	0.5-20	5-40 Plate
Mica	2.8-2.9	2.5-4	1.55-1.70	5-1000	20-100 Plate
Wollastonite	2.9	4.5	1.63,1.65	1-500	5-30 Fiber
Silica (precipitated)	1.9-2.1	5.5	1.46	0.005-0.1	~1 Round
Quartz	2.65	7	1.54,1.55	1-100	1
Carbon black	1.7-1.9	2-3	black	0.014-0.25	~1 Round
Dolomite	2.85	3.5-4	1.68	1-30	~1 Round
Barium sulfate	4.0-4.5	3-3.5	1.64	0.1-30	~1 Round
Kaolinite	2.6	2	1.54,1.56,1.57	0.2-8	10-30 Plate
ATH $Al(OH)_3$	2.42	2.5-3	1.57,1.57,1.59	5-80	1-10 Plate
MDH $Mg(OH)_2$	2.4	2.5-3	1.56, 1.58	0.5-8	1-10 Plate
Diatomaceous earth	2-2.5	5.5-6	1.42-1.48	4-30	2-10 Varies
Magnetite	5.2	5.5-6	black	1-50	~1 Blocky
Hematite	5.2	5.5-6	red	1-50	~1 Blocky
Halloysite	2.54	2.5	1.548 (dried)	1-20	5-20 Tubular
Zinc oxide	5.6	4.5	2.00	0.05-10	1 Round
Titanium dioxide	4.23	6	2.609	0.1-10	1 Round
Diamond	3.52	10	2.418	1-1000	1

Table 3 Properties of assorted functional fillers for plastics and elastomers (TiO_2 values depend on type)

Mechanical properties

The mechanical properties of polymers and composites have been well described in books such as Mechanical Properties of Polymers and Composites by Nielsen and Landel[25] or Mechanical Properties of Reinforced Plastics by Clegg and Collyer[26]. In some books there tends to be a lot of focus on theoretical treatment of properties which is often of little practical value. Instead, it is simpler and more useful to consider empirical trends as one varies parameters such as particle size, shape and surface area.

Testing is most often done in a tensile (pulling) mode or flexural (bending) mode but compression (pressing) tests are sometimes helpful. Reinforcement is a term used when modulus and strength are improved simultaneously.

Modulus

Modulus simply means stiffness. It is the amount a sample deforms under the influence of a force, i.e. the initial slope of the stress-strain curve. Most fillers are far stiffer than polymers, so addition of fillers almost always increases modulus. However, all fillers are not created equal (Table 3). Low aspect ratio fillers like calcium carbonate (calcite) give moderate improvements in modulus. Medium aspect ratio fillers, typified by wollastonite and talc, give even better modulus. Lastly, high aspect ratio fillers like chopped glass fiber or very high aspect ratio phlogopite mica give the most increase in modulus. One must be careful as cheaper, lower aspect ratio grades of talc, wollastonite, mica or glass fiber will not perform as hoped. The higher aspect ratio fillers are susceptible to damage if too much energy is applied during compounding. For instance, glass fiber and mica should not be dosed in the main hopper of an extruder where the viscosity is extreme as the polymer transforms from solid to liquid.

Neither particle size nor surface area affect modulus in most cases because modulus is tested at such low stress and strain that the adhesion between filler and matrix is not challenged. The exception is the testing of the "modulus" of elastomers which is performed under high elongations of 100% or more. In that case, the adhesion between the elastomer and the filler is tested and so it is observed that higher surface area fillers and fillers with coupling agent perform better.

Strength

Like modulus, strength also depends on the aspect ratio of the filler. Low aspect ratio fillers like calcium carbonate or silica spheres tend to result in a slight decrease in strength. Medium aspect ratio fillers preserve or slightly increase strength (i.e. they reinforce). High aspect ratio fillers give a substantial boost in strength.

Strength is tested at higher stresses and strains than modulus, so strength does depend on the surface area and adhesion between filler and polymer matrix. It is easy to understand why by considering the analogy of gluing two pieces of wood together. The strength of the bond can be improved by sanding the wood (increasing surface area) or by using better glue (improving coupling). Finer fillers and fillers with appropriate coupling agent applied, show better strength.

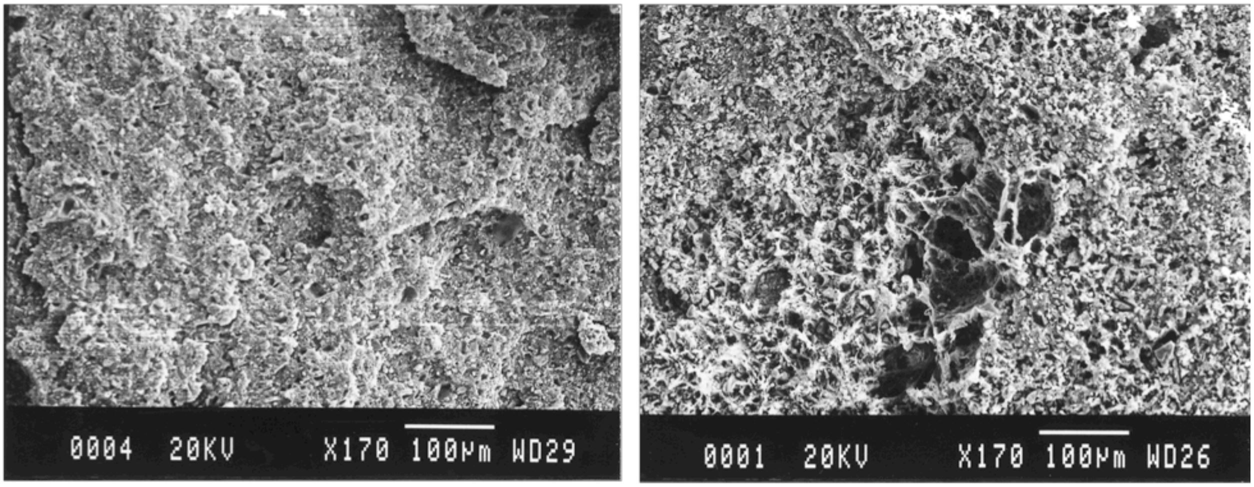
HDT/Vicat

HDT and Vicat normally follow each other closely as they both relate to the temperature at which the composite softens and falls below a defined modulus. Fillers do little to improve the softening temperature of amorphous (non-crystalline) polymers because such polymers soften at their glass transition temperature (Tg) irrespective of the presence of filler. In contrast, semi-crystalline polymers such as PE, PP, PA6, PA6,6, PBT and PEEK benefit tremendously from the addition of high aspect ratio reinforcement. Just 10-20 weight% of chopped glass fiber or other high aspect ratio particles can elevate the HDT/Vicat far above Tg and almost to the melting point of the polymer.

Impact resistance

Impact resistance depends on flaws in the polymer composite. When exposed to an impact, a crack will form and propagate from the largest particle or agglomerate in the part because that is where stresses concentrate. Therefore, impact resistance depends not on the average particle size (D_{50}) of the filler but on the tails of the particle size distribution e.g. the D_{10} and D_{98}. The D_{10} can be important because very fine particles agglomerate to form large particles (Figure 3). Two grades with the same D_{50} can behave very differently depending on how they were milled and whether the larger particles were removed by classification.

Interestingly, while fillers tend to reduce impact resistance in impact resistant polymers like PP copolymer, HIPS or ABS, they can actually improve the impact resistance of some brittle polymers such as uPVC and PP homopolymer. It is observed that 10-20 weight % of fine calcium carbonate treated with stearic acid helps impact resistance by causing the polymer to cavitate in many locations upon impact. This spreads the impact energy over a greater volume of polymer. As the particles debond, encouraged by reduced adhesion caused by the stearic acid coating, a foam is created (Figure 4).



Brittle 20 kJ/m² - Untreated 2 Micron $CaCO_3$ Ductile 40 kJ/m² - Stearic acid treated 2 Micron $CaCO_3$

Figure 4 Stearic acid coated calcium carbonate can increase impact resistance by filler debonding

Elongation to break

Elongation follows the same principles as impact. Larger particles and agglomerates are to be avoided if high elongation to break is the goal. Occasionally, one wishes to encourage low elongation to break, for example in a blister pack or a multi-pack of yoghurt that is designed to snap apart. Here, the intentional addition of a few percent of coarse particles can be advantageous.

Wire and cable formulations often require 400% elongation at high filler loadings of 60 weight % or more. A narrow particle size distribution without fines and without a coarse tail is beneficial. Surface treatment of the filler with an effective dispersant, good mixing and selection of a flexible polymer matrix such as EVA, all help to achieve the goal.

Creep

Polymers are said to be viscoelastic which means that they behave like a solid under short terms tests but can display liquid-like properties over longer time spans. Thus, a thermoplastic may flow slowly under load and this is referred to as creep. Well-bonded high aspect ratio fillers are highly effective at eliminating creep. As a rule of thumb, fillers reduce creep to the same extent that they increase modulus. So, if a filler increaseds stiffness by 50%, then creep would be reduced by a similar amount.

CLTE

The coefficient of linear thermal expansion (CLTE) is a measure of the expansion and contraction of a material when it is heated or cooled. Common fillers have far lower CLTE than polymers. High aspect ratio reinforcements give the lowest CLTE but only along the long dimension(s) of the particles. If glass fibers are aligned by processing in one direction, then CLTE along that direction will be low, but it will be almost unchanged in the two perpendicular directions. Such mismatches of CLTE can lead to warpage as the part cools. If one wishes to reduce shrinkage and warpage in a glass fiber filled material, then the best solution is to add some high aspect ratio mica, which solves the issue while maintaining excellent mechanicals.

Optical properties

Fillers can alter the optical properties in several ways. Usually, fillers make polymers opaque to light because light is scattered by the filler particles. However, the situation is rather more nuanced than that. For example, one can make the polymer brilliant white by adding one filler or transparent by adding a different filler. So, what properties govern the outcome?

Fillers that dramatically alter the colour of plastics are known as pigments. One example is carbon black. By absorbing all visible frequencies, carbon black creates a deep black colour. It also absorbs other light wavelengths. By absorbing UV light, carbon black acts as a powerful UV protectant against degradation in sunlight. By absorbing infrared light, carbon black makes plastics heat up more readily in sunlight.

Titanium dioxide (also known as titania or TiO_2) is a powerful white pigment. It works by scattering, such that incident light is reflected back at the observer. Why is it such a powerful light scatterer? That comes down to its very high refractive index (ability to bend light) and to particle size. Commercial TiO_2 grades tend to have a particle diameter of 0.25 microns because that gives maximum light scattering in plastics and coatings.

Many of the typical fillers have slightly different refractive index to the polymer they are in, so that they scatter light and act as weak white pigments. For example, calcium carbonate filled PP is milky white in appearance and is therefore more difficult to colour than unfilled PP. The opacity caused by the filler blunts the effect of the coloured pigment. More pigment must be added to achieve the desired colour, which means more cost. Some very intense colours may no longer be attainable, no matter how much pigment is used.

The equations also enable us to find the properties required to give minimum scattering, i.e. the route to transparent composites. To create a transparent composite requires a filler with exactly the same refractive index as the polymer. A refractive index mismatch of more than about 0.003 units is enough to generate visible haze[27]. The filler must also be isotropic (have only one refractive index) in order to achieve a match with the polymer. Many fillers appear white when viewed as the dry powder but may look very different and coloured, when wetted out by polymer. A simple way to test this is to mix the filler into an oil with the same refractive index as the polymer. That way, it is possible to see how it will look without wasting a lot of time and money making the compound. An example is paraffin oil, which has the same refractive index as cellulose acetate. Sometimes a designer is looking for the so-called "piano black" appearance. That is achieved by making a transparent material and then adding black dye. The material must be transparent because the piano black effect occurs only when light penetrates well beneath the part surface.

Gloss is a term describing the reflectivity of the part surface. As mentioned elsewhere in the chapter, gloss depends on processing conditions, mold surface and the material composition. High gloss is attainted using low viscosity polymer plus small, well-dispersed filler particles and a smooth mold surface. Low gloss, i.e. a matte surface is achieved by reversing these parameters.

Thermal properties

Thermal conductivity, diffusivity & specific heat capacity

The flow of heat through plastics is important during plastics processing. If the plastic can be heated and melted more quickly, then time is saved. The same is true for cooling from the molten state. Both these effects translate directly into productivity and therefore cost savings. Likewise, for thermoset resins and other polymerization systems, the addition of filler greatly helps absorb and transfer heat given out during the exothermic chemical cure reaction. Fillers can prevent thermal runaway accidents where the reaction temperature accelerates out of control.

The conductivity and diffusivity are terms used to describe the flow of heat through a material. Plastics are not very good conductors of heat. We know from our everyday lives that plastics are used as insulators to protect us from heat. Typical mineral fillers such as calcium carbonate, silica, mica and barium sulfate have thermal conductivities approximately ten times greater than plastics. Therefore, in general, fillers greatly enhance the transfer of heat in and out of polymer materials. The increase in thermal conductivity is quasi linear with the volume percentage filler loading. Unlike the case of electrical conductivity, no distinct percolation threshold is observed.

Some applications, such as plastic heatsinks for laptop computer processors, require very good heat transfer and using specialty fillers, notably hexagonal boron nitride, performance rivalling metals can be realized. Where more modest thermal conductivity is sufficient, other less expensive fillers such as talc, hematite or magnesium oxide may be considered. It is not widely recognized that the thermal diffusivity depends on the modulus of the material, so reinforcing fillers can give a boost. Other thermally conductive fillers include aluminum nitride, alumina and diamond. Using a high loading of alumina of ~67 volume %, one can create a composite with a thermal conductivity of ~3 W/mK). An effective surface treatment is mandatory in order to control viscosity at such high loadings. Small diamonds are less expensive than one might expect because the price of larger jewelry diamonds is artificially inflated. If electrical conductivity can be tolerated then copper, silver and graphene are options. A recent review by Zilles[28] gives more information.

Material	Thermal Conductivity (W/mK)
Silica aerogel	0.02
Polyurethane foam	0.023
Polystyrene foam	0.033
Hollow ceramic spheres	0.1
Hollow glass spheres	0.1 - 0.2
Polymers	0.2 - 0.3
Silica	1.4
Barium sulfate	1.7
Calcium carbonate	2.3
Talc	2 ⊥, 11 ǁ
Mica	0.5 ⊥, 4 ǁ
Magnetite	5.1
Hematite	12.5
Alumina	35
Magnesium oxide	42
Silicon carbide	60 - 200
Aluminium nitride	140 - 180
Hexagonal boron nitride	30 ⊥, 600 ǁ
Graphite	10 ⊥, 300-500 ǁ
Copper	400
Diamond (natural)	2000 - 2200

Table 4 Thermal conductivity of various solids (⊥ - perpendicular, ǁ parallel to plate broadest side)

If one wishes to use a material to store heat, then a material with high heat capacity per unit volume is ideal, but it has been found that most solids have essentially the same value[29], namely 2.3 MJm^{-3} K^{-1} ± 20%. However, few exceptions do exist. Magnetite has an anomalously high volumetric specific heat capacity and is used commercially to store heat. Hematite iron oxide and diamond also lie outside of the normal range.

Electrical properties

Most plastics are very good electrical insulators. There are some specialty polymers like polypyrrole, polyaniline and polythiophene that are electrically conductive, but they are expensive and used only in niche applications. Usually, when we need electrical conductivity, we add a conductive filler to a common plastic like PE, PP, nylon, PBT or epoxy. Note that electrical resistivity is simply the inverse of the conductivity, so high conductivity is synonymous with low resistivity.

As noted for the other properties, electrical conductivity also depends on the volume % of conductive filler but in this case, the dependence is not at all linear. Instead we see a distinct step at a filler concentration known as the percolation threshold. The abrupt change in conductivity marks the point where a continuous pathway forms between conductive particles (Figure 5). The volume percentage at which it occurs depends on particle size, particle shape and mixing conditions. Finer, high aspect ratio fillers give lower percolation thresholds. High structure carbon blacks foster a low percolation threshold and care must be taken not to apply too much mixing energy and thereby destroy that structure.

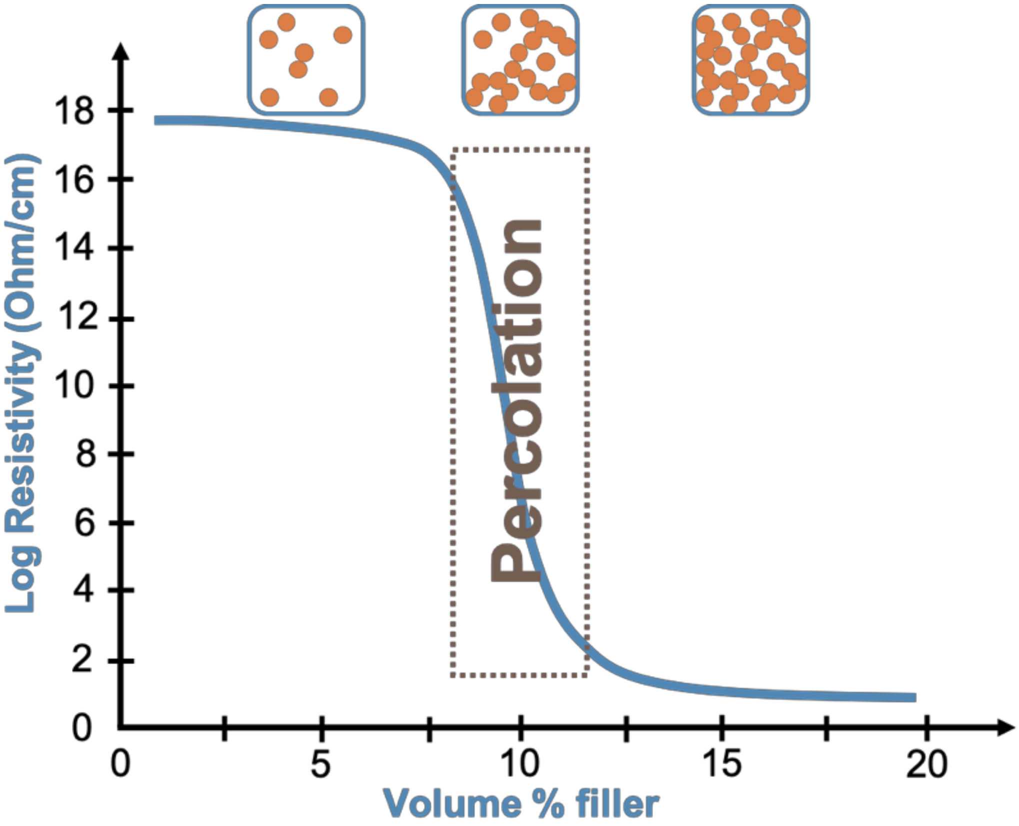


Figure 5 The percolation threshold marks formation of a continuous network of particles

The amount of electrical conductivity needed depends on the effect sought. So, for example, an anti-static effect is achieved at a much lower conductivity than is needed for EMI shielding. Because of the steep change at the percolation threshold, it is a challenge to precisely hit a given conductivity / resistivity target. In the percolation range, any slight shift in particle size, shape, dispersion or even temperature can lead to a conductivity shift of an order of magnitude or more. This issue can be avoided by selecting fillers that have just enough conductivity and formulating such that the compound is in the flat region above percolation.

Conductivity may be measured at the surface or in the bulk of the material and the two may not give the same result. For example, injection molded parts often have a thin skin of material where filler is absent. In such a case, one might be above percolation and have good electrical conductivity inside the part but none at the surface.

One interesting application is self-switching heating jackets for pipelines. A formulation is made in an elastomer where the filler is just above percolation. A current is run through the material which causes the desired heating to prevent the pipe from freezing. The heating causes the rubber to expand and this increases the separation of the conductive filler particles so that they are now below the percolation threshold. Therefore, current no longer flows and the heating stops until the material has cooled sufficiently to contract and restart heating. This so-called PTC material enables self-regulated heating without the need for external sensors. The PTC effect is even stronger in cross-linked semi-crystalline polymers where crystal melting creates the expansion.

Electrically conductive fillers include silver, copper, metalized glass beads, metal-coated glass flake, many different types of carbon black, indium tin oxide plus semi-conductors such as magnetite, hematite and doped silicon or zinc oxide.

Fillers as crystal nucleating agents

The ability to accelerate crystallization and solidification of a polymer from the melt is very useful and valuable. Semi-crystalline polymers including PE, PP, PBT, PA6, PA 6,6, and PEEK, rely on crystallites for many of their properties. As a molded part cools, it solidifies when sufficient crystallization has taken place. At that point, the mold can be opened ready to make a new part. Thus, speed of crystal formation has a direct influence on cycle time (productivity) and overall cost of production parts. Nucleating agents are additives that help crystals form at higher temperatures, helping to improve productivity. Many of the most effective example are dissolved in the polymer and are therefore known as homogeneous nucleating agents. Fillers can act as heterogeneous nucleating agents by providing a surface for the crystals to form.

There is no satisfactory theory to predict whether a particle will nucleate crystal formation. Initially, it was thought that nucleation was caused by high surface energy solids but that was subsequently disproven. At present, it is believed to depend on microstructure of the filler surface which acts as a template for polymer adsorption followed by crystal growth.

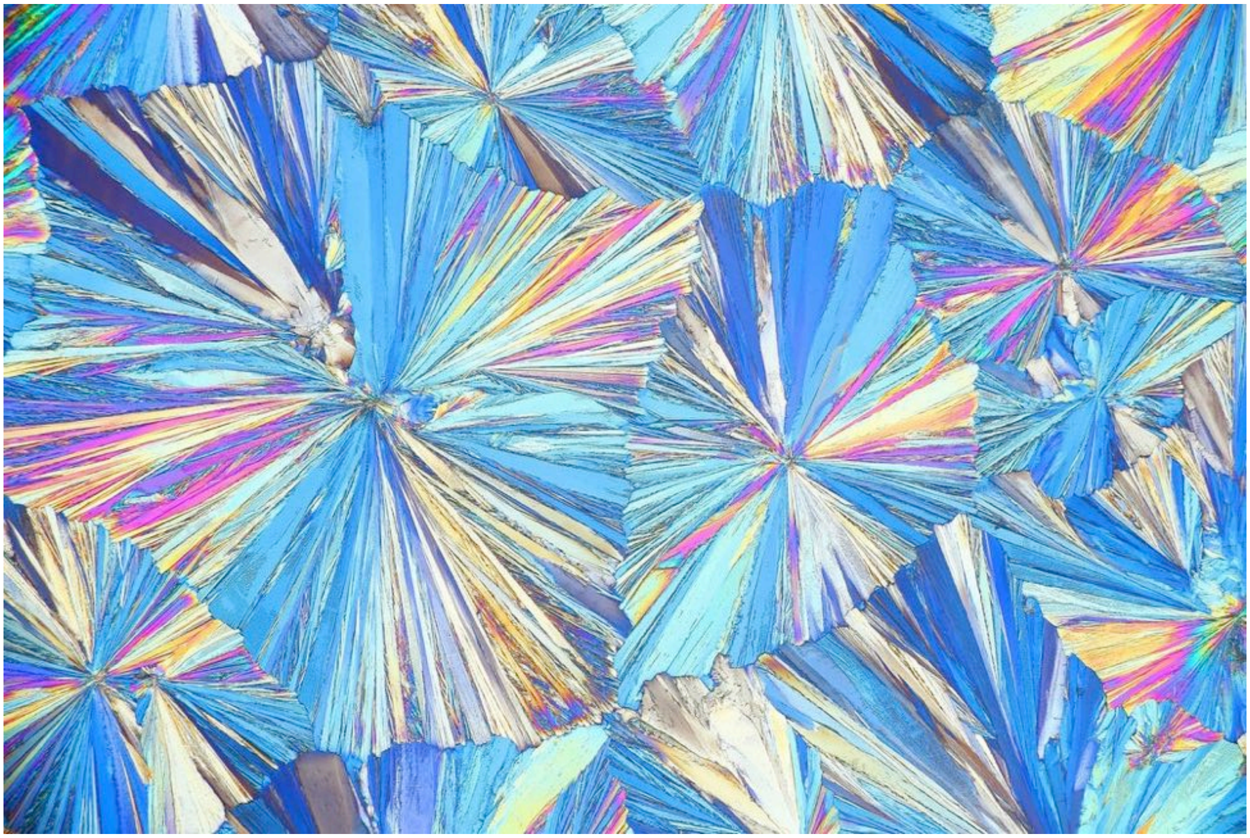


Figure 6 Large crystals are formed with no nucleating agent is present

Talc is found to be effective in a range of plastics including PP, PET and PLA. Dolomite is a mild nucleating agent for PP. Halloysite works well in a range of polymers including PP, PBT, PLA, nylon 6 and nylon 12. Surprisingly it is also effective in polyethylene[30], which is notoriously difficult to nucleate. Micaceous iron oxide is a lesser-known nucleating agent for PP. Sometimes, nucleation occurs unintentionally as a result of certain pigments such as phthalocyanine blue in PP. This infamous combination has led to many issues with unexpected mold shrinkage leading to parts, especially closures, with incorrect dimensions.

Heterogeneous nucleation depends on the surface area of the filler so finer, often sub-micron grades, are more efficacious. Surface treatment of the filler can inhibit nucleation by preventing the filler surface and the polymer from coming into intimate contact.

Fillers as foam nucleating agents

Foams are used extensively as they possess many attractive properties. Using air as a filler means significant savings in the polymer needed to create a certain volume of material. Furthermore, foams have good thermal insulation, good dielectric properties and are useful for sound damping.

Good foams tend to have small cell size and an even distribution of cells. Foam nucleating agents are used to bring about such a structure. In simple terms, the filler particles give the gas bubbles somewhere to form in much the same way that bubbles in a beer glass appear only where the glass is dirty. Thus, addition of fine, well-dispersed solid particles to a polymer will result in the formation of many, well-distributed foam bubbles i.e. a good foam structure. Surface modification of the filler particles can help dispersion and to improve nucleation by altering the filler surface energy. Typically, just 1 weight % filler is needed to give good results.

Magnetic properties

Plastics are not susceptible to magnetic fields but sometimes, we would like them to be. For example, a perfume bottle cap that needs to be held in place by a magnet. Magnetite iron oxide is the natural material that is most strongly attracted to a magnet, so that is the filler most often selected. Magnetite is not itself a magnet, but it is attracted to magnets, which is an important distinction. The hematite form of iron oxide is very weakly attracted to magnets, about one hundred-fold less so than magnetite.

The flexible magnets used to close fridge doors and attached to the front of such doors are made using a soft polymer or elastomer plus a filler that can be magnetized. Appropriate fillers include hard ferrites with the formula $MFe_{12}O_{19}$ where M is usually barium or strontium. Samarium cobalt and neodymium iron boride[31] are alternatives. Some fillers lose their magnetic properties above a certain temperature, so that must be taken into consideration when formulating. Magnetic fillers tend to have high density and so high loadings, on a weight basis, are used.

Barrier properties

Plastic packaging is a very large market. Plastics have enabled a dramatic reduction in food waste. Food production has an alarming environmental burden and it has been shown that plastic packaging helps the environment by helping food stay fresh, so less is wasted. Interestingly, fillers are used to improve barrier properties and also to decrease them. For example, platy fillers like talc, kaolin, mica, graphene or nanoclay, can be aligned in a polymer film or coating, presenting a tortuous path to liquids or gasses. For well-aligned high aspect ratio platelets, the reduction in permeability can be dramatic. Most fillers are impermeable to liquids and gasses, so addition of such a filler would be expected to always reduce the permeability of the polymer. However, there are exceptions.

If the filler particles are not fully wetted out by the polymer, then an air gap remains at the filler-polymer interface. This air gap is the path of least resistance to a molecule attempting to permeate through the material, so gas and liquid permeability are increased, despite the presence of impermeable filler. Liquids may be wicked into the composite along a polymer-glass fiber interface. This has been observed experimentally and the problem was eliminated by surface treating the filler to improve wetting by the polymer and strengthen filler-polymer adhesion[32].

Breathable films are used extensively in diapers and other sanitary products, which is a huge market. They are microporous polyolefin films made using filler that is designed to have poor adhesion to the matrix polymer. Calcium carbonate particles are coated with stearic acid which forms a waxy layer. When the filled film is intentionally stretched, the particles debond, leading to extensive void formation. The end result is a foamed film where the debonded particles are trapped within the foam pores. Such films are hydrophobic, so they prevent water droplets from penetrating, but they are an open-cell foam that allows moisture vapor to pass through. Controlling the filler size distribution and precise application of the surface treatment are of paramount importance.

Compounding and part production

It would be a mistake to think that the properties of a composite depend solely on the types and amounts of its constituents. While the formulation is indeed important, the processing and part production steps can make or break the result.

Compounding

Compounding is a general term used to describe processes used to mix polymer, fillers and other additives[33]. Each has a unique set of advantages and drawbacks. For example, single screw extruders are less expensive but relatively poor at mixing. Some filled plastics are prepared on single screw extruders, but twin screw extruders are preferred due to their superior mixing ability. The screw configuration can be varied widely and is somewhat of an art, although understanding has come a long way in recent years.

Flame-retardant systems are a special case because they usually require ≥60% of filler by weight (~35 volume %), so the viscosity is relatively high. Furthermore, such fillers (ATH, MDH, HMH) are temperature sensitive and decompose when heated to excess. Twin screw extruders can be used for such compounds but Buss Kneaders, TriVolution® or FCM™ machines give superior results because they are better able to achieve good dispersion while avoiding extreme shear that can damage the polymer.

The overall goal is to convey the liquid polymer while dosing in the various ingredients and removing any gasses, such as water vapor, that may be given off. Failure to remove gasses results in a product with voids. Sometimes a foam is the desired result, but in most instances, a vacuum is applied to remove volatiles and prevent air bubbles from affecting the mechanical properties and surface appearance of the final part. It is good practice to measure the density of the compounded material. If it is lower than predicted based on its composition, then voids may be present.

Part production

Once a compound has been made, it must be formed into the intended shape. This additional processing step also has an influence on the final properties of the material.

Rotational molding - A powdered plastic, usually polyethylene, is placed in a heated mold that is then rotated such that the powder melts and coats the inside of the mold. Upon cooling, the solidified part may be removed. This process is especially suited to large simple parts such as storage tanks. Addition of filler to the polymer powder results in bad mechanical properties because the filler concentrates at the boundary between polymer particles and prevents them from fully fusing together. In addition, the concentration of filler is very uneven whereby the original polymer particles contain no filler and the boundary regions contain a large amount. Fillers can be used in rotational molding, but the filler must be pre-compounded into the polymer powder. The orientation of filler in the part will be random, which minimizes warpage and leads to isotropic mechanical properties, i.e. the properties are the same in every direction.

Compression molding - This is mainly useful for the production of large flat, or moderately curved items. The polymer pellets are placed in an open mold whereupon the mold is closed with the addition of heat and pressure. The filler should be pre-compounded to ensure good mixing and the product is a part with random filler distribution leading to isotropic properties.

Extrusion - Extrusion involves pushing a molten polymer through a hole (called a die) that is shaped like the desired part. It is ideal for products like pipes, cables, sheets and fibers. Because the flow is rapid and directional, there can be orientation effects in the material. Polymer chains can align in the flow direction and so can fillers. In particular, platy and fibrous fillers align preferentially in the flow direction. The parts produced therefore display anisotropic properties. For example, strength and modulus are higher in the flow direction than in the perpendicular direction. This can be advantageous. For example, platy particles can align to substantially improve the barrier properties of the composite material.

A high gloss extrudate is usually a good indicator that filler is well dispersed. Conversely, a matte extrudate may indicate poor filler dispersion, which is undesirable in most instances. However, sometimes a matte surface is the goal. One example would be house siding, made from extruded PVC. In that case, large filler particles can be added, and extrusion conditions adjusted, to induce surface roughness which results in light scattering and thus low gloss.

Injection molding - This technique is ideal for complex parts. A molten stream of polymer is pushed into a mold at high speed. The high shear induces noticeable alignment of platy or fibrous fillers and that can induce anisotropic properties in the part. Warpage can result because of differential shrinkage as the part cools. Gating positions may be altered to intentionally disrupt alignment and thereby decrease warpage. During flow at high speed, filler particles move away from the walls such that injection molded parts often have no filler at the part surface, leading to enhanced gloss.

Health and safety

Fillers are usually selected for their safety. Many are generally recognized as safe (GRAS), some even have indirect food contact approval. It is important to note that all naturally occurring minerals are, by definition, TSCA listed but they are not actually in the list by name. Sometimes this leads to confusion in companies where the person responsible for safety is not aware of this rule.

Asbestos is the best-known case of a mineral filler that was later discovered to be unsafe. Nowadays, the major concern comes from impurities in the minerals. Most naturally occurring minerals contain a measurable amount of crystalline silica, in the form of quartz. The International Agency for Research on Cancer (IARC) classifies quartz as Group 1 - Carcinogenic to humans. Simply put, quartz can cause cancer when particles are breathed in. Therefore, regulations exist to monitor and control exposure to respirable quartz, usually defined as particles less than 10 microns in diameter.

Confusion may arise when mineral analysis is reported based on XRF. The XRF results report every element as if it is present as the oxide. This can be highly misleading, especially to non-chemists. An XRF analysis of 100% pure calcium carbonate $CaCO_3$ would state that the sample contains a high percentage of calcium, expressed as the oxide CaO, even though there is actually no calcium oxide at all in the sample. Similarly, an analysis of silicate minerals like talc and mica show high values for SiO_2 even when no actual silica is present. This occasionally leads people to unjustified worries about mineral silica content and safety.

It is not just the chemistry of the filler that matters. Studies have shown that the particle size and shape can be just as important. For example, asbestos fibers lose their propensity to cause mesothelioma if they are ground up smaller or if longer fibers are used. Conversely, an otherwise safe mineral can become dangerous, like asbestos, if it occurs in fibers of a size and shape similar to asbestos. In such cases the mineral is said to be “asbestiform”. The most dangerous fibers were found to be under 0.25 microns in diameter and over 8 microns in length but fibers up to 1.5 microns in diameter and over 4 microns in length were also found to be problematic[34]. The toxicity can be reduced by coating the filler with a surface treatment[35].

The danger is primarily via inhalation of particles and once encapsulated in a polymer composite, they can no longer be inhaled. However, one should take care when cutting or sanding, as such operations have the potential to liberate airborne particles.

Flame retardant fillers

With regulations steadily eroding the availability of brominated flame retardants, companies have turned to FR fillers to fill the role. However, loadings of 60 weight% or more are needed to achieve a suitable FR rating, so careful formulation and processing are a must. A detailed look at FR fillers has been published by Hewitt and Hull[36].

Aluminium trihydrate (ATH) – $Al(OH)_3$

ATH is the most common flame retardant filler. It decomposes when heated above 180-200°C, at which point it absorbs heat and releases water to quench the flame. The low decomposition temperature is suitable for polymers that are processed at under 200°C like PE, EVA and EBA. However, ATH cannot be used in PP and most other polymers because the ATH decomposes during compounding. ATH does occur naturally as the mineral Gibbsite but most FR grades are purer, synthetic precipitated products. Surface treatments are required because high loadings, in the region of 60 weight % are needed to get a good flame retardant rating, e.g. UL94 V-O. The surface treatment helps reduce the viscosity in such highly filled compounds. Large amounts of ATH are used in synthetic marble countertops (so-called solid surfaces) and those grades are usually surface treated with an unsaturated organosilane coupling agent to improve bonding to the acrylic matrix polymer. A dispersant may be added as well as a coupling agent.

Magnesium hydroxide (MDH) – $Mg(OH)_2$

Magnesium hydroxide is selected for PP and other polymers that are processed at higher temperature because it has higher thermal stability than ATH. Endothermic (heat absorbing) decomposition starts at 300°C whereupon water is released to combat the fire, in much the same way as described for ATH. MDH does occur naturally as the mineral brucite but deposits are relatively rare, and the natural product suffers from impurities and sub-optimal particle shape for the high loadings needed. Thus, synthetic grades are more popular, although far more costly, than either brucite or precipitated ATH. Coated grades are available, where dispersants lower processing viscosity and coupling agents improve bonding and thereby the strength of the composite. Surface treatments are also used to improve wet electrical performance.

Huntite / Hydromagnesite (HMH) blends – $Mg_3Ca(CO_3)_4$ / $Mg_5(CO_3)_4(OH)_2{\cdot}4H_2O$

Huntite and hydromagnesite occur, almost invariably, as mixtures in nature. Commercial deposits are rare, mainly in Greece and more recently in Turkey. The hydromagnesite starts to decompose at 220°C (open air) or 250°C (under pressure in an extruder), which is high enough so that it can be used in polypropylene. It also finds use in PE, EVA and EBA. The hydromagnesite gives off water and absorbs heat, much like ATH and MDH do. In contrast, the huntite decomposes above 400°C, absorbing heat but liberating only carbon dioxide. As a natural mineral product, it is inherently less expensive than precipitated ATH or MDH. Hydromagnesite has a low aspect ratio but huntite is a medium aspect ratio platy material which alters polymer melt flow behavior and provides some reinforcement. HMH is gaining popularity because it has the higher onset temperature of MDH combined with the low cost of ATH.

High density fillers (and x-ray detectability)

There are numerous applications where added density is beneficial. One example is to control noise or vibration. Both barium sulfate and iron oxide are used in cars for just that reason. Sometimes one is simply looking for heft, which can impart the perception of high-quality. High density fillers are also able to block x-rays. This makes them useful for dental implants or in a hospital environment to protect patients. In order to maximize density, high filler loadings are commonly employed. As an example, 70 weight % of iron oxide in PP may seem high and potentially hard to process due to high viscosity. However, that loading translates to just 31 volume percent, so flow is not a problem.

Barium Sulfate (Barite or Blanc Fixe) – $BaSO_4$

White in powder form, it occurs naturally as the mineral barite and the corresponding synthetic version is referred to as Blanc Fixe. The two main attributes are high density (4.0-4.5 gcm^{-3}) depending on purity and radio opacity. It is therefore added to polymers to make them heavy, e.g. for sound damping or to make them x-ray visible for implants, for example. It is highly unreactive (inert) and because the particles are blocky in shape it is a non-reinforcing filler.

Magnetite iron oxide – Fe_3O_4

A black lustrous powder with unusual properties. Often used for its high density (5.2 gcm^{-3} for pure grades). It also has high electrical conductivity and quite high thermal conductivity. It is x-ray opaque and can be used to block radiation. Magnetite is non-reinforcing due to the low aspect ratio of the particles. The many unusual properties are detailed in a chapter by DeArmitt[37]. Magnetite heats very rapidly in a microwave oven and can be used to block radar. The heating rate of magnetite-filled plastics can be tuned by adjusting the filler loading. Although black in colour, magnetite is a rather weak pigment, so that coarse magnetite-filled plastics can still be coloured by adding other pigments.

Hematite iron oxide – Fe_2O_3

Coarse, pure hematite is a shiny gunmetal grey colour but when ground finer, below about 5 microns in size, the particles change colour and are rust red. This red colour is used as a pigment and is the basis for rouge used in cosmetics. Hematite has the same density (5.2 gcm^{-3} for pure grades) as magnetite and is highly effective in sound deadening applications, but is normally less expensive making it an attractive alternative to magnetite. Hematite heats rapidly when exposed to microwaves and can reach 400°C in 2 minutes. Hematite absorbs radar which can be useful in stealth applications. Hematite has very high thermal conductivity (12.5 W/m.K) which is 4-5 times higher than typical mineral fillers. This leads to very low cycle times when molding hematite-filled plastics. Until recently, pure hematite was not available as a filler for plastics but in 2016 it was launched commercially in the US[38] under the tradename DenzFlex®.

A special platy form of hematite called micaceous iron oxide is also available, e.g. under the tradename MIOX®. It is used as a nucleating agent, a mild abrasive and for anti-corrosion coatings as a partial replacement for zinc.

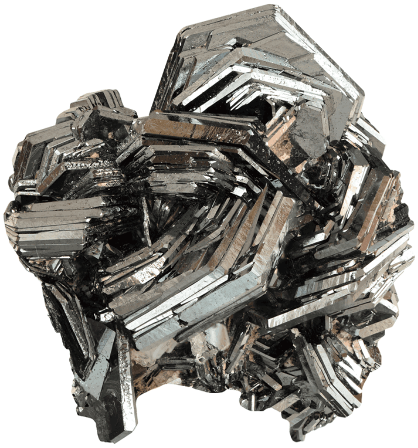


Figure 7 Micaceous iron oxide – a special platy form of hematite Fe_2O_3

Tungsten – W

Tungsten is a pure elemental metal used for very high-density composites such as lead replacement. Tungsten itself has a density of 19.25 gcm^{-3} and the name comes from Swedish where “tung” means heavy and “sten” means stone. It is far more expensive than barium sulfate or magnetite and also much harder, causing machine wear.

Others

Several other dense, radiopaque, filler options are available including bismuth subcarbonate, bismuth oxychloride and bismuth trioxide.

Specialty fillers

The fillers covered above are of most importance in terms of volume used but many other types are selected to achieve particular effects.

Dolomite – $CaCO_3 \cdot MgCO_3$

Dolomite is similar to calcium carbonate (calcite) but with some subtle differences. It is also a soft white powder, but it is much rarer to find deposits of sufficient whiteness for polymer applications. It is slightly harder and denser than calcite and has greater resistance to attack by acids. Note that it is not a mixture of calcium carbonate and magnesium carbonate but rather, a chemically distinct mineral.

Magnesium oxysulfate (MOS) fiber – $5Mg(OH)_2 \cdot MgSO_4 \cdot 3H_2O$

Although this product has been manufactured and used for several decades, it is not at all well known. With a fiber diameter of 0.5 microns and mean length of 15 microns, the aspect ratio is approximately 30:1 as supplied. After processing into polymer that is reduced somewhat, but is still enough to provide reinforcement in PP and other polymers. Strength is improved by using MOS fibers but modulus and HDT are very good. Stearic acid has been used successfully as a dispersant and silane grafted PP can be used as a coupling agent to boost strength. Although fibers with these dimensions normally have asbestiform behaviour, MOS fiber is water-soluble, non-persistent[39] and therefore considered safe.

Halloysite – $Al_2Si_2O_5(OH)_4$

Halloysite is an aluminosilicate and member of the Kaolin group of minerals. It has identical chemistry to kaolinite but instead of platy particles, the silicate sheets are rolled up in a scroll-like fashion to create nanotubes. These are typically 50nm in diameter and a few microns long to give an aspect ratio of 10-20:1 and thus moderate reinforcement similar to wollastonite. Although many potential applications have been proposed[40], commercialization in polymers has been very slow to take off.

Titanium Dioxide – TiO_2

Normally thought of as a pigment and used at 1-2% by weight, TiO_2 is sometimes used at much higher loadings (10-30 weight %) more typical of fillers. As expected, these are exceptionally white compounds with superior UV resistance but the TiO_2 also lends surprisingly good mechanical properties because the particles are small (~0.25μm), with a narrow particle size distribution and surface treated to enhance dispersion.

Desiccant Fillers

Certain fillers can absorb or chemically react with moisture. This can be used to protect hydrolytically sensitive materials such as polyesters. Desiccants can also be useful for preventing foaming due to water vapor evolution during processing.

Calcium oxide – CaO

This desiccant reacts chemically with water to form calcium hydroxide which creates alkalinity that may affect some types of polymer. The reaction is irreversible under most circumstances, as it requires heating in excess of 500°C to revert to the oxide. The oxide can scavenge about 30% of its own mass in water and interestingly, the particles expand significantly as they react and convert to the hydroxide form.

Zeolites

Zeolites are normally thought of as synthetic but less expensive natural types are mined commercially as well. Zeolites are a family of aluminosilicates containing tiny pores and channels that can adsorb small molecules. The 3 Å and 4Å type zeolites have pores of the right size to hold water molecules and can typically adsorb 15-20% of their own mass in water. Such zeolites may be regenerated by heating to 175-260°C whereupon they release the bound water molecules. That temperature range overlaps with processing conditions for several plastics, so one must be aware that there is the potential for water to be liberated from the zeolites.

Antimicrobial fillers

Zinc oxide, silver and doped zeolites are all available and can be used as antimicrobials. They work by releasing metal ions, so controlling the release rate is essential. Too fast a release and the additive is expended too soon, too slow of a release and the efficacy is lost.

Surface treatments – dispersants & coupling agents

Earlier, we mentioned the importance of the filler surface and surface area on properties. At various points, we have mentioned certain advantages to surface treating filler particles. Such treatments can bring worthwhile advantages and we will discuss them briefly here, although this is a topic usually covered in dedicated texts, for example by DeArmitt and Rothon[41,42]. These additives are usually added at 1-5 weight% relative to the weight of filler and bring about remarkable improvements considering the low amount needed. The ideal concentration of surface treatment depends on the surface area and reactive site concentration of the filler. They can be pre-treated onto the filler surface, or the treatment may be performed in-situ during compounding.

Dispersants

Dispersants are amphiphilic molecules, meaning that they are composed of two dissimilar parts. One part is designed to bond to the filler surface and the other part is designed to have an affinity for the polymer. A simple example is stearic acid, which is widely used to coat calcium carbonate. The carboxylic acid group anchors itself to the filler surface and the polyolefin-like tail is in contact with the surrounding polymer. One can picture this as a waxy coating bonded to the filler particles. The effects are manifold.

The waxy, hydrophobic coating makes the filler less sensitive to moisture pick-up, e.g. due to high humidity. More importantly, it provides a lubrication effect so that when two filler particles come into contact, there is less friction. The result is reduced viscosity which is especially valued in highly filler flame-retardant compounds. Higher flow enables greater filler loadings and gives increased extruder output, which saves money.

As their name implies, dispersion is also improved, leading to better gloss, better impact resistance and better elongation to break, due to the elimination of flaws in the form of agglomerates. Dispersants decrease the attraction between particles but also the attraction between the particle and the polymer. The chemistry needed to anchor the dispersant depends on the surface chemistry of the filler (or pigment) and the dispersant "tail" portion is selected to match the polarity (Solubility Parameter) of the polymer.

Stearic acid is the most common dispersant for fillers. While better options exist, stearic acid is an abundant and inexpensive natural product. Other dispersants include the titanates and some of the organosilanes. Stearates (stearic acid salts) are used as well but are usually less effective than the free acid form.

Coupling agents

Coupling agents are also amphiphilic molecules, comprised of two different segments. One part must bond strongly to the filler surface and the other part must bond strongly to the polymer, either by chemical bonds or via chain entanglements. By improving interfacial adhesion, coupling agents lead to stronger composites and they enable composites to better survive extreme heat and humidity without losing their mechanical and electrical properties. An improperly chosen coupling agent may end up performing as a dispersant instead. That happens when the surface modifier bonds to the filler, but the chemistry is incorrect, so it does not bond to the polymer. The most common coupling agents are the organosilanes and the maleated polyolefins. If the coupling agent is doing its job, then you will see an increase in strength. More polar polymers, like nylons, interact strongly with the filler without the need for coupling agents.

Filler myths and misconceptions

This section addresses some misunderstandings that continue despite clear evidence to the contrary.

Iron content and polymer stability

It is widely thought that iron content in fillers directly correlates to the long term and heat stability of the compound. In fact, the situation is more complex. Iron and other transition metals such (e.g. copper, vanadium, manganese) can indeed decrease the thermo-oxidative stability of polyolefins by catalyzing free radical attack. Some companies purchase filler and set prices according to these trace impurities, normally present in the ppm concentration range. However, there is no direct correlation between iron content and polymer stability. Some talcs have very low iron but that iron is present in a very catalytically active form that causes stability issues. Other talcs and micas contain much larger amounts of iron but have little or no effect on polymer stability. As an extreme example, pure magnetite iron oxide contains >600 000ppm of iron and yet it has been shown to have no major effect on the stability of PP[43]. The best approach is to actually test the oven ageing stability with the filler grades of interest.

Abrasion and wear

In the plastics industry, people observe wear of their equipment, e.g. extruders and attribute that wear to the filler. Even soft minerals such as talc and calcium carbonate are blamed for wear. This is intuitively nonsense because talc is so soft that it is scratched by a fingernail. So, what is the explanation? Studies have proven that common fillers are too soft to cause appreciable wear and that almost all wear observed is due to traces of hard impurities, usually quartz, in the mineral[44]. This is an important finding because wear means maintenance costs and downtime. Larger amounts of quartz and larger quartz particles cause excessive wear that can be avoided by using purer grades of filler[45]. This needs to be factored in when choosing filler grades.

One can easily assess the propensity to cause wear using the Einlehner Abrasion test where a bronze mesh is exposed to a 10 or 15 weight % slurry of the filler for a set number of revolutions, and the weight loss from the screen is recorded. More abrasive materials lead to greater weight lost from the mesh.

Datasheet particle size and aspect ratio

Fillers are often specified based on the datasheet parameters such as the particle size or aspect ratio. However, the properties one obtains using a filler depend not on the datasheet but on the size and shape of the particles once they have been compounded into the polymer. For example, a nanofiller may lead to 200 micron agglomerates in the polymer with correspondingly catastrophic consequences to the impact resistance of the material. Similarly, high aspect ratio mica or glass fiber added in the main hopper will be ground up and the aspect ratio destroyed, such that no reinforcement is achieved. This happens regularly in practice, even when the filler supplier provides explicit instructions about correct filler dosage methodology.

In order to understand composites, it is good practice to do microscopy to see the size and shape of the filler in the final compound or part. One can also ash the composite, i.e. burn away the polymer and then do particle size analysis on the filler that is left.

Nanofillers

A lot of hype has sprung up around the topic of nanofillers. This is surprising for a couple of reasons. Firstly, because nanofillers are not new[46,47]. Nano-silica and carbon black have been in our tires for decades and constitute a billion dollar a year business. Secondly, there is nothing surprising about the performance observed when using nanofillers. Colloid scientists have understood the nano / surface realm for over half a century. Let us look briefly at the attributes of nano-particles.

- The small particle size, in the nanometer range, actually turns out to be the least important factor. Small size can lead to some useful properties such as transparent composites, but usually, the size is a problem because small particles give rise to huge viscosity and severe difficulties with dispersion.

- The high surface area, often in the hundreds of m^2/g means huge contact area with the surrounding polymer. This leads to higher strength but also requires very large amounts of surface treatment to cover the surface.

- The platy nanoclays have very high aspect ratio making for excellent reinforcement. However, they can only be used at low loadings and do not perform better than standard reinforcements.

The extreme level of interest in nano-composites is therefore unwarranted.

Conclusions

Plastics are an invaluable and irreplaceable part of our modern lifestyles. Their success is largely because of their versatility and functional fillers have taken plastics to new levels of performance. Filled plastics is a multi-disciplinary field so an understanding of plastics, fillers, processing and surface science are all needed in order to create successful new formulations. This chapter is designed to give insights into all of those aspects in a simple, practical way so that a new generation can get a head start in this dynamic and fascinating field.

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