

# Fillers and surface treatment

Fillers are widely used in thermosets, thermoplastics and elastomers. Current estimates put the global market for fillers at between 12 and 18 million tonnes per year. Originally, their main function was seen as reducing the cost of the compound. However, in recent years it has become more widely recognized that fillers can enhance the processability and mechanical properties of compounds. The term functional fillers is now used to emphasize the positive benefits achieved through the addition of fillers. Even in cases where fillers are added primarily to reduce cost, they still alter the properties of the compound and it is therefore important to understand the changes that fillers bring about. Dr. Chris DeArmitt and Professor Roger Rotheron describe the key filler characteristics that influence the manufacture and final properties of compounds - illustrated with specific examples for common fillers. In addition, they cover the use of surface treatments for fillers and how the judicious use of surface treatment additives can further enhance filled plastic compounds.

## Common filler types

The most common fillers are natural calcium carbonate and carbon black. Each accounts for around 30 to 40 per cent by weight of all filler consumption. Glass fibre is third at around 15 per cent market share. Precipitated silicas, precipitated calcium carbonates, aluminium hydroxide and talc each account for about three per cent.

Other significant fillers include clay, wollastonite, mica, wood fibre, dolomite and glass beads. In value terms, the market leader is carbon black, followed by glass fibre, precipitated silica, aluminium hydroxide and precipitated calcium carbonates.

While fillers are used in all polymer types, elastomers are the main market by both volume and value, largely due to the tyre industry. Among the other polymers,

polyvinyl chloride (PVC) probably consumes most filler by volume, while unsaturated polyester and polypropylene consume most filler in terms of value.

Some key properties of these more common fillers are listed in Table 1.

## Filler properties

There are many factors that influence the behaviour of fillers in the polymer. The most important include particle size distribution, surface area, shape, colour, refractive index, impurities, density, hardness, moisture content, thermal stability, modulus, surface chemistry and toxicity. Particle size distribution is one of the most important factors. This determines how many particles will be present at a given loading, how close to one another the particles will be, and how much filler surface there will be. All of these affect the

properties of the compound. The weight percentage of filler is often given, but the compound's mechanical, physical and electrical properties depend on the volume percentage of filler, not the weight percentage. For example, modulus and yield strength vary linearly with the volume percentage of filler.

Mineral fillers have substantially higher moduli than polymers, so the compound's modulus is increased by addition of filler. High surface area and anisotropy also contribute to a higher modulus. Yield strength is another key property and is sensitive to particle size (surface area) and shape.

Spherical fillers usually decrease the yield strength of the compound relative to the unfilled polymer, unless the particles have exceptionally high surface area - increased surface area and anisotropy increase the magnitude of reinforcement.

**Table 1: Key properties of some common fillers**

Filler	Shape	Density	Moh hardness	Chemical formula	Colour
Calcium carbonate	Spherical	2.7	3	CaCO <sub>3</sub>	White
Dolomite	Spherical	2.85	3.5	CaCO <sub>3</sub> •MgCO <sub>3</sub>	White
Talc	Platy	2.7	1	Mg <sub>3</sub> (Si <sub>4</sub> O <sub>10</sub> )(OH) <sub>2</sub>	Grey/white
Mica	Platy	2.76-2.88	2-2.5	KM(AlSi <sub>3</sub> O <sub>10</sub> )(OH) <sub>2</sub>	White/brown
Wollastonite	Acicular	2.9	4.5	KM(AlSi <sub>3</sub> O <sub>10</sub> )(OH) <sub>2</sub>	White
Clay (Kaolin)	Platy	2.6	2.5-3	Al <sub>2</sub> O <sub>3</sub> •2SiO <sub>2</sub> •2H <sub>2</sub> O	White/brown
Glass fibre	Fibrous	2.59	6.5	SiO <sub>2</sub> based	Colourless
Carbon black	Spherical	1.7-1.9	1	C(83-99%)	Black
ATH		2.4		Al(OH) <sub>3</sub>	White
Precipitated silica	Spherical	2.0	7	SiO <sub>2</sub>	White

Platy fillers and especially fibrous fillers are able to reinforce; that is they enhance yield strength.

In general, particles that are too large will act as stress concentrators and significantly reduce the compound's strength and toughness, even if they are only a small fraction of the total filler amount.

On the other hand, particles that are too fine can be very difficult to disperse and can form agglomerates that act as large particles. Even when well dispersed, the high amount of filler surface associated with fine particles can detrimentally affect polymer structure, often leading to high stiffness but low toughness.

The optimum particle size will vary with application and polymer type. Elastomers generally utilize the finest particles, with reinforcing fillers such as carbon blacks and silicas being a few tens of nanometers in diameter and with specific surface areas of over 100 m<sup>2</sup>/g. For thermoplastics sizes are usually from 500-1000 nanometers, while thermosets can utilize significantly coarser particles.

Particle shape is also very important for impact properties. Round particles flow and disperse well and cause least problems with stress concentration. Needle-like (acicular), fibrous and platy particle shapes can be harder to disperse and can

act as stress concentrators, which reduces impact strength.

Platy particles can also be useful for reducing gas permeability properties. The special shapes (known as structure) of particles like reinforcing carbon black are important in controlling several crucial properties of filled elastomers.

Both particle size and shape distribution are also important in determining how well particles pack together. This is important where very high filler loadings are required, such as in flame retardant compounds, polymer concretes, magnetic formulations and dental resins.

Particle size and shape also affect health hazards, with fine fibrous particles being of special concern, even if present at low levels. Asbestos is an example of a fibrous filler that once used to be in widespread use, but is now generally avoided because of health and safety concerns.

Almost all fillers are significantly denser than common polymers and therefore result in compounds with increased density. This is often undesirable, but tolerated. An exception is in sound deadening compositions, where very high density fillers such as magnetite or barium sulphate are preferred.

At the other end of the scale, hollow glass beads or expanding polymer microspheres, for example Expancel<sup>®</sup>, are used as fillers when very low densities are needed, such as in buoyancy aids.

Fillers vary greatly in their hardness, from the very soft talc, through to the very hard silicas, such as quartz. Excessive hardness should be avoided, because it causes problems with wear of machinery. However, in some cases hard fillers are essential, particularly where good abrasion and wear resistance is needed in thermoset compounds.

Free moisture content generally has to be minimized, because it can cause voids to form during compounding and may also lead to the degradation of polymers such as polyamides. Some moisture is, however, needed for optimum performance of some types of surface modifier. On the other hand, bound moisture (for example in hydrates and hydroxides) can be used to obtain flame retardancy, without the smoke and toxicity concerns associated with some other methods.

In this instance, it is important for the water to be lost at a temperature above that at which the polymer is processed, but at, or below, that at which it decomposes. Aluminium and magnesium

hydroxides are the most widely used flame retardant fillers.

The importance of optical effects, such as colour and refractive index, depend on the application. It is generally preferred that fillers are white, or colourless. The scattering power of fillers and therefore their pigimentary ability depends on the refractive index difference between the filler and polymer.

For most fillers this is small and they have little pigimentary effect compared to a material such as titanium dioxide. Some fillers have two or more refractive indices and this can give rise to complex effects, when their refractive indices are close to that of the polymer.

Toxicity is of obvious concern. The effect of particle shape has already been mentioned. The presence of crystalline silicas of a certain particle size can also be a problem in some instances.

The chemistry of the filler particle surface is important, as it determines how well the particles interact with the polymer matrix and how they respond to surface modifiers. Consequently carbon blacks show a strong interaction with elastomers, without the need for any surface modifiers.

Fillers with reactive surface hydroxyls such as silicas, silicates, and hydroxides respond well to organo-silane treatments, while calcium carbonate does not and must be modified using different chemistry.

## Surface treatment

There are two principle classes of filler surface treatment; non-coupling and coupling. Both of these may act as dispersants, but only coupling bonds the filler strongly to the polymer matrix. The non-coupling types give a relatively weak filler to polymer interface.

The main uses of the non-bonding types are:

- Aiding filler production and handling.
- Improving the processing of filled polymers.
- Improving filler dispersion and the properties associated with it.
- Reducing machine wear.

- Reducing moisture pick-up of the filler and compound.
- Reducing the adsorption of expensive additives, such as antioxidants.
- As a result of the weak interface, the compound strength may be somewhat reduced, but impact strength can often be enhanced.

The principle non-coupling surface treatments are long chain (C16-20) fatty acids and their salts. These can bond strongly to the surface of basic and amphoteric fillers, especially calcium carbonate. The most cost-effective forms of these additives are mixtures obtained from natural products. The principal aim of coupling agents is to provide strong and environmentally stable, interaction between the filler and the polymer. This improves strength properties and particularly their retention under adverse environmental conditions.

Carefully selected, coupling agents can also provide some of the benefits of the non-coupling types, especially improved processing and dispersion. However, while of great importance, this is not usually a consequence of the strong filler to polymer interaction itself.

The main class of coupling agent is the organo-silanes. In these materials, a silicon atom is usually attached to three alkoxy groups and, through a silicon to carbon bond, to some organic functional group, chosen so that it capable of reacting with a particular polymer matrix. Bonding to a filler surface is through hydrolysis of the alkoxy groups and condensation of the resulting silanols with surface hydroxyls.

The main polymer reactive functionalities used are amino, epoxy, mercapto, polysulphide, methacryloxy and vinyl. Most fillers can be successfully treated with organo-silanes, the main exceptions being calcium carbonates and carbon blacks. Due to its use with precipitated silica in tyres, the polysulphide is probably used in greatest volume, with the amino- and vinyl forms coming next.

Other organo-metallics, notably organotitanates, aluminates, zirconates and zirconoaluminates, are also promoted as coupling agents, but none approaches the use levels of the silanes.

Another approach to achieving a strong polymer to filler attachment is to pre-graft a filler reactive group onto a polymer backbone, giving what is known as a functionalized polymer.

Acidic groups (notably carboxylic or succinic anhydride) are the main functionality used, although alkoxy silanes are also used. Such functionalized polymers are available based on polyethylene, polypropylene, ethylene vinylacetate and polybutadienes.

The acid and anhydride functional polymers are mainly effective with basic and amphoteric fillers (such as calcium carbonate and aluminium hydroxide). Glass fibre, silica and some silicates may need priming with a layer of amino-silane, which can form an amide linkage with the derivatized polymer.

Surface modifiers can be pre-coated onto the filler surface or can be added during compounding of the filler with the polymer. Both approaches have advantages and limitations and each is widely used.

## Reference

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