Polymers and Polymeric Composites:
A Reference Series

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Roger Rothon *Editor*

# Fillers for Polymer Applications

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Roger Rothon
Editor

# Fillers for Polymer Applications

With 164 Figures and 117 Tables

Springer

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# Preface

Written by industry and academic specialists, this volume focusses on the production, choice, and use of fillers in polymers. The principal focus throughout is on particulate rather than fibrous fillers, as the latter are covered in other chapters. Acicular fillers like Wollastonite are however included, as are plates such as clays.

Particulate fillers play a key role in many applications and are essential to today's industrial age, whether it be vehicle tires, printed circuit boards, or environmentally friendly flame retardants for a host of construction, transport, and communications applications. It is estimated that 25–30 million tons of particulate fillers are used in polymers globally (source Rothon Consultants).

The main fillers by volume are natural carbonates (principally calcium carbonates), carbon blacks, kaolins, talcs, aluminum hydroxide, precipitated silicas, and wood flour. Carbon blacks, precipitated silicas, and aluminum hydroxide are the leaders by value. All of these fillers, together with many of the more specialized, lower volume ones, are included.

Most filler publications seem to focus on thermoplastic applications alone, but thermosets and especially elastomers are also very significant users of particulate fillers. Indeed, the majority of carbon blacks and precipitated silicas are used in the rubber industry, especially as vital reinforcing agents in vehicle tires. All of these polymer types are covered here, with all three polymer classes having their own chapter highlighting the aspects of most significance to them.

Surface modification, especially the use of coupling agents, is also a very important factor in optimizing performance in many composite applications, and this is given due prominence throughout, as well as having a chapter devoted to the basic features involved in this technology. The main (but not sole) purpose of surface modification is to alter the interaction between the filler and polymer matrix. In many cases (for example, tires) increased adhesion is sought, and this is where coupling agents are employed. However, this is not always the case and reduced adhesion can sometimes be required, with fatty acid coated calcium carbonate in microporous film being a good example.

At the time of writing, environmental issues relating to sustainability and recycling are emerging as an important consideration for the composites and, by inference, the fillers industries. One of the principal emphasis here is on the large volume products such as tires, but there are many other examples. These subjects are still evolving with the current state of the art addressed throughout the Volume and also in a dedicated chapter. In addition, the related topic of fillers produced from organic sources is given its own chapter.

The sometimes controversial topic of nano-fillers is also addressed. A few years ago, one class of these, the nano-clays, was seen as the “next big thing” for composites and about to take the fillers market by storm. Inevitably, this was over promoted and has failed to deliver anything near what was promised. As a result, interest in nano-fillers has declined markedly. What is not appreciated is that they are nothing new and in the form of carbon blacks and precipitated and fumed silicas have long been a stalwart of the fillers industry.

The Volume itself is a transition from what was originally a series of contributions for an Encyclopedia. Most of the chapters are thus rather short with their main aim being to give a good overview of the topic and point the reader to the best of the detailed literature. Something also needs to be said about the literature referenced. Filler technology is very much industry, rather than academic, based. Thus, the best literature is often found in trade journals and even patent applications, rather than in the leading academic journals. Much of the fundamental work on the established fillers was also published some time ago and still remains the go-to reference.

# Contents

# About the Editor

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**Professor Roger Rothon** is an independent consultant, company director, and a visiting professor at Manchester Metropolitan University.

Professor Rothon has spent over 30 years working in the fields of inorganic filler production, surface modification, and filled polymer composites. The first 15 of these were spent in ICI, where he developed new types of coupling agents and also new types of magnesium mineral flame retardants. Later he was technical manager for Flamemag International, where he worked with CSIRO Minerals Division in Australia on the development of new processes for the manufacture of magnesium hydroxide flame retardants. He is now an independent consultant and also a director of ECOfillers, a company involved in recycling of polymers and particulate materials.

Professor Rothon has a number of relevant patent applications and many scientific publications, including a highly regarded book on particulate filled mineral composites. He also authors reports on global markets for fillers for a number of leading companies where he specializes in flame retardant fillers and in fillers for tire rubber applications. His current research interests include the recovery of nano-sized silica particles from geothermal power plants and their use as specialized fillers.

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# Part I

# Fundamentals and Principles

# Particulate Fillers, Selection, and Use in Polymer Composites

# 1

Christopher DeArmitt and Roger Rothon

## Contents

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**Abstract**

Fillers have been incorporated into all polymer types, thermoplastics, elastomers, and thermosets, from the very beginning, and it is probably true to say that the development of many polymers would not have been possible without them. They continue to play a vital role today.

One of the original purposes was simply to reduce cost, but this is less important today, as polymers have become less expensive and more of a commodity. Fillers have distinctly different properties to polymers, and by their judicious selection one can produce composite materials with enhanced properties for a given use. It is important to recognize that while benefitting some properties, a filler may be detrimental to others and considerable skill is needed to arrive at the best compromise for any application.

The main reasons for using particulate fillers today vary with the polymer type but include improved processing, increased stiffness, heat distortion temperature and creep resistance, better abrasion and tear resistance, and flame retardancy.

Key properties include cost, specific gravity (density), hardness, purity, particle size and shape, surface chemistry, and thermal stability. Optical, thermal, and electrical properties can also be critical in some applications.

**Keywords**

Filler • Mineral • Polymer • Thermoplastic • Thermoset • Elastomer • Particle size • Particle shape • Composite

## Definition

Particulate fillers are powdered substances, with particles usually less than 100 μm in size, which are added to polymers to reduce cost, to improve processing, and/or to modify one or more properties. Nanoparticle fillers are those where at least one dimension is in the 1–10 nm range, but fibers and nanoparticle fillers are outside of the scope of this entry. A particulate-filled polymer composite is an admixture of a polymer matrix with particulate fillers.

## Introduction

Fillers have been incorporated into all polymer types, thermoplastics, elastomers, and thermosets, from the very beginning. Indeed, it is true to say that the development of many of today’s polymers would not have been possible without them. One of the original purposes was simply to reduce cost, especially in the early days when polymers were relatively expensive. Today, as polymers have become more of a commodity and less expensive, addition of fillers to reduce cost is less important and other reasons have come to the fore. Typically, the filler and the polymer have very different properties, and by judicious blending of the two, one can achieve a spectrum of materials with properties intermediate between those of the two ingredients. If one looks at the commercial polymers on the market, there are performance gaps between them, incorporation of fillers can bridge such gaps and extend performance capabilities to address a much broader market. In some cases, such as elastomers, particulate fillers are essential to develop acceptable properties for most applications.

In selecting particulate fillers, one must first understand the performance criteria for the material in use and then select or create a material that matches those criteria at a competitive cost. There is no ideal polymer or filler; so the skill is to blend ingredients to maximize certain properties and mitigate against loss of others. In essence, the winner is the one able to make the best compromises by understanding materials better than their competitor. There are at least 30 properties that can be altered by filler addition so you may be adding a filler to increase modulus but discover that most of the other properties are changed, possibly detrimentally, even though that was not the intent. Burditt (1991) listed 21 reasons that fillers are added to polymers. His list, with some modifications and updating, is:

Reduce cost
Increase heat resistance
Increase stiffness
Reduce creep
Reduce shrinkage during polymerization or molding
Reduce cure exotherm
Change electrical properties
Reduce flammability
Modify specific gravity (density)
Modify flow
Increase compressive strength
Increase lubricity
Improve abrasion resistance
Decrease permeability (today we could add also increase permeability)
Improve tensile and flex strengths
Improve impact strength
Improve dimensional stability
Improve thermal conductivity
Improve processability
Improve moisture resistance
Increase degradability (e.g., starch filler added to produce biodegradable film)
Modify adhesion, either to itself (e.g., antiblocking) or to other substrates
Change appearance, opacity, and gloss

It is important to remember that not all fillers improve all of the above properties and that some can actually be decreased by certain fillers.

## The Main Important Characteristics of Particulate Fillers

### Cost

The cost of fillers varies enormously, with the spread from the crudest clays and carbonates to specialist synthetic types being over 100-fold. Large price variations are even experienced within one filler type, such as calcium carbonate, depending on factors such as color, purity, particle size and shape, and surface treatment. Transportation costs can also be very significant for the lowest-cost fillers and may well determine the choice of filler type and supplier. With increasing globalization, uniformity of filler grades across the world is becoming an important issue.

In considering potential cost savings from use of fillers, one must always bear in mind that they are generally considerably denser (two- to threefold) than the host polymer. Filler prices are generally quoted on a weight basis, but most applications are based on volume, and hence a significant correction has to be performed for a fair comparison to be made. A simplified view of the relative volume costs of fillers and polymers is presented in Table 1.

Factors other than the raw material cost also have to be taken into account in assessing whether cost savings will be obtained. One of the most important is any additional processing cost incurred. In many cases, the use of fillers increases processing costs due to the need for different equipment and higher energy costs and/or lower throughput. On the other hand, their use can give better heat transfer, speeding up cooling, and reducing cycle times. Any extra cost is much reduced with polymers that already have to be processed (e.g., to add curatives and stabilizers), and it is no accident that fillers are most widely used in such polymers (elastomers, thermosets, and PVC).

Filler effects on other ingredients, such as antioxidants and curatives, can also be significant. One would generally expect a reduction in the use of these per unit volume when filler is replacing some polymer. On the other hand, some fillers can negatively impact on polymer stability and also deactivate antioxidants and curatives, leading to the opposite effect. As with so much in this field, one has to consider each case on its own merits.

**Table 1** Approximate relative volume costs of some common polymers and polymer grade particulate fillers (Note: commodity polymer and some filler prices are very much influenced by the price of oil so the above relationships must be treated with caution)

| Polymer or filler | Approximate volume cost |
|---|---|
| Common thermoplastics and elastomers | 0.9 –1.5 |
| Common thermosets | 1.4 –2.6 |
| Ground carbonates | 0.15–0.3 |
| Coated ground carbonates | 0.25–0.5 |
| Talcs | 1.0 –1.5 |
| Precipitated silicas | 2.0 –3.0 |
| Carbon blacks | 1.6 –2.2 |

Despite the above, there are still significant areas where fillers are used principally because they give useful cost savings. These will particularly be where suitable compounding is already taking place to introduce other additives, as is the case with polyvinyl chloride (PVC), elastomers, and most thermosets, and where relatively expensive polymers, such as polyamides, are being used.

## Chemical Composition

In most cases, the actual chemical composition of the filler is not of direct importance, as long as it is inert, insoluble, nontoxic, and sufficiently thermally stable. The presence of deleterious impurities is often of more concern. These vary with the application but are usually those that can affect color (e.g., humates, iron compounds), equipment wear (e.g., quartz), polymer stability (many metal compounds), electrical properties (soluble materials), and toxicity (crystalline silicas, asbestos). In some cases, even a few parts per million (ppm) of these impurities can be detrimental.

## Surface Chemistry

While the bulk chemical composition is of little direct importance, surface chemical composition is very relevant for a number of reasons.

First and foremost is its effect on the strength of interaction between the particles and the polymer matrix. This interaction is critical to many composite properties and can vary from strong to weak. While strong interaction is often best, some applications, such as microporous films, require weak interaction. Chemical treatments such as coupling agents and fatty acids are often used to alter the amount of interaction.

Carbon black is the main example of a filler whose own surface is able to interact strongly with most polymer types and where little use is made of surface treatments. Fumed and precipitated silicas are examples of inorganics where the surface is able to interact strongly with some polymers, notably silicone elastomers.

The surface of most mineral fillers leads to weak interaction with nonpolar polymers, especially when polar additives, such as many processing aids and dispersants, are present. These are often more strongly attracted to the filler than the polymer is and collect at and weaken the interface. In these cases, the interaction can often be boosted by the use of coupling agents (chemicals which can react with both the filler surface and the polymer). In some cases, noncoupling treatments are used, such as fatty acids, and these reduce the already weak interaction. Polar polymers such as polyamides and polyesters are able to interact strongly with many filler surfaces, especially carbonates. Even so, coupling agents still help in many cases, especially with siliceous fillers. As a very rough rule of thumb, where strong interaction is required, one usually finds siliceous fillers with silane coupling agents. Where low interaction is required, one usually finds carbonate fillers with fatty acids.

Deleterious impurities are often concentrated at the filler surface and can have a disproportionate effect compared to their bulk concentration on composite properties such as water absorption and polymer stability. This is particularly true for high surface area fillers.

Untreated filler surfaces can also adsorb important additives such as processing aids, stabilizers, and curatives. Such interactions result in removal of the additive from the bulk matrix and deactivation of their desired effects. Additive adsorption can be countered using simple filler surface treatments such as fatty acids. When adsorbed, the latter occupies the sites on the filler surface that would otherwise have attracted and deactivated polar additives in the formulation.

## Specific Gravity (Density)

The more common mineral fillers have densities in the range 1.5–3.0 g cm$^{-3}$, whereas commodity plastics tend to lie in range 0.9–1.4 g cm$^{-3}$, meaning that fillers usually act to increase density. It seems obvious that the density of the composite would be proportional to the weight percentage of each component, but that is not the case. Plotting density versus weight percentage of filler leads to curves (Fig. 1), whereas plots made against volume percentage filler are linear. An extreme illustration of this is the use of air as a filler. Adding just one weight percent of air leads to a density decrease around 50% with a radical change in properties simply because half of the polymer has now been replaced. This illustrates the importance of thinking in terms of volume percentages.

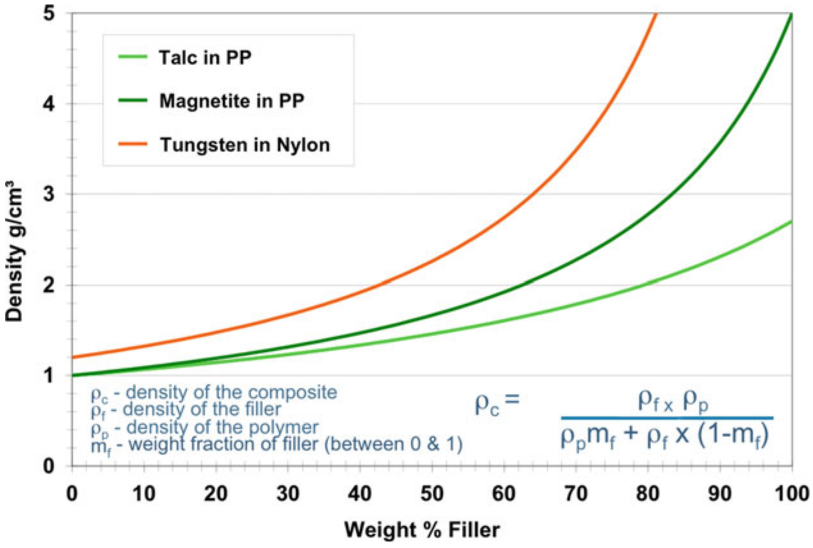


**Fig. 1** Dependence of density on filler concentration

**Table 2** Approximate Mohs' hardness of common fillers (because of the mineralogical origin of the scale, several common mineral fillers are reference points with exact numbers)

| Filler | Mohs' hardness | Comments |
|---|---|---|
| Talc | 1.0 | The softest mineral known |
| Gypsum | 2.0 | $CaSO_4.2H_2O$ |
| Kaolin | 2.5–3.0 | Varies with purity |
| Aluminum hydroxide (ATH) | ~3.0 | Flame retardant filler $Al(OH)_3$ |
| Calcite | 3.0 | $CaCO_3$ |
| Wollastonite | ~4.5 | $CaSiO_3$ |
| Quartz | 7.0 | $SiO_2$ |

There are some instances where the effects of fillers on specific gravity are exploited. Typical examples are the use of high density fillers in sound deadening compositions (e.g., magnetite or barium sulfate) and of lightweight fillers (e.g., hollow glass beads) in buoyancy aids.

## Hardness

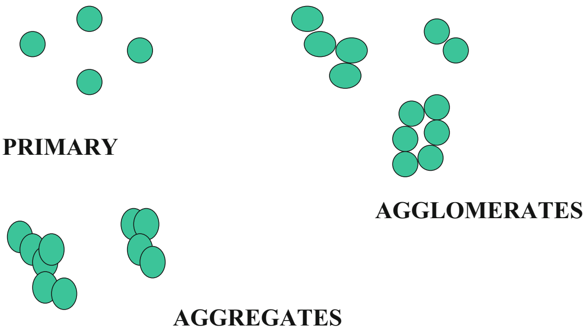
The hardness of minerals is usually measured according to the Mohs' scale, as used in mineralogy. This scale is based on the ability of one mineral to scratch another and goes from talc (softest) with a hardness of 1 to diamond with a hardness of 10. The scale is approximately logarithmic and so small, numerical differences can have a significant impact.

The hardness of the main fillers is given in Table 2. Most commonly used fillers have a Mohs' hardness below 4. The hardness of fillers is important to polymer processing, where soft fillers are preferred to minimize equipment wear and the accompanying pickup of metal contamination. The harder fillers can also lead to undesirable degradation of fiber length when used in conjunction with glass fiber reinforcements. Hard fillers, such as crystalline silicas, are used when high abrasion resistance is required, particularly in thermosets. Solid surfaces for use in kitchen sinks are a good example.

## Morphology (Particle Size and Shape)

The size and shape of filler particles are critical factors in the processing and final properties of particulate fillers. Although they seem to be simple concepts, their adequate measurement and description provide significant challenges. One reason for this is that except in rare instances, the particles exhibit a wide range of size and shape within any given sample. Another is the effect that composite processing can have in significantly altering the particle size and shape from that in the original powder on which most measurements are usually based.

**Fig. 2** The concept of primary particles, agglomerates, and aggregates (with permission of Smithers Rapra)



The terminology used can also give rise to some confusion; this is particularly noted with the description of particle types as primary particles, aggregates, and agglomerates. The term primary particle normally refers to the smallest unit that the filler can be sensibly thought to be composed of. With very fine fillers, these primary particles are often strongly attached to each other, usually by some intergrowth or fusion, and these assemblies of particles are referred to as aggregates. Both primary particles and aggregates can then form weaker structures which are easily broken down and these are referred to as agglomerates. (Care must be exercised here, as the terms aggregate and agglomerate are sometimes reversed in the literature.) These concepts are illustrated in Fig. 2.

The larger size solid glass sphere fillers provide an example of a simple type which only consists of primary particles (and probably very weak agglomerates). Carbon blacks provide a good example of the two extremes. The larger thermal blacks are essentially composed of single, nonfused particles. The furnace blacks, on the other hand, show various levels of strong aggregation caused by partial fusion (this is discussed further in the section dealing with shape).

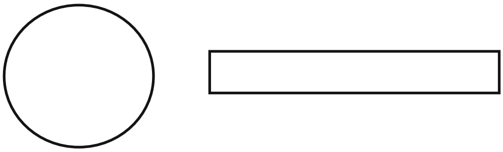
As briefly mentioned above, processing can affect the size of particles. This is especially true where aggregates are involved (such as can occur with high-structure carbon blacks). The degree to which these are broken down and dispersed will depend on their strength relative to the processing conditions. Hollow glass spheres provide an extreme example. In some processing, the spheres survive intact and can be regarded as primary particles, while in others they can be broken down into fragments.

The measurement and application of size and shape are discussed in more detail below.

## Particle Size

This is the most widely used parameter for filler morphology but is subject to a lot of misunderstanding and needs careful explanation. Particle size is usually measured in microns ($10^{-6}$ of a meter), and despite the fact that on its own, it is fairly meaningless, many data sheets give this as a single number usually called the average particle size. To make some attempt at allowing for irregular sizes, this number is often what is

**Fig. 3** How two different shapes can have the same ESD (reproduced with permission of Smithers Rapra)



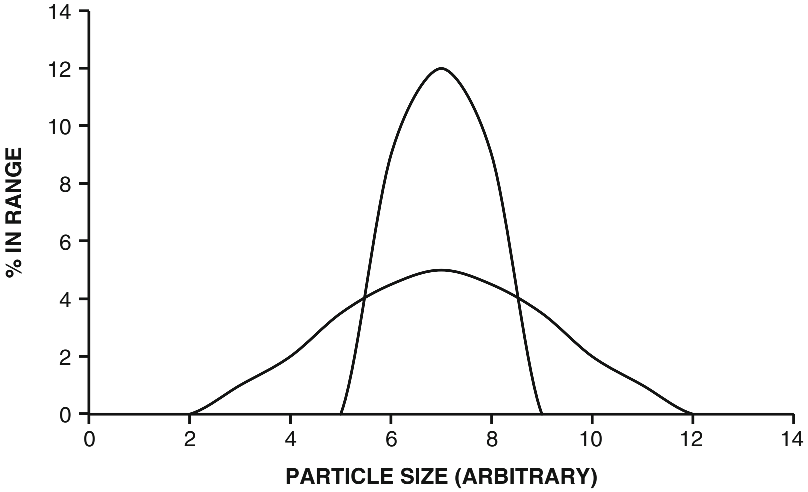


**Fig. 4** How different particle size distributions can have the same average particle size (reproduced with permission of Smithers Rapra)

known as the equivalent spherical diameter (ESD), which is the diameter of a sphere having the same volume as that of the particle. As shown in Fig. 3, the same ESD can be derived for a plate and a sphere, although they clearly have different sizes.

The average can also be determined by weight or by number, with the by weight method being the commonest and giving the larger value. The term D50 is often used for the average, and this is the size with 50% of the particles above and 50% below (usually by weight, but can be by number if specified). As shown in Fig. 4, markedly different size distributions can give the same average value. Sometimes an indication of the width of the size distribution is also given, usually by providing a top and bottom size value. The top size is frequently given as a value such as D98, which means that 98% of the particles are below this number. The bottom size, on the other hand, is usually given by the percent less than a certain fixed value. The fixed value is often a convenient sieve size.

## Specific Surface Area (SSA)

An alternative measure of particle size is provided by the SSA, which is the area of surface present per unit weight of the filler and usually given the units $m^2g^{-1}$.

The SSA is obviously related to the particle size distribution of the filler and with materials of the same density and shape, a higher specific surface area means a smaller particle size.

An indirect method for expressing particle size, SSA, has some advantages, especially for very small particles. Fillers in common use have SSAs ranging from under 1 to more than 200 $m^2g^{-1}$. In some cases, the SSA is calculated from the ESD particle size information, but it is more usually measured by adsorption methods, such as nitrogen or dye adsorption. The most rigorous method is nitrogen adsorption using the BET (Brunauer, Emmett, Teller) procedure. This is a very reproducible method, but requires relatively expensive equipment not always possessed by filler producers. As nitrogen is a very small molecule, it can access surface features that may not be accessible to polymer molecules and thus give a falsely high result for practical purposes. Dye adsorption uses much larger molecules adsorbed from solution and is less expensive to carry out and can come closer to the value relevant in polymer composites. The carbon black industry uses a surfactant (CTAB, cetyltrimethylammonium bromide) for this purpose.

## Particle Shape

Shape is an important factor in the use of fillers in polymers, affecting processing and composite properties. Typical particulate filler shapes are illustrated in Fig. 5. Anisotropy, or aspect ratio, is particularly important, being valuable in improving factors such as stiffness and heat distortion temperature. Despite this, shape is poorly described in the literature and filler specifications. This is due to the difficulty of carrying out meaningful measurements, especially as aspect ratio is often significantly affected (reduced) during processing operations.

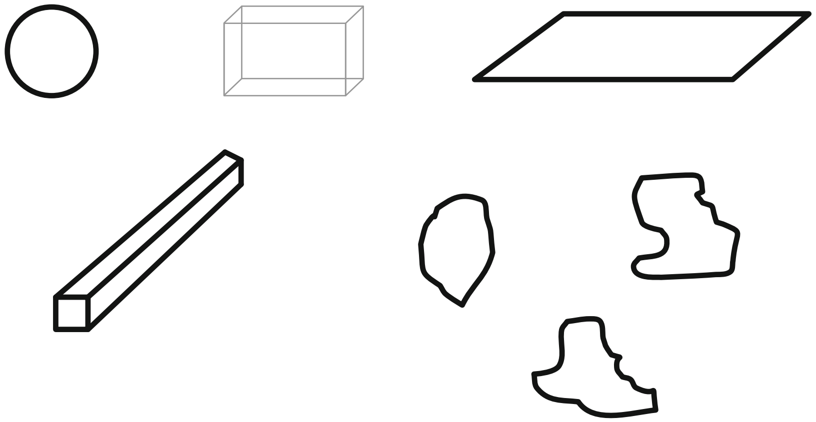


**Fig. 5** Various filler particle shapes (reproduced with permission of Smithers Rapra)

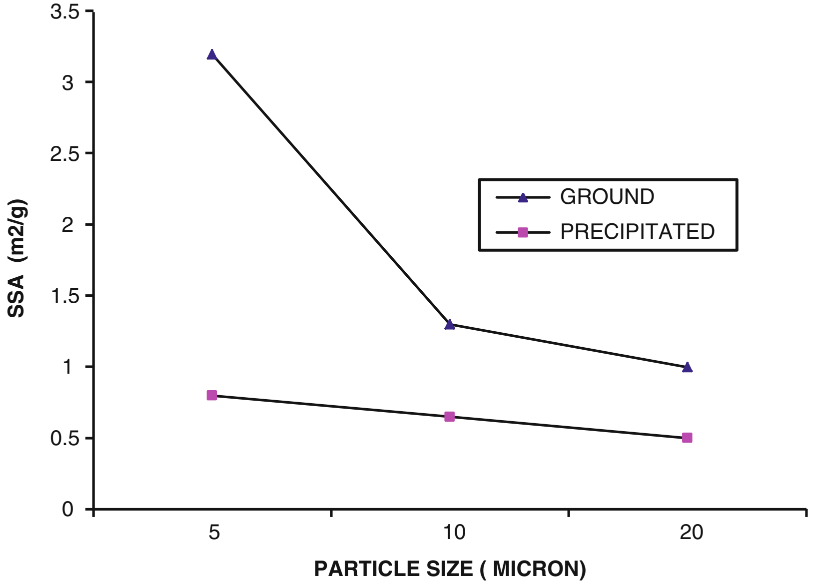


**Fig. 6** Variation of SSA with particle size for two types of aluminum hydroxide

The difference in the measured SSA from that calculated from the size distribution, assuming a spherical shape, can sometimes be used as an indication of anisotropy or porosity. This is illustrated by the data in Fig. 6, where the SSA of various grades of ATH is plotted against particle size. The ground materials, which are known to be more platy than the precipitated, are seen to have a higher SSA, especially at the smaller sizes, where the milling process leads to the biggest increase in aspect ratio.

For most polymer applications, the aspect ratio is the most important shape property. This is generally defined as the width divided by the height where the width is the larger value. When dealing with particles, it can be regarded as the ratio of the largest to the smallest dimension and has a big influence on processing and many important composite properties. Particulate fillers can be described as follows: approximately isotropic, platy, and acicular as shown in the diagram. Both the platy and acicular ones have significant aspect ratios. Care must be taken to differentiate the acicular particulates from true fibers, although there can be some overlap. The aspect ratio of acicular fillers will be no more than 20:1, while fibers will generally be much greater. The isotropic ones can be further subdivided into spherical or irregular shapes, with truly spherical particles (e.g., glass beads) being the ultimate. Most filler particles have low-aspect ratio, for example, calcium carbonate, dolomite, barium sulfate, or silicas, which tend to have round or blocky morphology. Those with higher ratios include wollastonite (acicular), talc (platy), mica (platy), and kaolin (platy). The type selected will depend

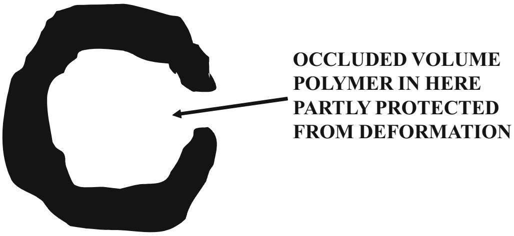


**Fig. 7** The concept of carbon black structure

upon the desired properties in the composite and the trade-off between different properties.

A further shape factor known as structure is recognized as being important for the very fine synthetic fillers (principally carbon black synthetic silicas) used in elastomer applications. These fillers consist of extremely small primary particles, partly fused together into larger structures (aggregates) which survive into the final compound. Because of their complex shapes, these aggregates can shield some of the polymer from deformation, and this can be usefully exploited to alter the balance of properties. This concept of structure is outlined in Fig. 7.

## Particle Packing

In many composite applications, it is necessary to achieve a high filler loading, either to minimize cost or to maximize some property that the filler provides. In these cases, the ability of the particles to pack together with minimum free interparticle space is the controlling factor. This packing ability is determined by the size and shape distribution of the particles.

The concept of maximum packing fraction (MPF or $P_f$) is important and is the maximum amount of filler that can be incorporated into a composite before particle-particle contact becomes inevitable. As a rule of thumb, it is usually accepted that (except for special cases such as electrical conductivity where percolation is required) it is best to work below 90% of the MPF.

The commonest measure related to MPF is the oil absorption (e.g., ASTM D-281) value of a filler. This can be measured using a simple test and, although subject to many complications, can, when carefully applied, be a very useful guide and is frequently seen in product data sheets and specifications. The measurement procedure is based on determining the amount of a selected oil that is needed to just form a continuous paste with the filler under standardized mixing conditions and is usually quoted as milliliters or grams of oil per 100 g of filler. The following equation can be used to convert from oil adsorption to the filler packing fraction in the final paste:

$$P_f = \frac{100}{100 + OA} \times \quad 100\% \ \ w/w$$

where OA is the oil absorption expressed in g/100 g.

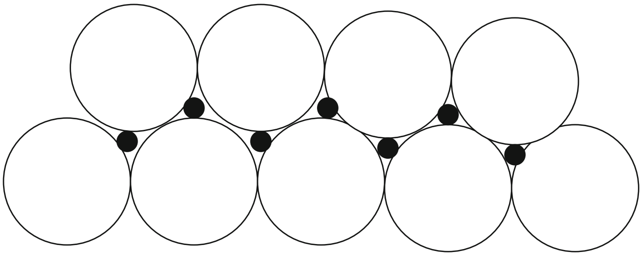


**Fig. 8** Use of the particle packing principle to maximize filler loading (reproduced with permission of Smithers Rapra)

The choice of oil is important, as its wetting ability for the filler will determine how easily the particles disperse in the test, and the oil should be chosen to mimic the polymer system if possible. For plasticized PVC applications, the plasticizer is often used as the oil and the value may be described as plasticizer demand.

Where very high filler loadings are needed, then special size (and sometimes shape) distributions are used. This is usually done by having a size distribution with just enough of the correctly sized fine particles to fit into the interstitial spaces between the larger ones. A simple example of this is given in Fig. 8. An excellent description of particle packing theory has been given by German (1989).

The relevance of shape depends largely on the polymer type and application. Low-aspect-ratio fillers are ubiquitous and widely used in all polymer types. They can usually be added at higher loadings and have less deleterious effects on processing than high-aspect-ratio fillers. Platy and acicular fillers are mainly used when their shapes support a key property in that application.

## Thermal Properties

The principal thermal properties of importance in particulate-filled polymer composites are specific heat, thermal conductivity, coefficient of expansion, and stability. Thermal properties generally vary smoothly with the volume percentage of filler added and do not show the marked percolation effect seen with electrical conductivity (see next section).

## Specific Heat

Specific heat capacity is the amount of energy needed to heat a given amount of material. Most books erroneously state that fillers help in this regard by having lower specific heat capacity than polymers. The misunderstanding comes from the units used. The specific heat capacity per unit weight of polymers is indeed ~3 times higher than that for minerals. However, the density of minerals is also ~3× higher. So it turns out that the specific heat capacity per unit volume is the same, and fillers do not help lower the amount of energy needed to heat and cool plastics. In fact, as a rule of thumb, it is known that the volume-specific heat capacity of all solid materials is about the same.

## Thermal Conductivity and Diffusivity

Thermal conductivity is a measure of how well a given material conducts heat. While the related property of thermal diffusivity takes the specific heat and specific gravity of the material into account and is a better guide to how well heat moves through it, most composite literature uses the term thermal conductivity. Many fillers are minerals and they have much higher volume thermal conductivities than polymers. This helps in processing because one can heat and cool the melt more quickly. Parts can be made faster and therefore more cheaply. Specialty fillers are used when high thermal conductivity is paramount, for example, in heat sinks for laptop computers where enormous amounts of heat must be managed in a confined space. One would imagine that the higher the thermal conductivity of the filler, the more effective it would be at increasing the thermal conductivity of the composite. This, however, turns out not to be the only factor; the elastic modulus of a composite also has a significant effect, and fillers that significantly increase this can perform better than expected.

## Coefficient of Thermal Expansion

Coefficient of thermal expansion (CTE) simply means the amount a material expands (or contracts) when heated. Polymers generally have high CTE and metals have much lower values. The coefficients of thermal expansion of most mineral fillers are also considerably less than those of polymers. Thus, mineral incorporation can significantly reduce the coefficient of expansion of a composite material. This effect is usually beneficial, reducing shrinkage when a part cools after molding. On the other hand, high-aspect-ratio fillers, especially when aligned by processing, will often give rise to anisotropic shrinkage, leading to problems of warpage. Some specialty fillers have been designed to have very low coefficients of expansion (e.g., some glass ceramics). Negative coefficients are also possible (e.g., zirconium tungstate and some zeolites).

## Thermal Stability

Particulate fillers need to be stable at the temperature reached during processing of the composites; this can be as high as 350 °C. While most fillers are stable at much higher temperatures, some can release water below this temperature, which can cause problems such as porosity in extrusions and moldings. This water can also come from impurities. Some polymers, notably condensation types, such as polyesters and polyamides are very susceptible to hydrolytic degradation during high temperature processing, and in such cases it is prudent to dry any fillers just before use.

Flame retardant fillers are a notable exception, as their effectiveness depends on an endothermic decomposition, accompanied by water release, and this needs to occur at or close to the temperature at which the polymer itself begins to decompose and release flammable gasses. These fillers decompose at temperatures in the range 200–350 °C, and therefore, processing conditions need to be carefully controlled.

## Electrical Properties

Filled polymers are used in applications requiring both electrical insulation (e.g., cable coating) and electrical conductivity. Their effects on the electrical properties of composites can thus be very important. The properties of most interest are conductivity and dielectric properties.

### Conductivity

Most particulate fillers have low electrical conductivity and this is good where insulation properties of a composite are being exploited. In this case, the most concern is over the presence of trace amounts of water-soluble ionic impurities, which can markedly increase composite conductivity under humid conditions, even if only present in trace amounts. Sodium chloride is a particular example. Tests on the filler, such as conductivity of aqueous extract, are often used for quality control purposes when this is an issue.

At the other end of the scale, there are a range of applications where fillers are used to make a polymer electrically conducting (antistatic and EMF shielding are examples). Carbon blacks are the predominant particulate (as opposed to fibrous) fillers used here. Others include metals, graphite, and doped zinc and tin oxides.

Unlike most other properties, electrical conductivity does not vary smoothly with increased filler content. Conductivity is dominated by percolation meaning that adding conductive fillers has little effect until enough is present to form a continuous particle pathway through the material. This concentration is known as the percolation threshold and is accompanied by a dramatic increase in the electrical conductivity of the composite. This is illustrated in Fig. 9. For mechanical properties, good dispersion is usually the goal, but for electrical conductivity, it can be counterproductive (indeed, electrical conductivity is used as a measure of dispersion quality in carbon black-filled elastomers, good dispersion being indicated by low conductivity). Perfectly separated particles cannot percolate so conductivity remains low. Instead, the goal is to have a controlled amount of agglomeration and to be able to keep it exactly the same from lot to lot. Particle size and shape have a big effect on the volume fraction at which the percolation starts, with smaller fillers and more anisotropic particles leading to lower percolation thresholds.

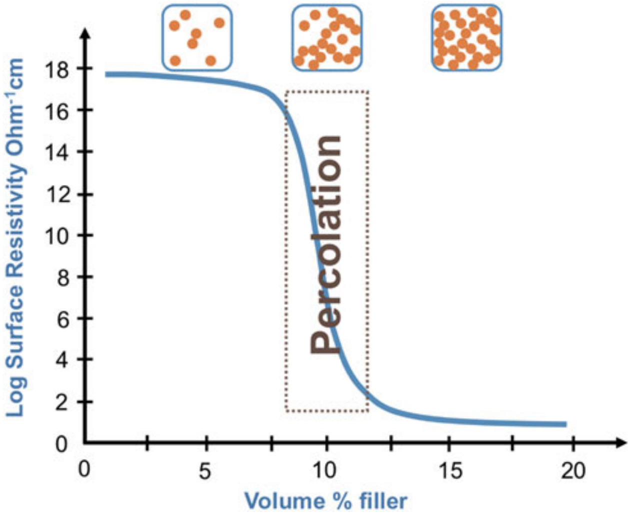


**Fig. 9** Percolation of electrically conductive particles

## Optical Properties

Color and refractive index are the most important optical properties for fillers. Most filler applications require them to be colorless, or white, but traces of impurities can have significant deleterious effects on this.

The comparative refractive indices of fillers and polymers play a very important role in the appearance of composites, controlling whether filler effects are due to scattering or transmission of incident light. When the refractive index difference is large, then scattering dominates (the extreme example is for a filler or polymer powder in air, where the difference is great and the particles are seen by scattered light). As the refractive index difference reduces, so scattering decreases and transmission through the filler becomes more important, until, when they are identical, there is no scattering, just transmission. All of this has a profound effect on the appearance of the composite, both in terms of its transparency and color. When a filler is seen by scattered light, then its bulk color dominates and it can appear quite white; when it is by transmitted light, then small levels of impurities, such as iron or organics, can give very dark colors. The refractive indices of most common fillers and commodity polymers are similar, and thus, transmission rather than scattering dominates in composites. Surprisingly dark colors can sometimes be found from fillers which look quite white, when viewed in air. One way of checking for this, without having to make a composite, is to make a paste of the filler in oil with similar refractive index to the polymer.

The scattering power also depends on the filler particle size, going through a maximum at a certain size. This is usually quoted as being when the particle size is about one-third of the wavelength of the light; but this is an oversimplification.

The position of maximum scattering depends on the difference in refractive index between the filler and polymer, moving to larger particle sizes as the difference in refractive index between filler and polymer deceases. The one-third rule applies to situations where the refractive index difference is large, such as with titanium dioxide pigments. With most fillers, the size of maximum scattering is actually several times the wavelength of the light.

A further complication is that many fillers have more than one refractive index, and this can also give rise to complex and undesirable interference effects. Such effects are absent with amorphous fillers, such as glass and precipitated silica, and these are used when highest clarity is required.

In addition to their intrinsic optical effects, fillers can have an influence on the appearance of a composite for other reasons. One of these is gloss, which depends largely on the surface roughness of the composite. Larger filler particles or agglomerates of smaller ones can give rise to an irregular surface and thus low gloss, especially as measured at low angles, for example, 20°. Therefore, anything that can be done to minimize particle size and optimize dispersion will improve gloss. So, where this is important, one would select a finer grade of filler, use a dispersant, and set up processing parameters for high dispersion. Sometimes low gloss is desirable and large or poorly dispersed fillers may be added to deluster the surface. Sidings for houses or car dashboards are examples of surfaces that need to have low gloss.

## Use of Particulate Fillers in Polymer Composites

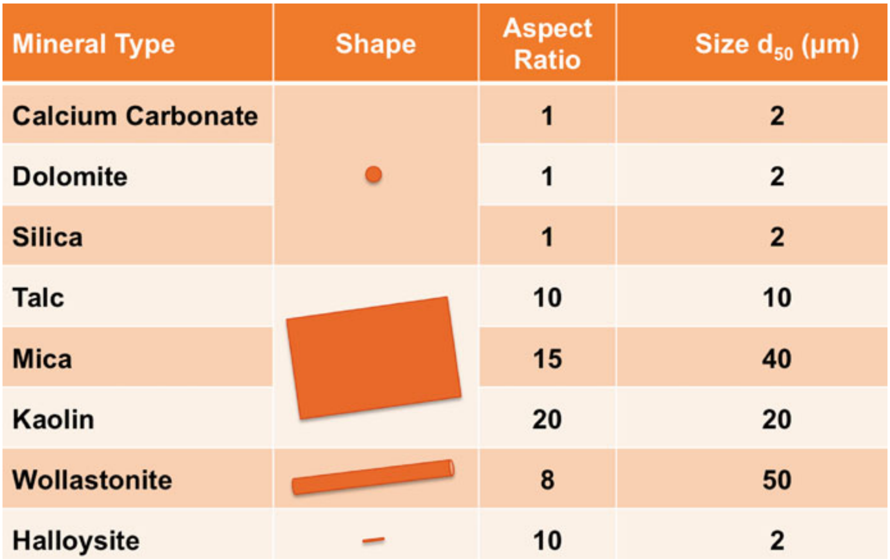
A brief description of the choice of fillers in the main polymer types follows. More details can be found in the separate chapters dealing with the use of fillers in elastomers, thermoplastics, and thermosets.

## Thermoplastics

The size and shape properties of the main fillers used in thermoplastics are given in Fig. 10.

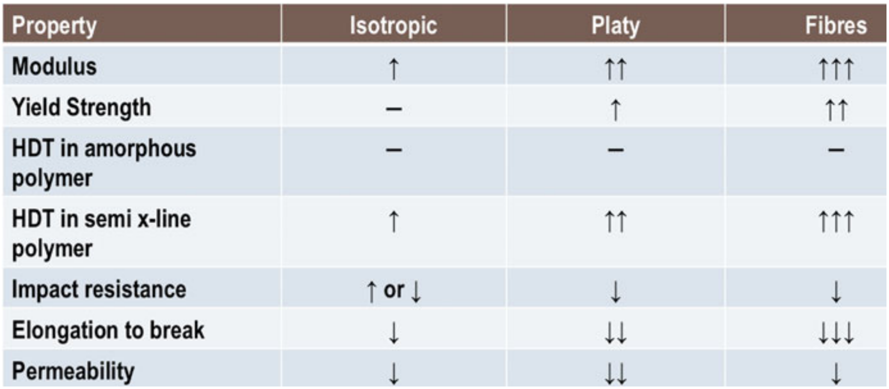
The principal fillers used are the low-aspect-ratio calcium carbonates and, where flame retardancy is required, aluminum or magnesium hydroxide. For most purposes, average particle size is in the range 1–5 μm, with minimal amounts over 50 μm and below 0.2 μm.

Two distinctions must be made when considering the effects of fillers in this class of polymer. The first is between amorphous and semicrystalline types (e.g., polystyrene and polyolefins, respectively). The second is between conventional- and impact-modified grades (often these contain a dispersed rubber phase or some copolymer as the impact modifier). Polypropylene is a good example of this for semicrystalline types; there are homopolymer, copolymer, and rubber-modified grades with subtle differences in filler effects in these various forms. Where the



| Mineral Type | Shape | Aspect Ratio | Size $d_{50}$ (µm) |
|---|---|---|---|
| Calcium Carbonate | ● | 1 | 2 |
| Dolomite | | 1 | 2 |
| Silica | | 1 | 2 |
| Talc | ■ | 10 | 10 |
| Mica | | 15 | 40 |
| Kaolin | | 20 | 20 |
| Wollastonite | ▬ | 8 | 50 |
| Halloysite | – | 10 | 2 |

**Fig. 10** Size and shape of the main filler types used in thermoplastics



| Property | Isotropic | Platy | Fibres |
|---|---|---|---|
| Modulus | ↑ | ↑↑ | ↑↑↑ |
| Yield Strength | – | ↑ | ↑↑ |
| HDT in amorphous polymer | – | – | – |
| HDT in semi x-line polymer | ↑ | ↑↑ | ↑↑↑ |
| Impact resistance | ↑ or ↓ | ↓ | ↓ |
| Elongation to break | ↓ | ↓↓ | ↓↓↓ |
| Permeability | ↓ | ↓↓ | ↓ |

**Fig. 11** The effect of filler shape on key properties of thermoplastics

polymer has inclusions, such as crystallites and/or rubber phase, the filler is often only found in the amorphous regions of the thermoplastic, and this significantly increases its effective volume fraction. In some special cases, the filler can also be present in the elastomer phase.

Shape, as well as size, is important, and a summary of the effects of filler shape on the key properties of thermoplastic composites is presented in Fig. 11.

Low-aspect-ratio fillers are used when it is necessary to retain good impact resistance. Higher aspect ratio fillers are more effective at reinforcing, that is, increasing strength and modulus. However, higher aspect ratio fillers can be very deleterious to impact resistance. This is a prime example of what composite design is all about, namely, making compromises.

Because they soften with heat, a property known as heat distortion temperature or heat deflection temperature (HDT) is often important for composites based on thermoplastics. This is a measure of the temperature at which the composite deforms under a given load. High-aspect-ratio fillers are preferred for increasing HDT, and this is related to their ability to improve modulus, especially at elevated temperature. It is not widely appreciated that HDT is not meaningfully improved by adding fillers to amorphous plastics but is very much improved in semicrystalline polymers. (HDT can be determined by the methods in ASTM D648, another test used for the same purpose is the Vicat softening point.)

It is often assumed that high-aspect-ratio fillers are intrinsically better than low-aspect-ratio types, but this is because their advantages are overestimated and their disadvantages underrepresented. When one sees data for reinforcement using mica, wollastonite, talc, and kaolin, the modulus and strength improvements are impressive. However, the data from tensile testing are unrealistically positive. When tensile test bars are injection molded, these fillers orientate in the direction of the melt flow. When the bars are tested, the reinforcement is optimal in the test direction. If the same bars were tested perpendicular to the flow direction, then far inferior results would be recorded. In the perpendicular directions, strength and modulus are equivalent to the values obtained using round or blocky shaped particles. In many commercial applications, it would be more realistic to find particles randomly orientated, and in that case the modulus and strength gain from using such fillers may be substantially less than half that for fully aligned particles.

There are other issues as well. For instance, high-aspect-ratio fillers are broken down by handling, extrusion, and injection molding. This is significant and much of the potential reinforcement performance can be lost. Furthermore, they are broken down by recycling so the properties worsen with every recycling pass. In contrast, low-aspect-ratio fillers like calcium carbonate, silica, and dolomite can be recycled multiple times without deterioration of properties. Aligned anisotropic particles induce warpage (differential shrinkage). Lastly, anisotropic fillers lead to weld lines or knit lines in molded parts. When two flow fronts meet, the particles misalign and create a weakened area. This can dramatically reduce the strength of the part.

Barrier properties are important in some applications, especially in packaging films and microporous membranes. Mineral fillers are impermeable so they can be added to polymers in order to reduce the overall permeability of the plastic to gasses and fluids. However, most fillers are not very effective in this regard. For example, adding 10 wt% calcium carbonate equates to only ~3 vol.%. So only 3% of the permeable plastic has been replaced with impermeable material. Even at 60 wt% filler, only ~20% of the plastic has been replaced. The so-called tortuosity effect is far more significant than simple volume replacement. When platy fillers are used and aligned in the same direction, they can provide a very good barrier because the permeant molecules are forced to travel around the long dimension of each plate. So the material behaves as if it were much thicker. This is illustrated in Fig. 12.

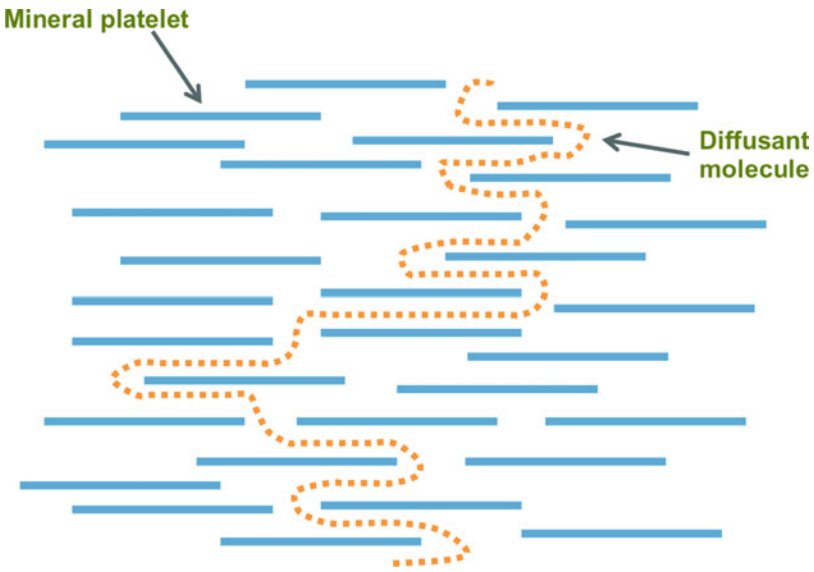


**Fig. 12** Reduction in permeability due to tortuosity effects of aligned platy particles

The low permeability of nanocomposites made from platy fillers is attributed to tortuosity. That is important but it has been shown to be only one of two important factors. The other is the interphase which is a layer of adsorbed polymer surrounding each filler particle. The polymer in the interphase has constricted mobility and reduced free volume and is thus less permeable. Fine particles have high surface area, meaning that a significant portion of the whole material is interphase with a concomitant reduction in permeability.

Fillers can also help if they nucleate crystal growth in the polymer and thereby increase the overall degree of crystallinity. Polymer crystals are virtually impermeable, whereas the amorphous phase is permeable; so more crystallinity means better barrier properties.

The effect of fillers on barrier properties depends very much upon whether the filler is wetted by the polymer. When properly wetted, particulate fillers decrease permeability; however, if there is a void around each particle, caused by poor wetting, a pathway for fast diffusion is provided, leading to a decrease in barrier properties. This is perfectly illustrated by the data in Table 3. Permeability actually increased with increasing levels of uncoated filler with poor wetting, but decreased when a surface treatment was applied. Factors that encourage wetting are predrying the filler, longer residence time, venting, and using a surface modifier to improve compatibility at the interphase.

It should be noted that improved barrier properties are not always the target. A huge application for fillers is in breathable films. Stearic acid-treated calcium carbonate is added to polypropylene film. Then the film is stretched to intentionally debond the filler from the surrounding polymer to leave voids around the particles

**Table 3** How permeability depends upon filler wetting (Steingiser et al. 1978)

| Filler type | Volume % filler | Permeability × $10^{-17}$ mol $m^{-1}$ $s^{-1}$ $Pa^{-1}$ |
|---|---|---|
| None | 0 | 1.3 |
| Calcium carbonate | 15 | 2.6 |
| Calcium carbonate | 25 | 5.3 |
| Surface-treated calcium carbonate | 25 | 0.4 |

allowing easy passage of water vapor. The stearic acid is used because it decreases the adhesion to the matrix polymer and thereby facilitates debonding. It also helps dispersion; it is vital to avoid large particles or agglomerates when making films.

## Elastomers

Elastomers are a large market for particulate fillers, where they are essential in making the polymer fit for use in many applications. The majority of the fillers used are very small particle, high surface area types, such as the carbon blacks.

Elastomers are mainly used in dynamic applications with repeated deformation and recovery and have a number of property requirements specific to this type of use. A key example of this is their use in tires. Three properties of the particles are recognized as being important. These are particle size, shape (especially a feature known as structure), and polymer/filler interaction. These have been extensively studied and the general trends for these properties are presented in Table 4.

While conventional filler shape properties such as aspect ratio have some importance, a property referred to as persistent structure (often just as structure) has particular importance in fillers used in elastomer applications and features is included in the table. This permanent (or persistent) structure is related strongly to aggregation and shape of the particles and in particular to their ability to trap or shield polymer from deformation. This trapped polymer does not experience the full stress field in the matrix, and in some ways this increases the effective volume fraction of the filler. This structure is a property of many types of filler, but is usually used with reference to carbon black, where it is particularly marked. Permanent structure is usually measured by a simple oil absorption test, with a high value indicating high structure. Oil absorption is usually included in the specification of fillers to be used in elastomers.

In addition, one may come across another type of structure, especially with reference to tire tread applications. This is known as transient structure and is the formation, at rest, of a network of interacting filler particles, which can be broken down during deformation. It is usually referred to in connection with carbon blacks and synthetic silicas.

The molecular architecture of elastomers means that they have high free volumes and high gas permeability. This is an important issue in applications such as tire inner tubes and liners, where a gas pressure has to be maintained. Until recently, this has

**Table 4** The direction and magnitude of the effects of the main filler properties on those of filled elastomers (adapted from Boonstra (1975))

| | Filler property | | | |
|---|---|---|---|---|
| Elastomer property | Particle size (decreasing) | Permanent structure (increasing) | Dispersion (increasing) | Interaction (increasing) |
| Hardness | ++ | ++ | – | + |
| Tensile strength | ++ | Little | + | + |
| 300% modulus | + | ++ | Little | ++ |
| Elongation at break | – | –– | ++ | – |
| Tear resistance | ++ | Little | Little | Little |
| Hysteresis | ++ | + | – | –– |
| Abrasion resistance | ++ | + | ++ | ++ |

Notes: + and ++ mean increase in that property and – and –– mean a decrease. They do not mean that the change is beneficial or detrimental. This depends very much on the application. For instance, high hysteresis loss is good for sound damping, but bad where heat buildup has to be avoided, for example, in tires

been tackled by using special elastomers. Interest is now turning to the incorporation of platy fillers to decrease permeability by creating tortuosity and increasing interphase (see barrier properties in the "Thermoplastics" section above).

## Thermosets

Many thermoset products contain fillers, often at very high levels. The most widely used particulate filler is calcium carbonate, although significant amounts of the flame retardant aluminum hydroxide are also used. As with the other polymer types, thermosets bring their own special characteristics and needs, which impact directly, or indirectly, on the filler choice. Differentiating features from other polymer classes are the incorporation of fillers at the prepolymerization stage, the widespread use of glass fibers (often in conjunction with particulates), and the ability to use larger particle size fillers than is usual with other types of polymer.

Thermosets are highly cross-linked materials formed by polymerization of low molecular weight precursors and are much more brittle than thermoplastics or elastomers. As a result, impact strength (more properly fracture toughness) is a key concern in many applications.

Fillers (and other additives) have to be incorporated before curing as the final polymer is an intractable solid. Thus, unlike the other polymer types, filler incorporation and dispersion is into a relatively low viscosity, often liquid, phase where the high shear that helps dispersion in the other types, especially elastomers, is missing. The polymerization process occurs during the forming of the part and is exothermic and generates high temperatures as well as giving high shrinkage. The cure exotherm and accompanying shrinkage are often problems for thermoset applications, and one of the important roles of fillers is to reduce these to manageable levels.

Key properties of thermosets in their main applications are stiffness, impact resistance (fracture toughness), and flammability. Fibers, especially glass fibers, are widely used to maximize stiffness and impact properties. In addition to the exotherm and shrinkage control referred to above, the main roles of fillers are cost saving, reduction in flammability, and improvements in thermal conductivity. Filler loadings can be very high (over 200 parts per hundred of polymer). The main particulate fillers used are aluminum hydroxides (for flame retardancy) and calcium carbonates. Some use is made of acicular and platy fillers such as wollastonite and mica. Very hard fillers, such as quartz and cristobalite, are used where excellent abrasion resistance is required, for example, in some solid surface applications. The polar nature of most thermosets means that they can wet and interact well with many types of filler, especially carbonates. This reduces the need for surface-modifying species, but dispersants and coupling agents may still be utilized, especially with siliceous fillers. Coupling agents are often used to help property retention under adverse environmental conditions rather than to improve initial properties.

In common with the other polymers, modulus increase is related to aspect ratio. This is usually dominated by glass fibers when they are present. Wollastonite (acicular) and mica, especially highly delaminated mica (often referred to as high-aspect-ratio mica or HAR), are more effective than carbonates and can be used to provide additional stiffening especially in glass fiber-free composites.

Impact resistance is another important property which is much affected by fillers, especially when no glass fiber is present. The relationship between filler properties, filler-matrix adhesion, and impact resistance is complex but has been well described by Jackson et al. (2003). Two distinct features are involved in determining overall impact resistance, crack initiation, and crack propagation, and the effects of filler loading and properties are different in the two cases. Fillers only have an influence on crack initiation if the particle size is above a value known as the critical (or inherent) flaw size, which can be tens of microns in many thermosets. This makes it possible to tolerate large particle sizes. Filler particles are also able to significantly decrease crack propagation through a mechanism known as crack pinning, and thus, they can give worthwhile improvements in overall impact resistance. A further refinement related to crack pinning is the need to consider the crack resistance of the filler itself. Those fillers that are readily delaminated (e.g., aluminum hydroxides and micas) can give less improvement in fracture toughness as a result.

## Future Directions

The future for conventional, nonnanoparticulate fillers looks fairly stable over the short to medium term. The principal recent changes of significance have been the emergence of precipitated silica as a filler for tire treads and of wood polymer composites for a range of applications such as decking. Despite great interest and much activity over the last several decades, the use of natural fibers, other than in wood polymer composites, has been slow in commercialization.

Environmental concerns and pressures are continuing to grow, with emphasis on sustainability in addition to emissions. We are already seeing significant activity and investment in the tire industry where some companies have a long-term goal of 100% sustainable tires. Currently this is mainly impacting the polymer and organic additives components, but will ultimately have an impact on the fillers. As examples, work is already underway to make carbon blacks from sustainable raw materials and to recover and recycle it. Some precipitated silica is now being produced from rice husks which is claimed to reduce emissions as well as being more sustainable.

A new area is the use of fillers as compatibilizers for immiscible polymer blends. Normally that task falls to expensive, tailor-made block copolymers, but it has been shown that fillers are effective and at a much lower cost. With the growing importance of recycling polymers and polymer blends, this could be an exciting new commercial application of fillers.

Nanofillers, other than the traditional carbon blacks and precipitated silicas and calcium carbonates, are outside of the scope of this entry. It can be said, however, that these have failed to live up to the great excitement that they were generating 10 years ago and that this is unlikely to change.

## Cross-References

- ► Compounding of Particulate-Filled Thermoplastics
- ► Particulate Fillers in Elastomers
- ► Particulate Fillers in Thermoplastics
- ► Particulate Fillers in Thermoset Plastics
- ► Surface Modifiers for Use with Particulate Fillers

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# Surface Modifiers for Use with Particulate Fillers

# 2

## Christopher DeArmitt and Roger Rothon

## Contents

### Abstract

The interface between a particulate filler and the polymer matrix plays an important role in determining the processability and properties of composites. The surface of most commonly used particulate fillers, with the exception of carbon blacks, is suboptimal for this purpose and surface modification is widely used, both to enhance wetting and to improve interaction with the polymer.

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A Reference Series, DOI 10.1007/978-3-319-28117-9_8

This modification is generally achieved by chemically reacting a suitable organic modifier with the filler surface.

Two distinct types of surface modifier can be recognized, noncoupling and coupling, depending on the type of organic group introduced. Both types have strong anchorage to the filler surface; but only the coupling type has strong interaction with the polymer. Fatty acids are the most common noncoupling treatment, while organo-silanes are most often used as coupling treatments.

Reaction of the filler surface can be carried out before addition to the polymer or during the polymer/filler mixing process. Both methods have advantages and limitations and are widely used.

**Keywords**

Filler • Surface • Modifier • Fatty acid • Stearic acid • Organo-silane • Organo-titanate • Zirco-aluminate

## Definition

Except for carbon blacks, the surface of commonly used particulate fillers is suboptimal for maximizing processing and properties of the polymer composites in which they are used. This is often remedied by treating the surface to enhance wetting and reaction with the polymer matrix. Surface modifiers are molecules which are chemically attached to the particle surface to improve compatibility. This differentiates them from weakly attached molecules that are physically adsorbed.

## Introduction

The surface of particulate fillers plays a vital role in determining both the processing behavior and properties of composites. Two factors are involved in the interaction between the filler and polymer: wetting and adhesion. The ease with which their surface is wetted by the polymer governs how easily they can be incorporated and how well they disperse. The strength of the interaction between the surface and the polymer determines the magnitude of many of the final composite properties.

The natural surface of most fillers is not ideal for adhesion to the polymer, and hence, surface modifiers are frequently used to improve performance.

While improved composite processing and end properties are the usual reasons for using modifiers, they can also produce other useful effects such as a reduction in the adsorption of curatives and stabilizers. The presence of surface modifiers can also affect filler handling properties, such as bulk density, powder flow, and dustiness.

In addition to their deliberate addition to improve wetting and adhesion, chemicals that can act as surface modifiers may also be present for other purposes. Typical examples are:

They may have been used as milling aids during grinding processes.
They may have been added to improve filtration and drying of precipitated products.
They may be used to protect the filler during storage. For instance, to reduce water pickup.

The presence of these additives is often not disclosed by the producer, with the use of milling aids being a prime example.

## General Principles

Virtually all surface modifiers work by chemically bonding an organic species to the filler surface with the nature of the organic molecule being chosen to have good compatibility with the polymer and in many instances to also be able to chemically interact with it, often during the curing process if there is one.

The general structure of a surface modifier can be thought of as an anchoring group, optionally a spacer and a polymer-compatible or reactive part. The role of anchoring groups is to react with the filler surface and bind the additive to it. The most common anchor groups are acids or acid precursors, such as anhydrides (for basic or amphoteric fillers) and alkoxysilanes (for fillers with metal hydroxyls present, especially siliceous fillers). The alkoxysilanes are frequently referred to merely as silanes. Other organometallics (titanates, aluminates, etc.) can also be used. The organic part of the molecule provides the polymer compatibility and reactivity. Spacer groups are not an essential part of the structure, but can be used to remove reactive functionalities from the vicinity of the anchor group and lift them proud of the filler surface.

Two distinct types of modifier can be recognized, depending on the type of organic group: noncoupling and coupling (see Fig. 1). Both have strong anchorage to the filler surface, but only the coupling type has strong interaction with the polymer. This interaction can be chemical or physical (e.g., entanglement). Fatty acids are the most common noncoupling treatment, while the silanes (see later for definition) are most often used as coupling agents (although noncoupling versions are available and are sometimes used).

### Methods of Using Surface Modifiers

Spreading of the modifier on the surface and chemical reaction is required to bring about the anchoring onto the filler, and this can be achieved in a number of ways.

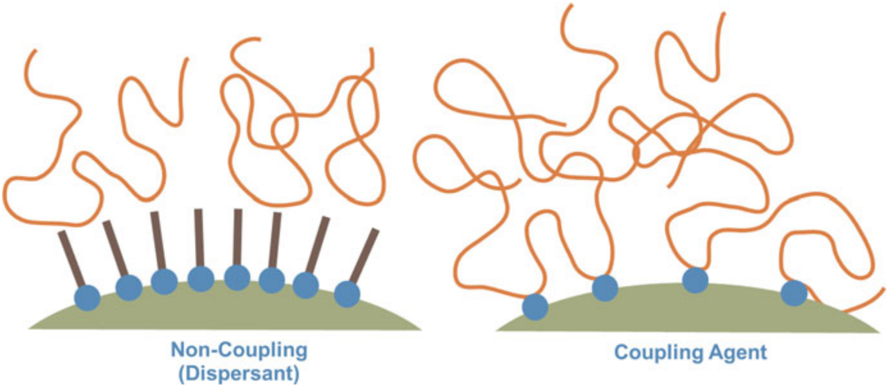

**Fig. 1** Noncoupling and coupling modifiers

**Table 1** A comparison of the precoating and in situ methods of filler treatment

| Precoating | In situ |
|---|---|
| Usually more expensive, but more efficient | Usually less expensive, but may require higher additive levels and more processing |
| Volatile reaction by-products such as alcohols are easily dealt with | Volatile by-products can be a problem |
| Better where improved composite processing is required | Not suitable where the coating is to be used to improve filler storage stability |
| Surface reaction and coverage can be more easily controlled. Interference from other compounding additives can be minimized | Careful processing is required to ensure complete reaction and there can be competitive adsorption from other compounding ingredients |
| Unable to treat any fresh surface generated during compounding | Able to deal with fresh surface generated during compounding |

The first differentiation is into “in situ” and precoating methods. In the “in situ” process, the coating agent is added during compounding and has to make its way to, and react with, the filler surface during processing. While it may seem to be a hit and miss procedure, it can often work very effectively and is widely used. The alternative is to prereact the filler with the additive prior to compounding (precoating).

The main advantages and disadvantages of the two procedures are summarized in Table 1. In some cases, especially where some newly exposed filler surface may be generated during processing, i.e., via breakdown of agglomerates/loosely bound aggregates, a combination of the two approaches is used.

Various precoating methods may be used, depending on circumstances. When the filler is produced in aqueous dispersion (e.g., wet milling, precipitation), it is often advantageous to add a soluble or water-dispersible form of the coating, prior to filtration and drying.

In the majority of other cases, a dry coating process is used. This can be during size reduction by grinding or in a specially designed mixer. The conditions used for dry coating must be carefully chosen to ensure complete coverage and surface reaction. The best form of mixer will depend on the additive and the filler.

## Coating Level

Choice and control of coating level is very important if properties are to be maximized and cost minimized. There are some generalizations to help identify the appropriate level, but final optimization usually requires experimentation.

The most important practical factors are the specific surface area (SSA) of the filler and the coverage factor of the additive. The SSA is usually measured in units of $m^2g^{-1}$ and the coverage of the additive in the same units. Dividing the SSA by the coverage then gives the ratio of additive needed to just treat the entire surface of that filler. As an example, if the filler SSA is 10 $m^2g^{-1}$ and the coverage of an additive is 100 $m^2g^{-1}$, then the required treatment level is 10 wt%. Levels found in practice range from under 0.1% w/w on low surface area (large particle size) fillers to nearly 10% w/w on high surface area ones.

The SSA can be readily determined by a number of methods (▶ Chap. 1, "Particulate Fillers, Selection and Use in Polymer Composites") and is usually part of product specifications.

Coverage factors are less easily determined and not so widely available. Only a brief discussion of the complexities is possible here; more details can be found in Rothon (2003). Some values from this work are presented in Table 2.

The idea of a monolayer is the underlying concept in arriving at the coverage factor. This is the amount of the additive that will produce a coating that is just one molecule thick. This can be calculated in various ways, including molecular modeling and experimental methods such as spreading pressure measurements.

There are problems with this concept, mainly caused by the fact that additive molecules are not spherical. Thus, several surface orientations are possible and will result in different thicknesses. This can be illustrated by a fatty acid modifier such as stearic acid. When the hydrocarbon tail is vertical to the surface, the coverage is 420 $m^2g^{-1}$, but if it lies flat, then the coverage rises to 1,800 $m^2g^{-1}$ (see Fig. 2).

Another complication is the need for the additive to find suitable sites to react with at the surface. This may not allow close packing of the additive molecules, and hence, the coverage will be less than calculated from geometric considerations alone.

**Table 2** Approximate surface coverage of some modifiers

| Modifier | Coverage ($m^2$ of available surface, per gram of additive) |
|---|---|
| γ-Aminopropyltriethoxysilane | 360 |
| γ-Mercaptopropyl trimethoxysilane | 350 |
| Vinyltrimethoxysilane | 525 |
| γ-Methacryloxypropyltrimethoxysilane | 315 |
| Stearic acid (C18) | 420 vertical, 1,800 horizontal |
| Oleic acid (unsaturated C18) | 940 vertical, 1,800 horizontal |

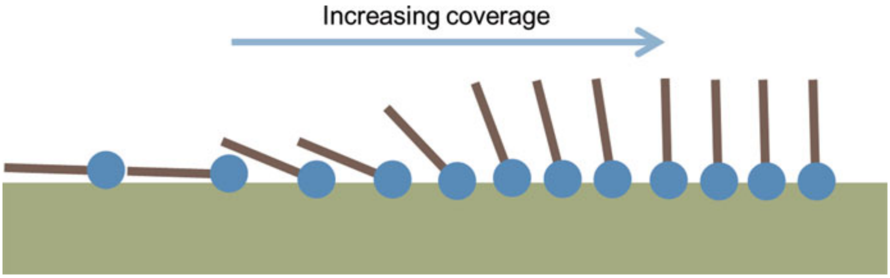

**Fig. 2** Different possible orientations of an adsorbed fatty acid chain

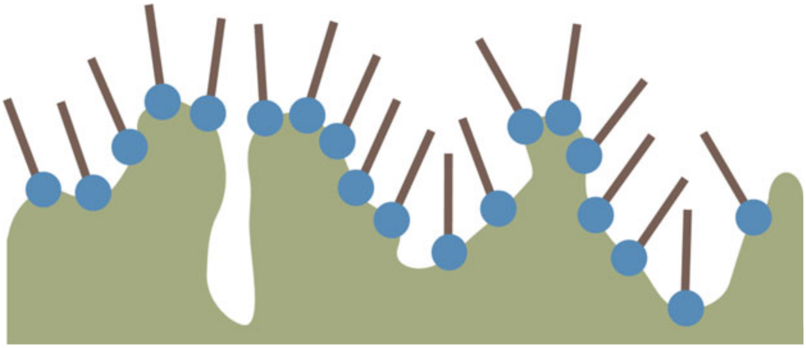

**Fig. 3** Inaccessible surface concept

Finally, as shown in Fig. 3, not all of the SSA may be accessible to the relatively large additive molecules.

Despite this, the intelligent use of SSA and coverage factors provides a useful starting point for any study. The next point to consider is what level of coverage is actually required. Most properties start to change well before complete surface coverage is reached, and in some applications, partial coverage may be sufficient. In many cases, the maximum effect is often found at about the monolayer level, but multilayers are found to be beneficial in other instances.

A good example of the effect of additive level and type (coupling and noncoupling) on a wide number of properties of a magnesium hydroxide-filled ethylene vinyl acetate copolymer can be found in the work of Rothon and coworkers (2002a). This includes effects on flame retardant properties and on aging. The latter is particularly interesting, as it was found that excess of the fatty acid led to a significant decrease in aging resistance. This was most marked when a commercial blend of fatty acid was used but was still very significant with pure stearic acid.

## Determination of the Amount of Additive and Its Distribution

Various methods can be used to detect the presence of a modifier and to determine the amount present. Simple chemical analysis suffices where the additive has an element that is easily distinguished from those on the filler. Pyrolysis is also successfully used in many cases, provided one is careful to allow for any weight loss due to the filler itself.

Dye adsorption is able to give an estimate of the amount of coated surface. The principle is simple and related to the use of dye adsorption to measure SSA. It relies on using a dye which strongly adsorbs on the uncoated filler surface, but not onto coated areas. The relative level of adsorption on coated compared to uncoated filler is then a measure of the amount of untreated surface.

More sophisticated instrumental techniques such as diffuse reflectance infrared fourier transform spectroscopy (DRIFTS) can be used to provide not only the amount present but also the information concerning its chemical structure.

The reader is referred to Liauw (2003) for a detailed discussion of the characterization of surface layers on fillers.

## Surface Modifier Types

The vast majority of surface modifiers fall into two chemical types depending on the anchor group. The first type uses carboxylic acid groups or their precursors for anchoring, with fatty acids being the prime example. These react well with amphoteric and basic surfaces, but not with acidic ones (in reality fillers generally have both basic and acidic sites present, but in most cases one type dominates). The other type uses metal alkoxy groups to provide the anchoring, especially silicon alkoxide groups. These react well with surfaces containing free hydroxyls, but not with carbonates, sulfates, and similar surfaces. Neither type is effective on carbon blacks, but fortunately, their surface is sufficiently reactive to achieve good interaction with many polymers.

### Carboxylic Acids and Related Compounds

For a recent review of this subject, see Rothon (2010).

Carboxylic acid groups provide a convenient method for anchoring organic species to basic and amphoteric fillers, as they can react with the surface to produce carboxylate salts. Additives containing them are widely used as surface modifiers, especially with calcium carbonates. In addition to the free carboxylic acid, it is possible to use a precursor, such as an acid anhydride. Carboxylate salts can also be used as additives themselves in some cases. It should be noted that the term “stearate” is used loosely in the literature and can mean stearic acid, sodium stearate, calcium stearate, zinc stearate, or ammonium stearate. Each of these is chemically unique and will not perform in exactly the same way.

The carboxylic acidic groups can be part of simple monomeric species or attached to a polymeric backbone. Finally, the additives can be either noncoupling or coupling, depending on the groups attached to them.

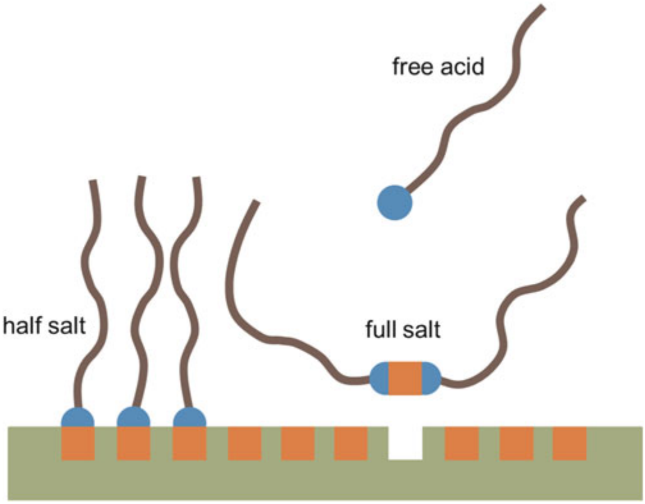

**Fig. 4** Idealized representation of the different states for a fatty acid modifier on a typical mineral filler with divalent metal ions (e.g., calcium carbonate)

Care has to be taken with the terminology and with the completely separate use of carboxylic acid salts as processing aids (e.g., internal and external lubricants). The following states can be distinguished in polymer composites containing carboxylic acid derivatives and fillers:

Free acid
Free salt of the acid (i.e., not chemically attached to the filler surface)
Bound salt of the acid, where the metal ion is still part of the filler surface

This is illustrated in Fig. 4.

The aim of surface modification is to maximize the bound salt. The importance of the other two types varies significantly with the system. Free acid is often detrimental, while the free salt may act as a processing aid (indeed, such salts are frequently added for this purpose).

## Saturated Fatty Acids

The main additives using carboxylic acid functionality as an anchor group are the saturated fatty acids. These are relatively inexpensive, are widely available products, and are the classic noncoupling workhorse surface treatment used on calcium carbonate and other basic fillers.

Fatty acids are usually derived from natural sources, where they occur as complex mixtures in both animal and vegetable matter. Separating out pure components from these mixtures is expensive, and economics dictates that blends of acids are normally used industrially. These blends are still quite complex, containing a number of different chain lengths and even small amounts of unsaturated acids and nonacid material. The composition of the blends used in precoating fillers is rarely specified and can vary markedly. Some of the minor components can cause problems in certain final applications and need to be minimized. Unsaturated acids (such as oleic) are a case in point and can adversely affect final properties such as color and heat stability.

Blends approximating to 18 carbon atoms are usually the least expensive and are those most often used for filler coating. They are often referred to as stearic acid or stearate coatings although this specific acid may be less than 50% of the overall composition.

Fatty acids are usually precoated onto fillers, and two methods of coating are generally employed: wet coating and dry blending. In the wet coating process, an aqueous solution of salt of the fatty acid is added to an aqueous slurry of the filler. If an alkali metal salt of the acid is used, then the coproduct containing it has to be washed out from the system. This can be circumvented by using the ammonium salt.

In the dry coating procedure, filler and fatty acid are usually reacted together in a high-shear mixer. Most fatty acids are solids and have to be melted before spreading and reaction can take place. In some cases, the shear action of the mixer generates enough heat, but external heating can also be used.

Very little information is available about the wet coating process although it has some commercial significance, especially in precipitated calcium carbonate production.

More information is available about dry coating methods, although it is still not extensive. Fekete and coworkers (1990) have shown that the adsorption and reaction are very dependent on the type of mixer and the exact conditions used.

While there has undoubtedly been much industrial interest in alternatives to the “stearic” acid blends, not much of this work has been published, and there is little evidence for the commercial use of alternatives. Iso-stearic acid is sometimes employed, probably because it is a liquid and easier to use in dry coating processes.

### Effects of Fatty Acid Coating in Composites

The saturated fatty acid chains are too short to entangle with the polymer matrix and have no means of chemically reacting, so they are noncoupling additives and result in low bond strengths between the filler and matrix and in filler debonding at relatively low stress levels. This leads to stress whitening and a decrease in ultimate tensile strength. On the other hand, there can also be useful improvements in other properties such as elongation and toughness.

Typical effects obtained as a function of coating level for a magnesium hydroxide-filled EVA compound are illustrated in Fig. 5.

The improvement in impact resistance obtained by using a fatty acid coating on calcium carbonate in a polypropylene homopolymer compound is illustrated in Table 3.

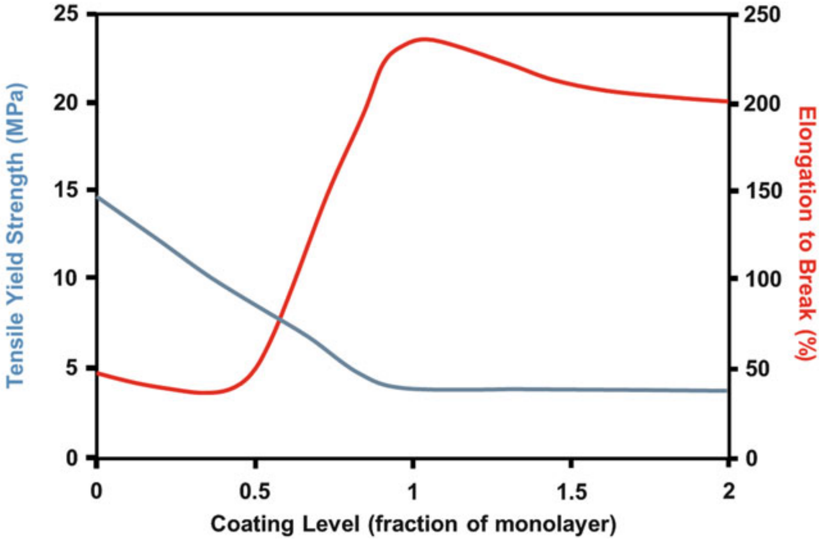

**Fig. 5** Effect of fatty acid coating level on the properties of a magnesium hydroxide-filled EVA compound (adapted from Rothon et al. 2002a)

**Table 3** Effect of fatty acid treatment level of calcium carbonate on the impact resistance of filled polypropylene homopolymer (50% w/w filler) (based on Hancock et al. (1980))

| Fatty acid coverage (% of theoretical monolayer) | Notched impact strength (normalized to uncoated = 1.00) |
|---|---|
| 0 | 1.00 |
| 8 | 1.24 |
| 15 | 1.15 |
| 39 | 1.45 |
| 77 | 1.51 |
| 115 | 1.80 |
| 153 | 1.50 |

Fatty acid coatings are predominately used in thermoplastic composites, where their combination of effects is of the most used. The general belief for these polymers is that fatty acid treatments reduce melt viscosity, improve filler dispersion, decrease modulus, reduce tensile strength, but improve elongation and impact resistance. While generally true, there are a significant number of exceptions reported.

In elastomers, the main fatty acid effects observed are reduced viscosity but also reduced filler polymer interaction (indicated by less bound rubber) and reduced reinforcement.

The effects of fatty acid surface modifiers also vary markedly according to the elastomer type. The effects are much more noticeable in solution-polymerized elastomers than in emulsion-polymerized ones. As shown by Rothon, this is due to the presence of large amounts of residual surfactants in the emulsion-polymerized case (1984). These can duplicate the effects of fatty acids.

Fatty acid treatments do not have much use in thermoset applications. Many of these (e.g., unsaturated polyesters) contain abundant acidic groups in any case.

## Unsaturated Carboxylic Acids and Related Compounds

The efficacy of the carboxylic anchor group has led to much interest in developing coupling-type modifiers based on it. The obvious way to do this would seem to be to replace the saturated hydrocarbon chain by an organic group containing some unsaturation. This has been extensively trialed but with limited success. The main candidates are unsaturated versions of fatty acids such as oleic acid and short chain species such as maleic acid and anhydride, acrylic acid, and methacrylic acid. The only commercial products of this type that the authors are aware of are based on unsaturated oligomeric carboxylic acids (Rothon et al. 2002b; Schofield et al. 2003).

As might be expected, the greatest success with the unsaturated systems has been in peroxide-cured polymers, such as unsaturated polyesters and some elastomers. Here the cure system is able to react with the unsaturation and lead to grafting. Less success has been obtained in sulfur-cured elastomers and especially in thermoplastics such as the polyolefins, where there is usually no added free-radical source.

While simple mechanical grafting is possible in polyolefins, this is usually limited by the presence of added antioxidant. This antioxidant interference can be overcome by the addition of a very small amount of peroxide.

## Dimaleimides

Dimaleimides can be thought of as derivatives of maleic anhydride, produced by its reaction with aromatic or aliphatic diamines and thus containing two very reactive double bonds. They have been shown to be effective coupling agents in particulate-filled polyolefins (Khunova and Sain 1995; Xanthos 1983) but do not appear to be used commercially.

## Polymeric Acids and Anhydrides

Using suitable polymeric backbones to carry the carboxylic acid functionality is a more promising approach for obtaining coupling in many cases. Two main classes of product are commercially available: one with a saturated hydrocarbon backbone and the other with an unsaturated one.

## Acid Functional Saturated Polymers

The main modifiers of this type are based on polyolefin homo- and copolymers. The acid functionality is usually introduced by the use of acrylic acid or maleic anhydride, and this can be done by grafting or by copolymerization. For various reasons, the level of acid functionality is relatively low compared to fatty acids.

These additives are for use in filled polyolefins, and coupling to the polymer matrix is thought to be due to processes such as chain entanglement and cocrystallization (Godlewski and Heggs 1989). They are usually used as additives to the formulation, rather than being precoated.

## Acid Functional Unsaturated Polymers

Unsaturated polymers offer the possibility of chemical bonding in addition to the physical methods described for the saturated versions. Polybutadienes (PBDs) have been found to be particularly suitable for this and can be made into excellent coupling agents for basic and amphoteric fillers. Just as for their nonpolymer equivalents, they are best in systems where some curing or cross-linking is taking place, but unlike the simple unsaturated acids, they are effective in both peroxide- and sulfur-cured materials.

The structure of a typical unsaturated polymeric acid anhydride surface modifier based on maleinized polybutadiene (MPBD) is shown in Fig. 6. The anhydride groups are believed to lead to the reaction with the filler surface, probably by salt formation, while the residual unsaturation is available for participation in various curing or cross-linking processes.

Much higher acid levels are possible compared to the functionalized saturated polymers and these give the best results. Moreover, high levels allow water-dispersible or even water-soluble forms to be made and used for precoating.

The effectiveness of an MPBD-type additive when precoated onto precipitated calcium carbonate is demonstrated in Table 4. This compares uncoated, fatty acid-coated, and MPBD-coated fillers in a cross-linked EPDM elastomer and clearly shows the benefits arising from the use of the MPBD.

It has been found that performance of the MPBD increases with both anhydride content and molecular weight but begins to plateau at about 10,000 molecular weight and 20–25% by weight of anhydride (Rothon 1990).

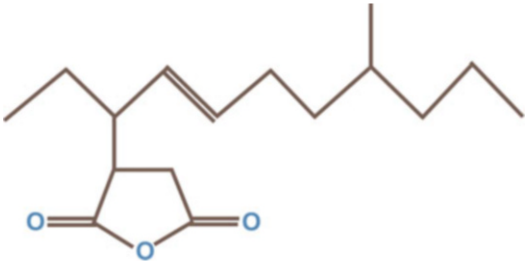

**Fig. 6** Structural elements of maleinized polybutadiene

**Table 4** A comparison of fatty acid and maleinized polybutadiene coating of precipitated calcium carbonate on performance in a sulfur-cured EPDM elastomer (100 phr filler, both coatings at 2.6% w/w on filler)

| Property | Untreated filler | Fatty acid coated | Maleinized polybutadiene coated |
|---|---|---|---|
| Tensile strength $MNm^{-2}$ | 10.0 | 4.5 | 13.3 |
| 300% modulus $MNm^{-2}$ | 2.3 | 1.4 | 3.7 |
| Tear strength $Ncm^{-1}$ | 1.6 | 1.0 | 2.4 |

## Organosilicon Compounds

### General

Silicon is one of the few metals which form stable bonds with carbon, and this offers unique opportunities for producing molecules that can react with both filler surfaces and polymer matrices.

The filler-reactive side is based around to the silanol (Si–OH) functionality. This will readily react with filler surface hydroxyls to form strong bonds. Silanols will also self-condense, however, and so they cannot be present in the starting compound but must be generated in situ during the coating process. Thus, some silanol precursor must be used. While halogens can do this, the most common approach is to use an alkoxide group as the silanol precursor. Thus, most modifiers are based on silicon alkoxides.

Groups such as vinyl, amino, epoxy, mercapto, and sulphido can be stably attached to silicon using Si–C bonds, and these provide the reaction sites with the host polymer. Where no reactivity is required, then a simple group such as methyl suffices.

The organosilicon coupling agents in commercial use generally have three filler anchor groups (alkoxy) and only contain one organic group attached to silicon, the general formula being

$$R - Si - (OR)_3 \ \ (R \text{ is usually } CH_3 \text{ or } C_2H_5)$$

They are often referred to simply as silanes.

### Filler Types Susceptible to Silane Treatment

Because they rely on reaction with filler surface hydroxyls to produce a stable layer, the organo-silanes are most effective on fillers with high concentrations of such sites. This includes silicas, silicates (including glass), oxides, and even hydroxides, although problems can arise if the surface has a high pH, when exposure to moisture may cause the bond to break down.

Silanes have little effect on carbon blacks. They are also not generally effective on surfaces such as sulfates and carbonates.

## Coating Techniques

As can be judged from the description of their chemistry, organo-silanes are complex species, which often have the potential of reacting with themselves as well as with filler surfaces. Careful control of the coating process is thus important.

The noncoupling silane versions are generally quite volatile, and filler coating is usually carried out in the gas phase by exposing the filler to their vapors. This ensures maximum reaction with the surface and minimum self-condensation.

On the other hand, the coupling versions are less volatile and are liquids at ambient temperatures. The filler can therefore be coated using the neat liquid or a solution of the latter in a suitable solvent. Silane coupling agents have been most used for coating glass fibers. In this specific application, prehydrolysis and partial self-condensation have been found to aid the coating process, and this is the usual procedure employed in much of the scientific work on silane treatment of particulate fillers. Unfortunately, this approach is not often used in real applications as it is too impractical. In many instances, the filler coating is actually carried out “in situ” during the compounding process, essentially utilizing the polymer matrix as the solvent and the mixer as the reactor.

## Reaction of Organo-Silanes with Filler Surfaces

While the reaction with the filler surface is critical to the functioning of the organo-silanes, it is a very complex topic, and only an overview is possible here. The reader is referred to Rothon (2003) for a more detailed discussion.

Reaction between the alkoxysilane and filler surface hydroxyls can proceed in one of the two ways.

When the system is very dry, then direct reaction takes place:

$$\mathrm{R-Si-OR+HO-Surface \rightarrow R-Si-Surface+ROH}$$

In the more common situation, when water is present, prehydrolysis can occur, followed by condensation:

$$\mathrm{R-Si-OR+H_2O \rightarrow R-Si-OH+ROH}$$

$$\mathrm{R-Si-OH+HO-Surface \rightarrow R-Si-Surface+H_2O}$$

These two processes occur at different rates and respond differently to factors such as temperature and pH, and it is not clear which path is followed in most commercial processes.

This simple model ignores the fact that the silanols can react with each other as well as with the surface thus allowing cross-linking in the coating and even the formation of unbound oligomeric silane species. There is even some evidence that the oligomeric species can be beneficial to processing.

## Applications of Organo-Silanes

The noncoupling types are mainly used to make filler surfaces hydrophobic and oleophilic and are principally used with fumed silicas (see “Cross-References”) for use in silicone elastomers. The trimethyl compounds are most widely used for this purpose, with both the chloro and methoxy derivatives being employed. Both of these give by-products that are difficult to remove from the system. This can be overcome by using hexamethyldisilazane (HMDS), $(CH_3)_3SiNHSi(CH_3)_3$. This reacts with surface moisture to form only volatile by-products and with surface silanols to release only ammonia, so the reaction is particularly clean. Cyclic azasilanes also react cleanly and are reported to be more reactive than the alkoxysilane types.

A considerable range of silane coupling agent types are available commercially or have been reported in the literature. Only the most commonly encountered types of silane will be covered here, together with limited examples of the effects they can produce. The reader is referred to excellent reviews by Plueddemann (1982) and Borup and Weissenbach (2010) for more details.

Virtually, all the commercial products are trialkoxy functional, and the first variable to consider is the nature of the alkoxy group. This is lost during the coating process and controls volatility and flash point, affects toxicity, and plays an important role in determining the rate of hydrolysis. The most common groups used are methoxy, ethoxy, and methoxy, ethoxy. The methoxy derivative gives the lowest flash point and fastest surface reaction.

The alcohols released from the alkoxy groups are under scrutiny because they are classed as volatile organic compounds (VOC). This is of particular concern where large amounts of the silane are used, such as in tire manufacture. Here products have been developed with much lower volatility alcohols that can remain in the matrix rather than being released into the atmosphere.

The other important variable is the chemical nature of the reactive (functional) group. This is chosen to ensure reactivity with the polymer matrix. The functional groups most used commercially in particulate-filled composites are vinyl, methacryl, amino, epoxy, mercapto, and polysulfide. These are briefly discussed below.

### Vinyl

Most products of this type have the vinyl group closely attached to the silicon atom. They are mainly used in systems that are cured by a free-radical process such as peroxide in which the vinyl unsaturation can participate.

### Methacryl

This is still mainly intended for peroxide cross-linking but is a more reactive group than vinyl, and the unsaturation is also generally further away from the silicon atom.

### Epoxy

Commercial products are based on 3-glycidoxy propyl trimethoxy silane. Although they can perform well in a number of systems, they are relatively expensive and mainly restricted to use in epoxies for which they are more suitable than other silane types.

### Amino

Amino functional silanes are fairly widely used. The commercial ones are usually based on the γ-aminopropyl functionality. They are very versatile and are used in epoxies, phenolics, urethanes, polyamides, and some elastomers. They can also be used in conjunction with acid functional polymers and in some polyolefins. In this case, they react with the acid functionality to form an amide linkage.

### Sulfur Functional

These are specialist coupling agents, specifically designed for use in sulfur-curing elastomers. The two principle forms are γ-mercaptopropyl trialkoxysilane and various polysulfidic silanes (especially tetrasulphide).

### Oligomeric Silanes

Another recent development is the use of oligomerized silanes. These are partly self-condensed products and have the advantage of reduced volatility and decreased alcohol release (Mack 2002).

## Examples of Silane Coupling Agent Effects in Filled Polymers

A brief account of the use of silanes in various polymer systems follows.

### Elastomers

Elastomer applications are a major consumer of silane coupling agents, largely due to the size of the tire market. The polysulfidic types have the bulk of the market, but mercapto, vinyl, and amino also have significant use. They are mainly used with precipitated silicas and clays, with the “in situ” method being far more common than precoating. One limitation of this method is the retention of some of the eliminated alcohol in the final product. This is important where high addition levels are used (e.g., in some tire applications) and can cause problems with VOC (volatile organic constituent) regulations.

There is also a specialized market for silane-modified fillers in silicone elastomers. Here the main filler is fumed silica and precoating is more common.

The silane coupling agents markedly improve the adhesion between the filler and polymer, especially at the high strains often encountered in elastomer applications. The main benefits to be observed from the improved adhesion are higher modulus, higher tear strength, better fatigue resistance, and higher abrasion resistance. The polysulfides used with precipitated silica have played a major role in the development of fuel-saving tire tread formulations (green or energy tires); details of this can be found in the chapter on elastomer (▶ Chap. 6, “Particulate Fillers in Elastomers”).

### Thermosets

Thermoset polymers are chemically cross-linked and are ideal for use with reactive modifiers such as silane coupling agents. Indeed, much of the early development of the silanes was in the glass fiber-filled thermosets. The silane types most commonly used are vinyl, methacryl, epoxy, and amino. Among the fillers, commonly treated are various silicas and silicates and the flame retardant aluminum hydroxide. As with elastomers, the “in situ” treatment method is favored over precoating, and there is the possibility of some alcohol remaining in the product.

In thermosets, the main effects of coupling agents are seen in property retention after exposure to moisture, rather than in initial properties. This property loss has long been a weak point of reinforced thermosets and so the effect is most important. In addition, improvements in initial impact strength are also often seen.

More details will be found in the chapter on thermosets (▶ Chap. 6, “Particulate Fillers in Elastomers”).

### Thermoplastics

For our purposes, we need to divide thermoplastics into two types: condensation polymers (such as polyamides and polyesters) and addition polymers (such as polyethylene and polypropylene).

The condensation polymers are polar and have groups that are able to react with certain silane functionalities, such as amino, during melt processing. It is thus easy to obtain beneficial coupling effects and silanes are most widely used with this type of thermoplastic.

The polyolefins, on the other hand, are fairly inert and much harder to react with, due to their chemical inertness. A number of approaches have been used in the past including, for a short time, a very reactive azido silane. The use of silane coupling agents as additives for thermoplastics has also been reviewed by Godlewski and Heggs (1989). Today, the favored approach for coupling fillers into thermoplastics is to use acid functional derivatives of the polymer matrix (see earlier). Where these cannot react with the filler directly (e.g., with silicas and silicates), then the filler can be pretreated with an amino-silane. Coupling is then achieved by amide formation between the amine and acid functionalities.

Both “in situ” and precoating methods are utilized, but unlike elastomers and thermosets, precoating is more common. This is due to the difficulties in adding liquids during melt processing and also to problems that can arise from alcohol release in compounding machinery.

The reader is referred to Borup and Weissenbach (2010) for a recent review on silane coupling agents.

## Other Organometallic Coupling Agents (Organo-Titanates and Zirconates)

Various other metals have groups similar to the silanols that could be used to react with filler surface hydroxyls, and the success of the organosilicon compounds has led to other organometallics being promoted for use as coupling agents. While they attempt to mimic the silane structures, they all have difficulty matching the hydrolytic and thermal stability of the silicon to carbon bond. The two principle types that may be encountered are based on titanium and zirconium.

### Organo-Titanates (Titanates)

The organo-titanates have aroused great interest and controversy in recent years. A recent review has been written by Monte (2010).

They can be regarded as derivatives of ortho-titanic acid, $Ti(OH)_4$, and hence are commonly known as organo-titanates rather than by their systematic names. The controversy is over their real structures and whether they act as true coupling agents or merely as very effective dispersants.

The idealized structures written for the organo-titanates are similar to silanes with alkoxy functionalities again providing the filler-reactive precursor. However, unlike the silicon to carbon bond, the titanium to carbon bond is very unstable and cannot be used to permanently attach organic groups to provide polymer reactivity. Thus, all these substituents have to be attached through titanium oxygen bonds, and their chemistry is dominated by the hydrolytic sensitivity of these. One of the more successful approaches is to use chelate groups attached to titanium, particularly where a five- or six-membered ring is formed. Titanates are much more reactive species than silanes and can exhibit a variety of cross-linking and catalytic effects of their own in polymeric systems, over and above any due to filler treatment. This makes understanding their role in filled composites very complicated. They are also sensitive to photoreduction, which can lead to unwanted color effects. These problems are largely eliminated if titanium is replaced by zirconium, and hence, organo-zirconates analogous to the organo-titanates have been developed, but they are considerably more expensive to produce than the titanates and hence are unlikely to completely replace them.

Based on the proposed mode of action, one would expect best performance on the same filler types as for the silanes (i.e., heavily hydroxylated surfaces such as silica, silicates, and hydroxides). Surprisingly, they also seem to produce beneficial effects on other fillers, notably calcium carbonates and carbon blacks, but this may be due to improved dispersion, or to the titanate reactivity mentioned earlier, rather than any coupling action.

While the organo-silanes are generally based on three alkoxy groups, the main titanates only have one.

In general, the simplest organo-titanates used as filler modifiers are nominally triacyloxy isopropoxy derivatives. They thus contain three potential polymer-reactive groups (as opposed to one with the silanes). These can be simple hydrocarbon or one or more of them can contain reactive functionality. Two examples are shown below (Fig. 7).

Despite the uncertainties over mechanisms, the titanates do appear to give some useful effects.

The most notable effects are in giving significant viscosity reduction in highly filled systems while maintaining good final properties. This is largely due to improved dispersion, and they must be judged against other products, such as the fatty acids, which can do the same thing at much lower cost. Unfortunately, very little data exists on which one can properly judge the relative merits of the organo-titanates and other treatments.

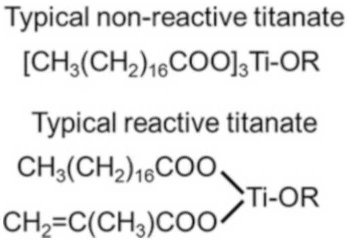

**Fig. 7** Typical reactive and nonreactive organo-titanate structures

The work of Sharma et al. (1982) is typical. They coated ground calcium carbonate with a nonfunctionalized titanate from toluene solution in a high-speed mixer. The filler was dry blended with polypropylene powder and compounded in a Buss Ko-Kneader. Test specimens were produced by both compression and injection molding. The coating was found to improve melt flow index, tensile elongation, and notched Izod impact strength relative to the uncoated filler. Scanning electron microscopy indicated better dispersion of the filler due to the presence of the titanate but gave no evidence of a chemical bond between the filler and matrix. Unfortunately, no comparison with a simple fatty acid treatment, which would be expected to give some, at least, of these benefits, was carried out.

### Aluminates and Zirco-Aluminates

There is some very limited use of both aluminates and zirco-aluminates, but information is limited.

The use of aluminates is being pioneered by Kenrich Petrochemicals (Ken react reference manual). They describe their products as chemically modified alkoxy aluminum chelates, but little more is known.

The zirco-aluminates have been available for many years but do not seem to have made much headway in the particulate fillers area. Structural details and useful scientific data are scarce. They are said to be based on a low molecular weight zirco-aluminate backbone carrying two ligand types. One ligand confers hydrolytic stability to the backbone, while the other contributes organo-functionality.

While described as coupling agents, the main benefits of the zirco-aluminates appear to be in dispersion and especially in producing low viscosity filler dispersions of excellent stability in liquid systems such as unsaturated polyester resin. The reader is referred to Cohen (1992) for more details.

### Phosphates and Borates

It is possible to devise structures of other organic acids which could mimic the effects of the carboxylates, and there has been some scientific interest, although no significant commercial application to date.

Borates have been proposed in a patent assigned to Dart Industries (Fein et al. 1978) and were found to give improved properties (melt flow, impact strength, elongation) in calcium carbonate-filled polypropylene homo- and copolymer compared to untreated filler.

Nakatsuka and coworkers (1982, 1985) have published details of their studies on the use of organo-functional dihydrogen phosphates (RO-$PO_3H_2$) as surface modifiers for calcium carbonate. They made compounds where the R group was a simple hydrocarbon (ethyl, butyl, hexyl, octyl) or contained additional functionality such as olefinic double bonds and methacryloxy, chloro, or mercapto groups. They applied the treatments to both ground and precipitated calcium carbonates and assessed them in elastomers such as SBR and EPDM.

Significant effects were observed in line with the type of functionality present in the modifier. Despite the apparent promise of these materials, they do not seem to have had much commercial success, probably because they are more expensive than other modifiers which achieve the same result.

## Conclusions and Future Directions

Surface modification can be used to produce a variety of useful effects in particulate-filled polymer composites and has been vital to the growth of particulate filler technology. This will continue to be the case going forward.

The main products in use fall into two types: coupling and noncoupling. While they each give different effects, both are useful depending on the application requirements.

The main commercial products are fatty acids (predominately noncoupling) and organo-silanes (predominately coupling). No new types are likely to emerge in the immediate future, but there may be some tweaking of composition to reduce issues with VOC emissions.

## Cross-References

- ▶ Compounding of Particulate-Filled Thermoplastics
- ▶ Particulate Fillers in Elastomers
- ▶ Particulate Fillers in Thermoset Plastics
- ▶ Particulate Fillers in Thermoplastics
- ▶ Particulate Fillers, Selection, and Use in Polymer Composites
- ▶ Precipitated and Fumed Silicas and Related Products

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# Particulate Fillers in Thermoplastics

# 3

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## Contents

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## Abstract

Although particulate-filled polymer composites are mature materials with a long history of application, their structure–property correlations are more complicated than usually assumed. The characteristics of all heterogeneous polymer systems including composites containing micro- or nanofillers are determined by four factors: component properties, composition, structure, and interfacial interactions. Several filler characteristics influence composite properties, but the most important ones are particle size, size distribution, specific surface area, and particle shape. The main matrix property is stiffness. Composite properties usually depend nonlinearly on composition, thus they must be always determined as a function of filler content. The structure of particulate-filled polymers is often more complicated than expected. Although segregation rarely occurs in practice, aggregation and the orientation of anisotropic particles take place quite frequently. The former usually deteriorates properties, while the latter determines reinforcement. Interfacial interactions invariably develop in composites; they lead to the formation of a stiff interphase considerably influencing properties. Interactions can be modified by surface treatment, which must be always system specific and selected according to the goal of the modification. Nonreactive coating helps dispersion and beneficial for impact strength, while coupling is needed for reinforcement. Particulate-filled polymers are heterogeneous materials in which inhomogeneous stress distribution and stress concentration develop under the effect of external load. These initiate local micromechanical deformation processes, which determine the macroscopic properties of the composites. Usually debonding is the dominating deformation mechanism in particulate-filled polymers. Although the number of reliable models to predict properties is relatively small, they offer valuable information about structure and interactions in particulate-filled composites. High compounding prices require the thorough consideration and utilization of all benefits of particulate fillers including large stiffness, strength, dimensional stability, increased productivity, etc.

## Keywords

Particulate-filled polymers • Interfacial interactions • Surface modification • Deformation and failure • Composition dependence of properties

## Definition

The characteristics of particulate-filled thermoplastics are determined by four factors: component properties, composition, structure, and interfacial interactions. The most important filler characteristics are particle size, size distribution, specific surface area, and particle shape, while the main matrix property is stiffness. Segregation, aggregation, and the orientation of anisotropic particles determine the structure. Interfacial interactions lead to the formation of a stiff interphase considerably influencing properties. Interactions are changed by surface modification, which must be always system specific and selected according to its goal. Under the effect of external load, inhomogeneous stress distribution develops around heterogeneities, which initiate local micromechanical deformation processes determining the macroscopic properties of the composites.

## Introduction

Particulate-filled polymers are used in very large quantities in all kinds of applications. The total consumption of fillers in Europe alone is currently estimated as 4.8 million tons (Table 1) (Rothon 2007). In spite of the overwhelming interest in nanocomposites, biomaterials, and natural fiber-reinforced composites, considerable research and development is done on particulate-filled polymers even today. The reason for the continuing interest in traditional composites lays, among others, in the changed role of particulate fillers. In the early days, fillers were added to the polymer to decrease price. However, the ever increasing technical and aesthetical requirements as well as soaring material and compounding costs require the utilization of all possible advantages of fillers. Fillers increase stiffness and heat deflection

**Table 1** Consumption of particulate fillers in Europe in 2007 (Rothon 2007)

| Filler | Amount (ton) |
|---|---|
| Carbon black | 2,000,000 |
| Natural calcium carbonate and dolomite | 1,500,000 |
| Aluminum hydroxide | 250,000 |
| Precipitated silica | 225,000 |
| Talc | 200,000 |
| Kaolin and clay | 200,000 |
| Fumed silica | 100,000 |
| Cristobalite, quartz | 100,000 |
| Precipitated calcium carbonate | 75,000 |
| Calcined clay | 50,000 |
| Magnesium hydroxide | 20,000 |
| Wollastonite | 20,000 |
| Wood flour and fiber | 20,000 |

temperature, decrease shrinkage, and improve the appearance of the composites (Katz and Milevski 1978; Pukánszky 1995). Productivity can be also increased in most thermoplastic processing technologies due to their decreased specific heat and increased heat conductivity (Wong and Bollampally 1999; Weidenfeller et al. 2005). Fillers are very often introduced into the polymer to create new functional properties not possessed by the matrix polymer at all, like flame retardancy or conductivity (Bertelli et al. 1989; Almeras et al. 2003). Another reason for the considerable research activity is that new fillers and reinforcements emerge continuously among other layered silicates (Alexandre and Dubois 2000; Pinnavaia and Beall 2001; Ray and Okamoto 2003), wood flour (Bledzki and Gassan 1999; Bledzki et al. 2002), sepiolite (Bokobza et al. 2004; Bilotti et al. 2008), etc.

The properties of all heterogeneous polymer systems are determined by the same four factors: component properties, composition, structure, and interfacial interactions (Pukánszky 1995, 2000). Although certain fillers and reinforcements including layered silicates, other nanofillers, or natural fibers possess special characteristics, the effect of these four factors is universal and valid for all particulate-filled materials. As a consequence, in this entry we focus our attention on them and discuss the most important theoretical and practical aspects of composite preparation and use accordingly. The general rules of heterogeneous materials apply also for nano- and wood-reinforced composites.

## Factors

All four factors mentioned in the previous section are equally important in the determination of composite properties, and they must be adjusted to achieve optimum performance and economics.

### Component Properties

The characteristics of the matrix strongly influence the effect of the filler on composite properties; reinforcing effect increases with decreasing matrix stiffness. True reinforcement takes place in elastomers, both stiffness and strength increases (Krysztafkiewicz 1988). This effect is demonstrated well by Fig. 1, in which the tensile yield stress of $CaCO_3$ composites is plotted against composition for two different matrices. LDPE is reinforced by the filler, while the yield stress of PVC containing the same filler decreases continuously with increasing filler content (Vörös et al. 1997). For the sake of easier comparison, the data were plotted on a relative scale, related to the yield stress of the matrix. The direction of the change in yield stress or strength is determined by the relative load-bearing capacity of the components (Pukánszky et al. 1988; Pukánszky 1990). In weak matrices, the filler carries a significant part of the load; it reinforces the polymer.

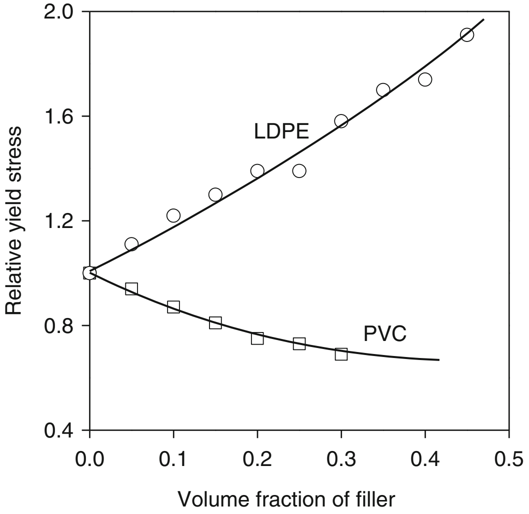


**Fig. 1** Effect of matrix properties on the tensile yield stress of particulate-filled composites. Particle size of $CaCO_3$, R = 1.8 μm

## Composition

Composition, i.e., the filler content of composites may change in a wide range. The effect of changing composition on composite properties is clearly seen in Fig. 1. The interrelation of various factors determining composite properties is also demonstrated by the figure; the same property may change in a different direction as a function of matrix characteristics or interfacial adhesion. The goal of the use of fillers is either to decrease cost or to improve properties, e.g., stiffness, dimensional stability, etc. These goals require the introduction of the largest possible amount of filler into the polymer, but the improvement of the targeted property may be accompanied by the deterioration of others. Since various properties depend in a different way on filler content, composite properties must be always determined as a function of composition.

## Structure

The structure of particulate-filled polymers seems to be simple; the homogeneous distribution of particles in the polymer matrix is assumed in most cases. This, however, rarely occurs and often special, particle-related structures develop in the composites. The most important of these are aggregation and the orientation of anisotropic filler particles.

## Interfacial Interactions

Particle/particle interactions induce aggregation, while matrix/filler interactions lead to the development of an interphase with properties different from those of both components. Secondary, van der Waals forces play a crucial role in the development of both kinds of interactions. They are usually modified by the surface treatment of the filler. Reactive treatment, i.e., coupling, is also used occasionally, although its importance is smaller in thermoplastics than in thermoset matrices.

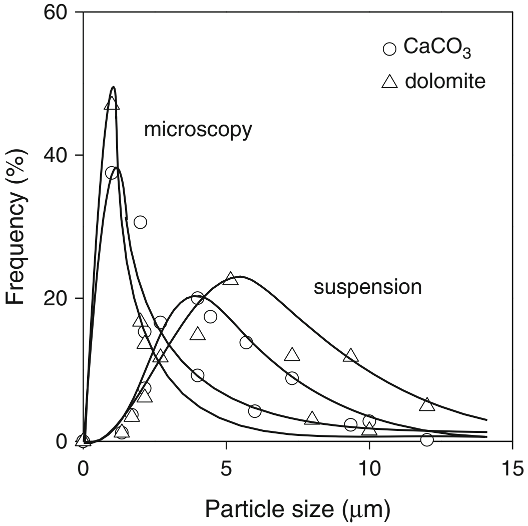
## Filler Characteristics

The chemical composition of fillers, which is usually supplied by the producer as relevant information, is not sufficient for their characterization (Pukánszky 1995); further physical, mostly particle characteristics are needed to forecast their performance in a composite for any application (Pukánszky 1995). A large variety of materials are used as fillers in composites. Besides $CaCO_3$ and carbon black (see Table 1), a large number of other materials like mica (Riley et al. 1990; Verbeek and Christopher 2012), short (Folkes and Wong 1987; Olmos et al. 2011) and long (Voelker 1991; Cilleruelo et al. 2012) glass fibers, glass beads (Meddad and Fisa 1997; Jerabek et al. 2010), sepiolite (Bokobza et al. 2004; Bilotti et al. 2008), magnesium and aluminum hydroxide (Hornsby and Watson 1989; Velasco et al. 2002), wood flour and cellulose (Bledzki and Gassan 1999; Bledzki et al. 2002; Dányádi et al. 2007a, b; Renner et al. 2009, 2010), wollastonite (Hadal et al. 2004a, b), gypsum (Molnár et al. 2009; Imre et al. 2012), clay (Riley et al. 1990), metal powders (aluminum, iron, nickel) (Bigg 1987; Maiti and Mahapatro 1989), steel fibers (Bridge et al. 1988), silicium carbide (Bigg 1987), phenolic microspheres (Zuchowska and Hlavata 1991), and diverse flame retardants (Bajaj et al. 1987) are also mentioned as potential fillers or reinforcements.

### Particle Size and Distribution

The mechanical properties of polymer composites containing uncoated fillers are determined mainly by their particle characteristics. One of the basic information supplied by the manufacturer is average particle size. Particle size has a pronounced influence on composite properties (Nielsen 1974; Pukánszky 1995). Modulus, sometimes strength increase, deformability, and impact resistance usually decrease with decreasing particle size. Particle size itself, however, is not sufficient for the characterization of any filler; the knowledge of the particle size distribution is equally important (Pukánszky 1995). Large particles usually deteriorate the deformation and failure characteristics of composites. Large particles easily debond from the matrix under loading often leading to the premature failure of the part. Debonding stress decreases with increasing particle size (Vollenberg 1987). The other end of the particle size distribution, i.e., the amount of small particles, is equally important. The aggregation tendency of fillers increases with decreasing particle size (Móczó et al. 2003). Extensive aggregation leads to insufficient homogeneity, rigidity, and low impact strength as aggregated filler particles act as crack

**Fig. 2** Particle size distributions of fillers showing a tendency for agglomeration. Dependence of distribution on the method of determination



initiation sites (Riley et al. 1990; Fekete et al. 1999; Móczó et al. 2003; Miltner et al. 2006).

The particle size distribution of fillers is usually determined in dispersion by light scattering. This, however, can be very misleading. The particle size distribution of two fillers is presented in Fig. 2. Both fillers have a tendency for aggregation, since they contain a fraction of small particles, and the particle size distributions determined by sedimentation and microscopy differ significantly from each other. These differences appear also in the properties of the composites.

## Specific Surface Area, Surface Energy

The specific surface area of fillers is closely related to their particle size distribution, and it has a direct impact on composite properties. The adsorption of small molecular weight additives, but also that of the polymer is proportional to the area of the matrix/filler interface (Pukánszky 1995). The adsorption of additives may change stability, while matrix/filler interaction significantly influences mechanical properties, first of all yield stress, tensile strength, and impact resistance (Pukánszky 1990).

The surface free energy of fillers determines both matrix/filler and particle/particle interactions. The former has a pronounced effect on the mechanical properties of the composite; the latter determines aggregation (Pukánszky et al. 1989; Pukánszky 1995). Both interactions can be modified by surface treatment. Nonreactive treatment leads to improved dispersion, but to decreased matrix/filler interaction (Pukánszky et al. 1989), while chemical or physical coupling results in improved strength (Okuno and Woodhams 1975). Some fillers and reinforcements are supplied with surface coating. The amount and character of the coating must be known for the successful application of the filler.

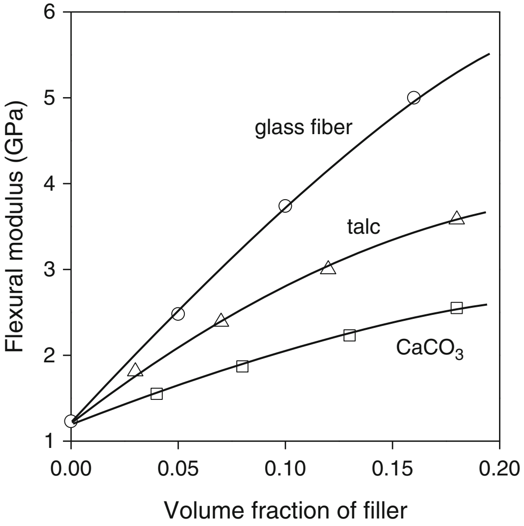


**Fig. 3** Effect of filler anisotropy on the flexural modulus of PP composites (Schlumpf 1983; Ramsteiner and Theysohn 1984)

## Particle Shape

The shape of the particles influences the reinforcing effect of the filler, which increases with the anisotropy of the particle. Fillers and reinforcements are very often differentiated by their degree of anisotropy (aspect ratio). Fillers with platelike geometry like talc, mica, or layered silicates reinforce polymers more than spherical fillers, and the influence of glass fibers is expected to be even stronger (see Fig. 3) (Ramsteiner and Theysohn 1984; Pukánszky 1995). However, based on published papers, it is difficult to obtain a clear picture about the effect of particle characteristics on composite properties for anisotropic fillers. Modulus seems to increase with aspect ratio (Busigin et al. 1984; Riley et al. 1990), although Parrinello (Parrinello 1991) found the stiffness of short-glass-fiber-filled PP to be independent both of the length and the diameter of the fibers. According to Riley (Riley et al. 1990), impact resistance increases with decreasing particle size, since large particles act as flaws, while large aspect ratio is claimed to result in increased stress concentration. Tensile strength is said to decrease with increasing particle size, although (Trotignon et al. 1986) did not observe any change in strength as a function of this characteristic. In spite of these contradictions, or just because of them, it is clear that the aspect ratio and its distribution also must be considered in the application of anisotropic fillers. Anisotropic fillers orientate during processing, and they reinforce the polymer only if their orientation is parallel to the direction of the load. Since orientation is often not determined, the real effect of aspect ratio or particle characteristics in general is difficult to judge.

## Other Characteristics

The *chemical composition* and especially *purity* of fillers have both direct and indirect effects on their application possibilities and performance. Traces of heavy metal contamination decrease the stability of polyolefins (Pukánszky 1995) and lead to the discoloration of the product. Fillers are surface coated in most applications; coupling agents must be chosen according to the chemical characteristics of both the filler and the polymer matrix. The *hardness* of the filler has a strong effect on the wear of the processing equipment (Pukánszky 1995), but the size and shape of the particles, composition, viscosity, and the rate of processing also influence the wear (Pukánszky 1995). The *thermal properties* of fillers usually have beneficiary effect on productivity and processing. Decreased heat capacity and increased heat conductivity decrease cooling time (Pukánszky 1995). Changing overall thermal properties result in the modification of the skin/core morphology of crystalline polymers and the properties of injection-molded parts. On the other hand, large differences in the thermal properties of the components may lead to the development of thermal stresses (Kerch and Irgen 1985; Stoklasa et al. 1985), which might be detrimental to properties.

Fillers are frequently added to polymers to achieve *functional properties* not possessed by the matrix polymer itself, like flame retardancy and conductivity (Bajaj et al. 1987; Bertelli et al. 1989; Hornsby and Watson 1989; Weidenfeller et al. 2005). The particle characteristics and physical properties of these additives have the same influence on the properties of composites as those of simple fillers. The characteristics of these modifiers must be optimized in order to achieve the desired goal, i.e., to produce composites with a given functional property but acceptable mechanical characteristics and aesthetics at the same time.

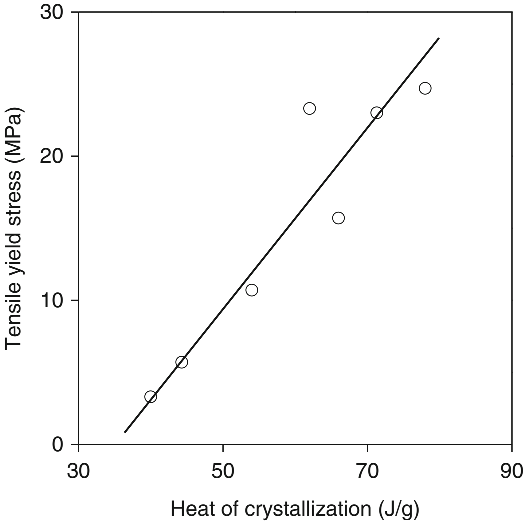
## Structure

Although the structure of particulate-filled polymers is usually thought to be very simple, often structure-related phenomena determine their properties. Structure is strongly influenced by the particle characteristics of the filler, the composition, and the processing technology used. The most important structure-related phenomena are homogeneity, the attrition of the filler or reinforcement, aggregation, and the orientation of anisotropic particles. Occasionally, fillers might modify the structure of crystalline polymers as well. All structure-related effects must be controlled in order to prepare products of high quality.

### Crystalline Matrices, Nucleation

The properties of crystalline polymers are determined by the relative amount of the amorphous and crystalline phases, crystal modification, the size and perfection of crystallites, the dimensions of spherulites, and the number of tie molecules (Samuels 1974). The most important effect of particulate fillers is their ability to act as nucleating agents. The very strong nucleating effect of talc in PP was proved many times (Menczel and Varga 1983; Fujiyama and Wakino 1991). Similarly to talc, layered silicates, and especially montmorillonite (MMT), were shown to

**Fig. 4** Correlation between the heat of crystallization and yield stress of PP/$CaCO_3$ composites (Maiti and Mahapatro 1990)



nucleate polypropylene quite strongly (Maiti et al. 2002; Pozsgay et al. 2002). The influence of other fillers and reinforcements is not so clear. Many fillers have shown weak nucleation effect in PP (Rybnikar 1991; Avella et al. 2006), while some others have shown no effect (Bajaj et al. 1987). A closer scrutiny of literature information and experimental data indicates that mostly physical and especially topological factors determine the nucleation effect of fillers. Fillers may influence also the crystal modification of the matrix. Introduction of talc into the β-modification of PP resulted in a complete change of crystalline structure; the higher crystallization temperature of the α-modification prevented the formation of the β-form (Varga and Tóth 1991). Similarly, in the presence of montmorillonite, polyamide was shown to crystallize mainly in the γ-form (Lincoln et al. 2001; Miltner et al. 2006) irrespective of the presence and/or type of organophilization (Choi et al. 2006).

Occasionally, strong correlation is claimed between the crystalline structure of the matrix and composite properties. (Hutley and Darlington 1984) found a more or less linear correlation between the crystallization temperature and the falling weight impact strength of particulate-filled PP, while (Maiti and Mahapatro 1990) observed an even better linear correlation between the crystallinity and tensile characteristics of PP filled with $CaCO_3$ (Fig. 4). However, the similar effect of the filler on two or more composite characteristics might lead to the linear correlation between tensile yield stress and crystallinity as observed by (Maiti and Mahapatro 1990) and often to erroneous conclusions. The detailed analysis of experimental results obtained on PP composites containing different fillers indicated that the effect of changes in crystalline structure may be neglected especially at large filler contents (Pukánszky et al. 1994a). A very efficient nucleating agent may change the modulus of PP from 1.4 to 1.9 GPa (Pukánszky et al. 1997), while the introduction of 30 vol.% talc results in a composite with a stiffness of almost 8 GPa (Pukánszky et al. 1994a).

## Segregation, Attrition

The segregation of a second phase during processing was observed in some heterogeneous polymer systems (Kubát and Szalánczi 1974; Karger-Kocsis and Csikai 1987). (Kubát and Szalánczi 1974) investigated the separation of phases during the injection molding of polyethylene and polyamide using the spiral test. The two polymers contained large glass spheres of 50–100 μm size and extremely long flow paths up to 1.6 m. They found that considerable segregation took place along the flow path; the glass content of a composite containing 25 wt% filler exceeded 40% locally at the end of the mold. Segregation was observed also across the cross section of the sample; the amount of filler was larger in the core than at the walls. Segregation depended on filler content and it became more pronounced with increasing size of the particles. The possible segregation of talc particles dispersed in a PP matrix was investigated under more practical conditions in injection-molded specimens of 4 × 10 × 150 mm dimensions. No differences were detected in filler content as a function of position; the particles were homogeneously distributed in the PP matrix independently of average filler content. Under practical conditions (small particles, relatively high filler content, normal flow path), segregation is of secondary importance; the filler is usually homogeneously distributed in the matrix polymer.

Another structure-related phenomenon is the change of particle dimensions during processing. The attrition of fibers, i.e., the change of fiber length and length distribution, is an intensively studied question in short-fiber-reinforced composites (Gupta et al. 1989). Attrition may occur also in composites filled with anisotropic particles with platelike geometry, e.g., mica and talc. The cleavage of these fillers is relatively easy, and considerable delamination may take place during processing, especially in injection molding at the very high shear stresses developing (Tausz and Chaffey 1982). Delamination of mica particles was shown to improve most properties, but decreasing particle size may lead to aggregation (Busigin et al. 1984). Contrary to traditional fillers, delamination or exfoliation would be very advantageous in layered silicate nanocomposites.

## Aggregation

Aggregation is a well-known phenomenon in particulate-filled composites. Experience has shown that the probability of aggregation increases with decreasing particle size of the filler. The occurrence and extent of aggregation is determined by the relative magnitude of the forces which hold together the particles, on the one hand, or try to separate them, on the other. Particulate-filled polymers are prepared by the melt mixing of the components; thus, the major attractive and separating forces must be considered under these conditions.

When two bodies enter into contact, they are attracted to each other. The strength of adhesion between two particles is determined by their size and surface energy (Adams and Edmondson 1987; Adams et al. 1987), i.e.,

$$F_a = \frac{3}{2}\pi W_{AB} R_a \tag{1}$$

where $F_a$ is the adhesive force between the particles, $W_{AB}$ is the reversible work of adhesion, and $R_a = R_1\,R_2/(R_1 + R_2)$ is an effective radius for particles of different sizes. In the presence of fluids, i.e., in suspensions, but also in the polymer melt during homogenization, further forces act among the particles. Depending on the extent of particle wetting, (Adam and Edmondson 1987) specify two attractive forces. When wetting is complete, viscous force ($F_v$) acts between particles separating them from each other with a constant rate. $F_v$ depends on the viscosity of the fluid, on separation rate, and on the initial distance of the particles. The viscous force might have some importance during the homogenization of composites. If the particles are wetted only partially by the fluid (melt), liquid bridges form and capillary forces develop among them. Four main types of electrostatic forces can hold charged particles together: Coulomb, image charge, space charge, and dipole forces (Balachandran 1987). The magnitude of all four is around $10^{-7}$–$10^{-8}$ N; they are significantly smaller than other forces acting among filler particles.

The number of forces separating the particles is smaller. Repulsive forces may act between particles with the same electrostatic charge. The mixing of fluids leads to the development of shear forces, which try to separate the particles. The maximum hydrodynamic force acting on spheres in a uniform shear field can be expressed as (Adams and Edmondson 1987)

$$F_h = -612\,\pi\,\eta\,R^2\dot{\gamma} \tag{2}$$

where $\eta$ is melt viscosity and $(\dot{\gamma})$ is shear rate.

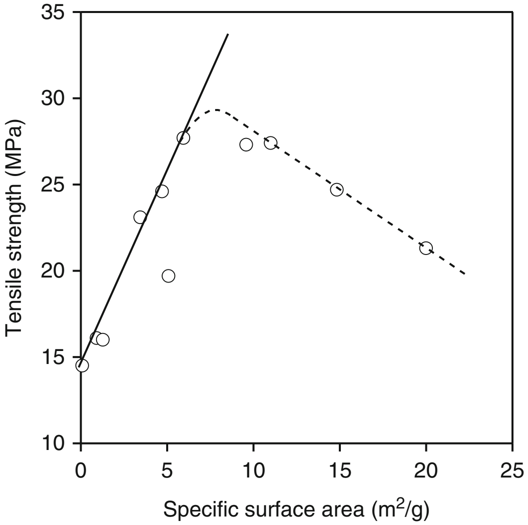
Both adhesive and hydrodynamic forces depend on the size of the particles. The estimation of the two forces by Eqs. 1 and 2 shows that below a certain particle size adhesion exceeds shear forces and the particles aggregate in the melt. Since commercial fillers have a relatively broad particle size distribution, most fillers aggregate to some extent, and the exact determination of the critical particle size, or any other filler characteristics at which aggregation appears, is difficult.

Since the relative magnitude of adhesive and shear forces determine the occurrence and extent of aggregation in a composite, the ratio of the two forces gives information about the possibilities to avoid or decrease it, i.e.,

$$\frac{F_a}{F_h} = k\frac{W_{AB}}{\eta\,\dot{\gamma}\,R} \tag{3}$$

where $k$ includes all constants of Eqs. 1 and 2. Increasing shear rate and particle size will result in decreased aggregation. Naturally, both can be changed only in a limited range, since excessive shear leads to degradation, while large particles easily debond from the matrix under the effect of external load leading to inferior composite

**Fig. 5** Strength of PP/$CaCO_3$ composites plotted as a function of the specific surface area of the filler. Effect of aggregation



properties. According to Eq. 3, smaller reversible work of adhesion also improves homogeneity. Nonreactive surface treatment invariably leads to the decrease of surface tension and $W_{AB}$ (see section "Type and Strength of Interaction"), thus to decreased aggregation, improved processability, and mechanical properties.

The presence of aggregates is practically always detrimental to the properties of composites as shown in Fig. 5. The strength of PP/$CaCO_3$ composites initially increases with increasing specific surface area of the filler, but it strongly decreases when aggregation takes place at small particle sizes. The effect is even more pronounced for impact properties; the fracture resistance of composites containing aggregated particles drastically decreases with increasing number of aggregates (Riley et al. 1990). Aggregates may act as fracture initiation sites, and depending on aggregate strength (Fekete et al. 1999; Móczó et al. 2003), they may break under the effect of external load, which results in the failure of the product. The phenomenon is demonstrated by Fig. 6 showing the initiation and propagation of a crack through an aggregate in a PP/$CaCO_3$ composite containing small particles.

## Orientation of Anisotropic Particles

Another processing-induced structural phenomenon is the orientation of anisotropic particles. Both the phenomenon and the resulting structure are similar in short-fiber-reinforced and particulate-filled composites. Platelike planar reinforcements, however, have some advantages over fibers; the orientation-dependent shrinkage of particulate-filled composites is significantly smaller than that of the fiber-reinforced

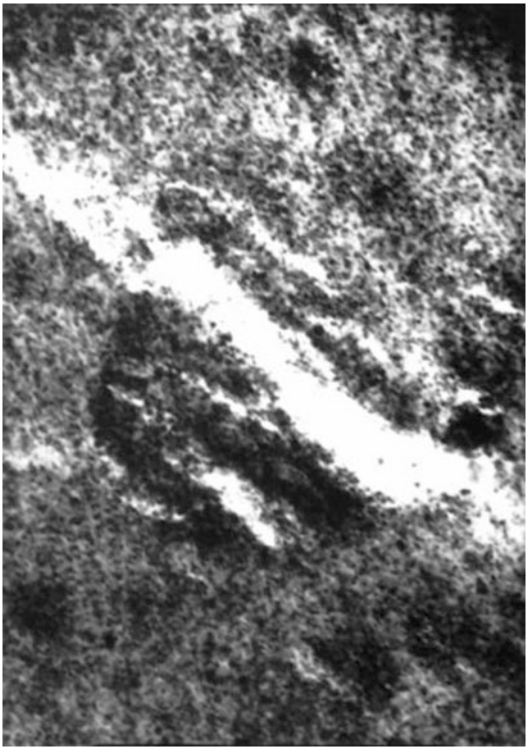


**Fig. 6** Initiation and propagation of a crack through an aggregate of $CaCO_3$ particles in a PP composite

ones (Pukánszky 1995). Orientation and orientation distribution strongly influence property distribution and the overall performance of the product (Kamal et al. 1986).

The orientation distribution of fibers and anisotropic particles is determined by the flow pattern and shear forces developing during processing (Sanou et al. 1985). Orientation is observed both in extrusion (Rockenbauer et al. 1985) and in injection molding, and even the relatively mild shearing conditions of compression molding may induce the orientation of filler particles (Rockenbauer et al. 1985). In injection-molded PP/talc composites, parallel orientation was observed at the wall, while more random distribution in the middle of the injection-molded plates. Average orientation shows significant composition dependence (Rockenbauer et al. 1985). The average orientation of particles relative to the direction of the external load determines properties. Increasing alignment results in increased reinforcement, i.e., larger modulus, yield stress, and impact strength (Mittal et al. 1987) (see Fig. 7).

The orientation of anisotropic filler particles has an especially pronounced effect on the strength of injection-molded parts containing weld lines. Fountain flow in the mold leads to the orientation of particles parallel with the melt front resulting in decreased weld line strength (Christie 1986). Increasing particle size and filler content result in a decrease of the weld line strength (Christie 1986), which can be

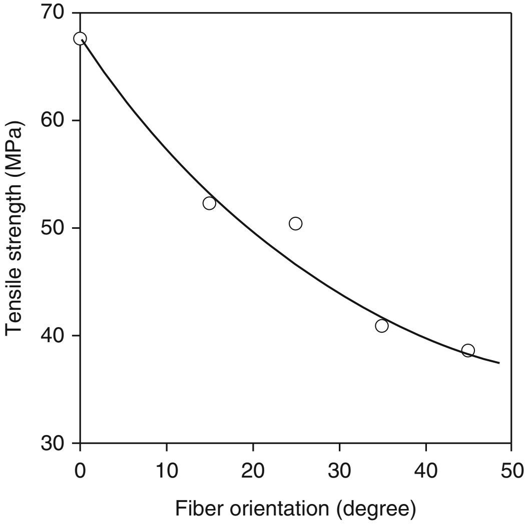


**Fig. 7** Effect of fiber orientation (alignment to external stress) on the strength of short-glass-fiber-reinforced PP composites (Mittal et al. 1987)

improved by changing particle characteristics (size, treatment, aspect ratio) (Christie 1986; Fisa et al. 1987) and mold construction.

## Interfacial Interactions, Interphase

Interfacial interactions play a decisive role in the determination of the mechanical properties of particulate-filled polymers, but they strongly influence other characteristics like processability or aesthetics as well.

### Type and Strength of Interaction

Both the polymers used as matrices in particulate-filled composites and the fillers or reinforcements have the most diverse physical and chemical structures; thus, a wide variety of interactions may form between them. Two boundary cases of interactions can be distinguished: covalent bonds, which rarely form spontaneously, but can be created by special surface treatments, and zero interaction, which does not exist in reality, since at least secondary, van der Waals forces always act between the components. In practice, the strength of the interaction is somewhere between the two boundary cases.

The theory of adsorption interaction is applied most widely for the description of interaction in particulate-filled or reinforced polymers. The approach is based on the theory of contact wetting, in which interfacial adhesion is created by secondary forces. Accordingly, the strength of the adhesive bond is assumed to be proportional to the reversible work of adhesion ($W_{AB}$), which is necessary to separate two phases with the creation of new surfaces. The Dupré equation relates $W_{AB}$ to the surface ($\gamma_A$ and $\gamma_B$) and interfacial ($\gamma_{AB}$) tension of the components in the following way

$$W_{AB} = \gamma_A + \gamma_B - \gamma_{AB} \tag{4}$$

Unfortunately, interfacial tension cannot be measured directly; it is usually derived from thermodynamic calculations. (Fowkes 1964) assumed that surface tension can be divided into components, which can be determined separately. The theory can be applied relatively easily for apolar interactions when only dispersion forces act between surfaces. Its generalization for polar interactions is more complicated and the geometric mean approximation gained the widest acceptance. This considers only the dispersion and a polar component of surface tension, but the latter includes all polar interactions (Wu 1974). According to the approach, interfacial tension can be calculated as

$$\gamma_{AB} = \gamma_A + \gamma_A - 2(\gamma_A\gamma_B)^{1/2} - 2(\gamma_A\gamma_B)^{1/2} \tag{5}$$

The surface tension of two thermoplastics and three fillers are listed in Table 2. Large differences can be observed both in the dispersion, but especially in the polar component. The surface tension of the majority of polymers is in the same range as shown in Table 2, in fact between that of PP and PMMA. The examples listed in the table represent the most important particulate fillers and reinforcements used in practice, since clean glass fibers possess similar surface tensions as $SiO_2$.

Although Eq. 5 tries to take into account the effect of the polarity of the surfaces to some extent, the role of acid–base interactions in adhesion became clear and theories describing them are more and more accepted. Fowkes (1981) suggested that the reversible work of adhesion should be defined as

$$W_{AB} = W_{AB}^{d} + W_{AB}^{ab} + W_{AB}^{p} \tag{6}$$

where $W_{AB}$ ab is the part of the reversible work of adhesion created by acid–base interactions. According to Fowkes, the polar component can be neglected, i.e., $W_{AB}$ p∼0; thus $W_{AB}$ can be expressed as

**Table 2** Surface tension of selected polymers and fillers, dispersion ($\gamma^{d}$) and polar ($\gamma^{p}$) components

| Material | Surface tension (mJ/m$^2$) | | |
|---|---|---|---|
| | $\gamma^d$ | $\gamma^p$ | $\gamma$ |
| PP[a] | 32.5 | 0.9 | 33.4 |
| PMMA[a] | 34.3 | 5.8 | 40.1 |
| $CaCO_3$[b] | 54.5 | 153.4 | 207.9 |
| Talc[c] | 49.3 | 90.1 | 139.4 |
| $SiO_2$[c] | 94.7 | 163.0 | 257.7 |

[a] Contact angle
[b] IGC
[c] Gravimetric measurement

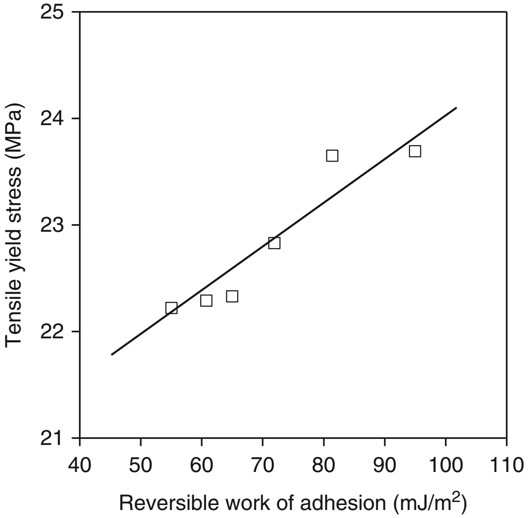


**Fig. 8** Effect of interfacial adhesion on the tensile yield stress of PP/$CaCO_3$ (covered with different amounts of stearic acid surfactant) composites; filler: $CaCO_3$, $\varphi_f = 0.1$, R = 0.9 µm

$$W_{AB} = 2\left(\gamma_A^d \gamma_B^d\right)^{1/2} + nf\,\Delta H^{ab} \tag{7}$$

where $\Delta H_{ab}$ is the change in free enthalpy due to acid–base interactions, $n$ is the number of moles interacting with a unit surface, and $f$ is a conversion factor, which takes into account the difference between free energy and free enthalpy ($f \sim 1$) (Fowkes 1981). The enthalpy of acid–base interaction, $\Delta H_{ab}$, necessary for the determination of the specific component of the reversible work of adhesion, can be calculated from the acid–base constants of the interacting phases by using the theory of (Drago et al. 1971) or (Guttman 1978).

In most cases, the strength of the adhesive bond is characterized acceptably by the reversible work of adhesion values calculated by the above theory. Often, especially in apolar systems, a close correlation exists between $W_{AB}$ and the macroscopic properties of the composite (Fig. 8). In spite of the imperfections of the approach, the reversible work of adhesion can be used for the characterization of matrix/filler interactions in particulate-filled polymers. The quantities necessary for the calculation of $W_{AB}$ can be determined by inverse gas chromatography (Fekete et al. 2004), while parameters related to interfacial adhesion can be derived from appropriate models (Pukánszky 1990; Pukánszky and Maurer 1995).

## Interphase Formation

As Table 2 shows, nontreated fillers and reinforcements have high-energy surfaces. During the almost exclusively used melt mixing procedure, the forces discussed in the previous section lead to the adsorption of polymer chains onto the active sites of the filler surface. The adsorption of polymer molecules results in the development of a layer which has properties different from those of the matrix polymer (Stamhuis and Loppe 1982; Maurer et al. 1985; Vollenberg and Heikens 1989). Although the character, thickness, and properties of this interlayer or interphase are much discussed topics, its existence is an accepted fact now.

The overall properties of the interphase, however, are not completely clear. Based on model calculations, the formation of a soft interphase is claimed (Maurer 1986), while in most cases the increased stiffness of composites is explained at least partly with the presence of a stiff interphase (Pukánszky 1990; Maiti and Mahapatro 1991). The contradiction obviously stems from two opposing effects. The imperfection of the crystallites and decreased crystallinity of the interphase should lead to smaller modulus and strength, as well as to larger deformability (Maurer et al. 1985). Adhesion and hindered mobility of adsorbed polymer chains, on the other hand, decrease deformability and increase the strength of the interlayer.

The thickness of the interphase is a similarly intriguing and contradictory question. It depends on the type and strength of the interaction, and values from 10 Å to several microns have been reported in the literature for the most diverse systems (Iisaka and Shibayama 1978; Maurer et al. 1982; Pukánszky et al. 1989; Akay 1990; Pukánszky and Tüdős 1990; Mansfield and Theodorou 1991; Vörös et al. 1997; Móczó et al. 2002). Since interphase thickness is calculated or deduced indirectly from measured quantities, it depends also on the method of determination. Table 3 presents some data for different particulate-filled polymers. Thermodynamic considerations and extraction experiments yield interphase thicknesses which are not influenced by the extent of deformation. In mechanical measurements, however, the

**Table 3** Interphase thickness in particulate-filled polymers determined by different techniques

| Matrix polymer | Filler | Method of determination | Thickness (μm) | Reference[a] |
|---|---|---|---|---|
| HDPE | $SiO_2$ | extraction | 0.0036 | 1 |
| HDPE | $SiO_2$ | extraction | 0.0036 | 2 |
| PP | $SiO_2$ | extraction | 0.0041 | 2 |
| PP | Graphite | Model calc. | 0.001 | 3 |
| PS | Mica | Dyn. mech. meas. | 0.06 | 4 |
| PMMA | Glass | Dyn. mech. meas. | 1.4 | 4 |
| PP | $CaCO_3$ | Young's modulus | 0.012 | 5 |
| PP | $CaCO_3$ | Tensile strength | 0.15 | 5 |
| PP | $CaCO_3$ | Tensile yield stress | 0.16 | 5 |
| PP | $CaCO_3$ | Tensile yield stress | 0.12 | 6 |
| LDPE | $CaCO_3$ | Tensile yield stress | 0.11 | 6 |
| PMMA | $CaCO_3$ | Tensile yield stress | 0.18 | 6 |
| PVC | $CaCO_3$ | Tensile yield stress | 0.23 | 6 |

[a] 1. Maurer et al. (1982)
2. Akay (1990)
3. Mansfield and Theodorou (1991)
4. Iisaka and Shibayama (1978)
5. Pukánszky and Tüdős (1990)
6. Móczó et al. (2002)

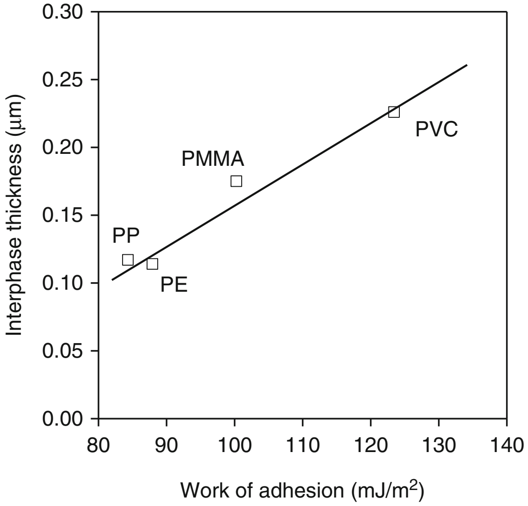


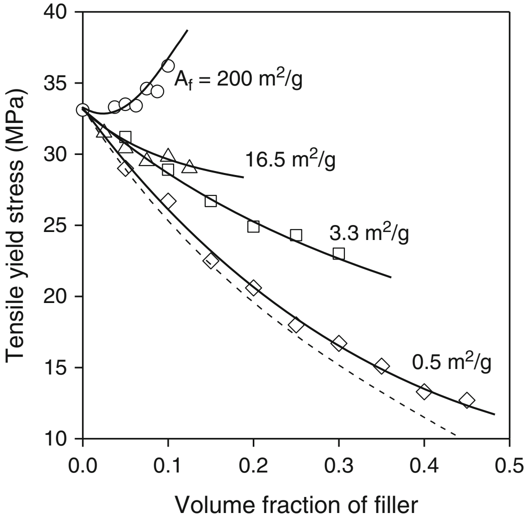
**Fig. 9** Effect of interfacial interactions on the thickness of the interlayer formed spontaneously in polymer/$CaCO_3$ composites

material is always deformed even during the determination of modulus. The role and effect of immobilized chain ends increase with increasing deformation, and the determined interphase thickness increases as well, which proves that chains are attached to the surface of the filler indeed (see Table 3).

The thickness of the interphase depends on the strength of the interaction. Interphase thicknesses derived from mechanical measurements are plotted as a function of $W_{AB}$ in Fig. 9 for $CaCO_3$ composites prepared with four different matrices: PVC, plasticized PVC (pPVC), PP, and LDPE. Acid–base interactions were also considered in the calculation of $W_{AB}$ (Móczó et al. 2002). The thickness of the interphase changes linearly with increasing adhesion. The figure proves several of the points mentioned above. The reversible work of adhesion adequately describes the strength of the interactions created mostly by secondary forces, and the thickness of the interphase is closely related to the strength of interaction.

The amount of polymer bonded in the interphase depends on the thickness of the interlayer and on the size of the contact area between the filler and the polymer. Interface area is related to the specific surface area of the filler ($A_f$), which is inversely proportional to particle size. Modulus shows only a very weak dependence on the specific surface area of the filler (Pukánszky 1992). Properties measured at larger deformations, e.g., tensile yield stress or tensile strength, depend much stronger on $A_f$ than modulus (Pukánszky 1992). Figure 10 shows that yield stresses larger than the corresponding value of the matrix can be achieved, i.e., even spherical fillers can reinforce polymers (Pukánszky 1990). If adhesion is strong, yielding should be initiated at the matrix value and no reinforcement would be possible. The reinforcing effect of spherical particles can be explained only with the presence of a hard interphase having properties somewhere between those of the polymer and the filler (Pukánszky 1990).

**Fig. 10** Effect of the size of the interfacial area on the yield stress of PP/$CaCO_3$ composites



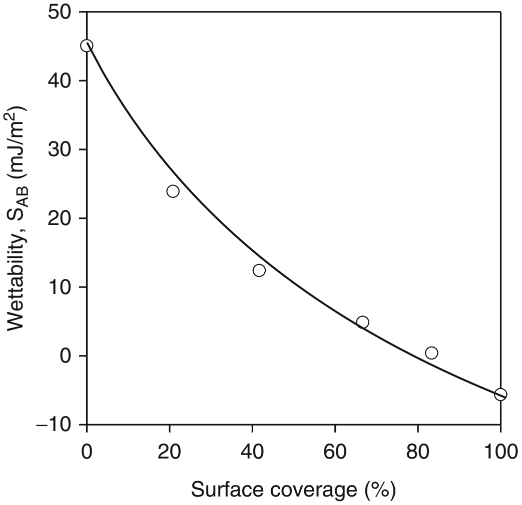
## Wetting

The maximum performance of a composite can be achieved only if the wetting of the filler or reinforcement by the polymer is perfect (Gutowski 1990; Felix and Gatenholm 1991). The nonreactive treatment of fillers with surfactants is claimed to improve wettability due to changing polarity. The improvement in mechanical properties as an effect of coating is often falsely interpreted as the result of better wetting and interaction. However, according to (Fox et al. 1955), the wetting of a high-energy solid by a low surface tension fluid is always complete. This condition is completely satisfied by polymers, including apolar ones like PP or PE, and all inorganic fillers (see Table 2). If wettability is characterized by the thermodynamic quantity

$$S_{AB} = \gamma_A - \gamma_B - \gamma_{AB} \tag{8}$$

where $\gamma_A > \gamma_B$, wettability decreases on surface treatment due to the drastic decrease of the surface tension of the filler. The correlation is demonstrated by Fig. 11 where $S_{AB}$ is plotted against the surface coverage of a $CaCO_3$ filler with stearic acid (Móczó et al. 2004). The larger the $S_{AB}$ is, the better the wettability is, and in the case of negative values, definite contact angle develops (partial wetting). As a consequence, wetting becomes poorer on surface coating, but it results in weaker interactions at the same time, which lead to a considerable decrease in aggregation, better dispersion and homogeneity, easier processing, and good mechanical properties and appearance. However, wetting has also kinetic conditions, which depend on the viscosity of the polymer, processing technology, and particle characteristics, which might not

**Fig. 11** Wettability of $CaCO_3$ by PP and its dependence on the surface coverage of the filler with stearic acid



always be optimal during composite preparation. As a consequence particle-related problems (debonding, aggregation) and insufficient homogenization usually create more problems than wetting.

## Surface Modification

The easiest way to change interfacial interactions is the surface coating of fillers. Surface modification is often regarded as a magic, which solves all problems of processing technology and product quality, but it works only if the compound used for the treatment (coupling agent, surfactant, etc.) is selected according to the characteristics of the components and the goal of the modification. Surface treatment modifies both particle/particle and matrix/filler interactions, and the properties of the composite are determined by the combined effect of the two. Besides its type, also the amount of the surfactant or coupling agent must be optimized both from the technical and the economical point of view.

### Nonreactive Treatment

The oldest and most often used modification of fillers is the coverage of their surface with a small molecular weight organic compound (Móczó et al. 2002, 2004; Fekete et al. 2004). Usually, amphoteric surfactants are used which have one or more polar groups and a long aliphatic tail. Typical example is the surface treatment of $CaCO_3$ with stearic acid (Pukánszky et al. 1989; Móczó et al. 2002, 2004; Fekete et al. 2004). The principle of the treatment is the preferential adsorption of the surfactant onto the surface of the filler. The high-energy surfaces of inorganic fillers (see Table 2) can often enter into special interactions with the polar group of the surfactant. Preferential adsorption is promoted to a large extent by the formation of ionic bonds between stearic acid and the surface of $CaCO_3$ (Fekete et al. 1990), but in other cases hydrogen or even covalent bonds may also form. Surfactants diffuse to the surface of the filler even from the polymer melt, which is a further proof for preferential adsorption (Marosi et al. 1987).

One of the crucial questions of nonreactive treatment, which, however, is very often neglected, is the amount of surfactant to use. It depends on the type of the interaction, the surface area occupied by the coating molecule, its alignment to the surface, the specific surface area of the filler, and some other factors. The determination of the optimum amount of surfactant is essential for efficient treatment. Insufficient amount does not achieve the desired effect, while excessive quantities lead to processing problems as well as to the deterioration of the mechanical properties and appearance of the product (Fekete et al. 1990). The amount of bonded surfactant can be determined by simple techniques. A dissolution method proved to be very convenient for the optimization of nonreactive surface treatment and for the characterization of the efficiency of the coating technology as well (Fekete et al. 1990). First, the surface of the filler is covered with increasing amounts of surfactant, and then the nonbonded part is dissolved with a solvent. The technique is demonstrated in Fig. 12, which presents a dissolution curve showing the adsorption of stearic acid on $CaCO_3$. Surface coating is preferably carried out with the irreversibly bonded surfactant ($C_{100}$); at this composition, the total amount of surfactant used for the treatment is bonded to the filler surface. The filler can adsorb more surfactant ($C_{max}$), but during compounding a part of it can be removed from the surface and might deteriorate properties. The specific surface area of the filler is an

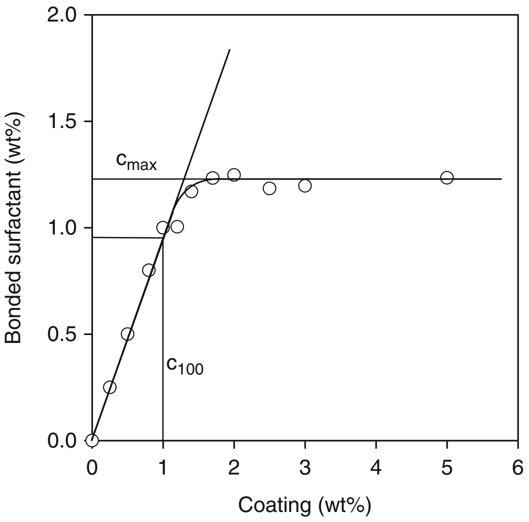


**Fig. 12** Dissolution curve used for the determination of surfactant adsorption on a filler. $CaCO_3$/stearic acid

important factor which must be taken into consideration during surface treatment. The irreversibly bonded surfactant depends linearly on it (Fekete et al. 1990).

As a result of the treatment, the surface free energy of the filler decreases drastically (Pukánszky et al. 1989; Fekete et al. 2004; Móczó et al. 2004). Smaller surface tension means decreased wetting (see Fig. 11), interfacial tension, and reversible work of adhesion (Fekete et al. 1990). Such changes in the thermodynamic quantities result in a decrease of both particle/particle and matrix/particle interaction. One of the main goals, major reasons, and benefits of nonreactive surface treatment is the first effect, i.e., to change interactions between the particles of fillers and reinforcements. As an effect of nonreactive treatment, not only particle/particle but matrix/filler interaction decreases as well. The consequence of this change is decreased yield stress and strength as well as improved deformability (Pukánszky et al. 1989; Jancár and Kucera 1990a). Strong interaction, however, is not always necessary or advantageous for the preparation of composites with desired properties; the plastic deformation of the matrix is the main energy absorbing process in impact, which increases with decreasing strength of adhesion (Allard et al. 1989; Pukánszky and Maurer 1995).

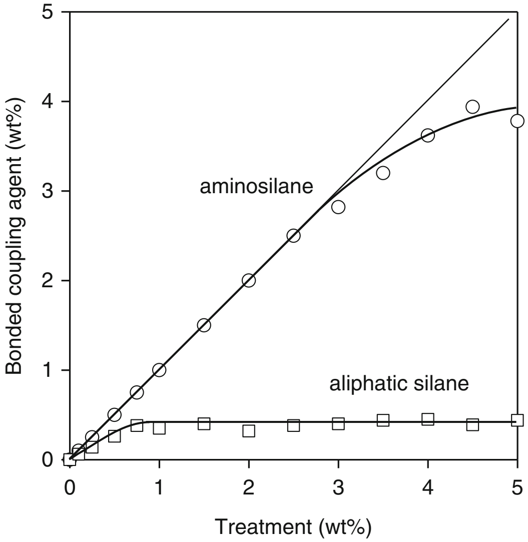
## Coupling

Successful reactive treatment assumes that the coupling agent reacts and forms covalent bonds with both components. Silane coupling agents are successfully applied for fillers and reinforcements which have reactive –OH groups on their surface, e.g., glass fibers, glass flakes and beads, mica, and other silica fillers (Matienzo and Shah 1986; Trotignon et al. 1986). The use of silanes with fillers like $CaCO_3$, $Mg(OH)_2$, wood flour, etc., were tried, but often proved to be unsuccessful (Vollenberg and Heikens 1990); sometimes, contradictory results were obtained even with glass and other siliceous fillers (Mäder and Freitag 1990). Acidic groups are preferable for $CaCO_3$, $Mg(OH)_2$, $Al(OH)_3$, and $BaSO_4$. Talc cannot be treated successfully either with reactive or nonreactive agents because of its inactive surface; only broken surfaces contain a few active –OH groups.

The adsorption of organofunctional silanes is usually accompanied by their polycondensation. The adsorbed amount of coupling agent, the structure, properties, and adhesion of the polysiloxane layer depend very much on the chemical composition of the organofunctional group of the silane. This is obvious if we compare the dissolution curve of two silanes, an aliphatic and an aminosilane, respectively, on $CaCO_3$ (Fig. 13). The different chemical structure of the silanes leads to considerably different adsorption isotherms. The figure shows also that the simple dissolution technique can be advantageously applied for the study of reactive coupling agents as well (Demjén et al. 1997).

Although the chemistry of silane modification of reactive silica fillers is well documented, much less is known about the interaction of silanes with polymers. Thermoplastics rarely contain reactive groups; thus, they cannot react chemically with silanes. Polycondensation polymers are the most reactive, and literature sources

**Fig. 13** Effect of the chemical structure of silane coupling agents on their adsorption on the surface of a $CaCO_3$ filler. Particle size 1.25 μm



offer sufficient evidence of reactive coupling, indeed. The strength of polyamide and polycarbonate composites increases on aminosilane treatment (Sadler and Vecere 1995; Zolotnitsky and Steinmetz 1995). Reactive treatment is the most difficult in polyolefins, since they do not contain any reactive groups. Some results indicate that polypropylene oxidizes during processing even in the presence of stabilizers, and the formed acidic groups react with aminosilanes resulting in reactive coupling (Demjén et al. 1999).

Considering the complexity of the chemistry involved, it is not surprising that the amount of coupling agent and surface coverage have an optimum here too, similarly to surfactants in nonreactive surface treatment. The optimization of the type and amount of coupling agent is crucial also in reactive treatment, and although "proprietary" coatings might lead to some improvement in properties, they are not necessarily optimal or cost-effective. The improper choice of coupling agent may result in insufficient or even deteriorating effects. In some cases, hardly any change is observed in properties, or the effect can be attributed unambiguously to the decrease of surface tension due to the coverage of the filler surface by an organic substance, i.e., to nonreactive treatment (Bajaj et al. 1989).

## Functionalized Polymers

The coverage of filler surface with a polymer layer which is capable of interdiffusion with the matrix proved to be very effective both in stress transfer and in forming a thick diffuse interphase with acceptable deformability. In this treatment, the filler is usually covered by a functionalized polymer, preferably with the same chemical

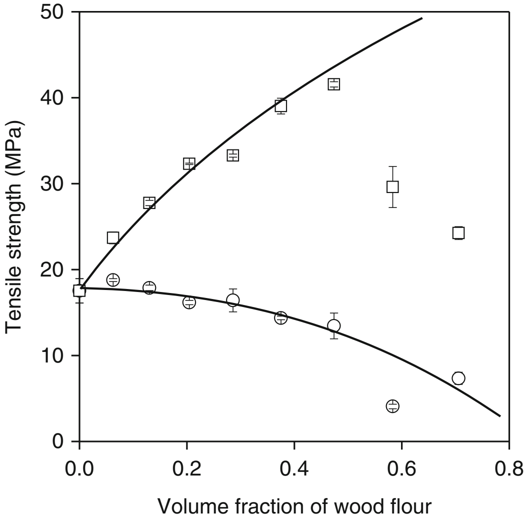


**Fig. 14** Dependence of the tensile strength of PP/wood flour composites on wood content and adhesion symbols: (○) poor adhesion, (□) good adhesion

structure as the matrix. The functionalized polymer is attached to the surface of the filler by secondary, hydrogen, ionic, and sometimes covalent bonds. The polymer layer interdiffuses with the matrix, entanglements form, and strong adhesion is created. Because of their polarity, in some cases reactivity, maleic anhydride or acrylic acid-modified polymers are often used for this purpose. The coupling agent adsorbs onto the surface of most polar fillers even from the melt. This treatment is frequently used in polyolefin composites, in which other treatments usually fail. Often, very small amounts of modified polymer (1–3 wt%) are sufficient to achieve significant improvement in stress transfer (Takase and Shiraishi 1989). The maximum effect of functionalized PP was found with fillers of high-energy surfaces (Chiang and Yang 1988) or with those capable for specific interactions, e.g., ionic bond with $CaCO_3$ (Jancár and Kucera 1990b) or chemical reaction with wood flour, kraft lignin, or cellulose (Takase and Shiraishi 1989). Figure 14 demonstrates the successful use of functionalized polymer in PP composites modified with wood flour.

## Soft Interlayer

The introduction of hard particles into the polymer matrix creates stress concentration, which induces local micromechanical deformation processes. Occasionally, these might be advantageous for increasing plastic deformation and impact resistance, but they usually deteriorate the properties of the composite. The encapsulation of the filler particles by an elastomer layer changes the stress distribution around the particles and modifies local deformation processes. Encapsulation can take place spontaneously, it can be promoted by the use of functionalized elastomers or the filler can be treated in advance. Such a surface modification is rarely done directly by covering the filler with a soft layer, but forms spontaneously during the preparation of multicomponent polymer/filler/elastomer composites (Pukánszky 1995; Vörös and Pukánszky 2001).

## Micromechanical Deformations

The introduction of fillers or reinforcements into a polymer matrix results in a heterogeneous system. Under the effect of external load, heterogeneities induce stress concentration, the magnitude of which depends on the geometry of the inclusions, the elastic properties of the components, and interfacial adhesion (Goodier 1933). Heterogeneous stress distribution and local stress maxima initiate local micromechanical deformations, which determine the deformation and failure behavior, as well as the overall performance of the composites. Stress concentration and local stress distribution can be estimated by the use of theoretical models or by finite element analysis (Bucknall 1977; Pukánszky and Vörös 1993). The interacting stress fields of neighboring particles are very complicated and change with composition. The most often used approach is the analysis of stresses around a single particle embedded in an infinite matrix, which was first proposed by (Goodier 1933). According to his model, radial stress has a maximum at the pole, where it exceeds almost twice the external stress. Micromechanical deformation processes initiated by local stress maxima around the particles are influenced also by thermal stresses induced by the different thermal expansion coefficients of the components, crystallization, or shrinkage during the curing of thermoset matrices (Kerch and Irgen 1985; Stoklasa et al. 1985). Although the importance of inhomogeneous stress distribution developing in particulate-filled composites is pointed out in numerous publications, the exact role of stress concentration is not completely clear, and contradictory information is published claiming either beneficial (Nakagawa and Sano 1985), neutral (Trantina 1984), or detrimental effect on properties (Riley et al. 1990; Maiti and Mahapatro 1991).

In particulate-filled polymers, the dominating micromechanical deformation process is debonding. The stress necessary to initiate debonding, the number of debonded particles, and the size of the voids formed all influence the macroscopic properties of composites. Several models exist for the prediction of debonding stress including the one below (Pukánszky and Vörös 1993):

$$\sigma^D = -C_1\sigma^T + C_2\left(\frac{W_{AB}\ E}{R}\right)^{1/2} \tag{9}$$

where $\sigma_D$ and $\sigma_T$ are debonding and thermal stresses, respectively, $W_{AB}$ is the reversible work of adhesion, and $R$ denotes the radius of the particle. $C_1$ and $C_2$ are constants which depend on the geometry of the debonding process. The validity of the model was checked in various particulate-filled composites. Initiation stress

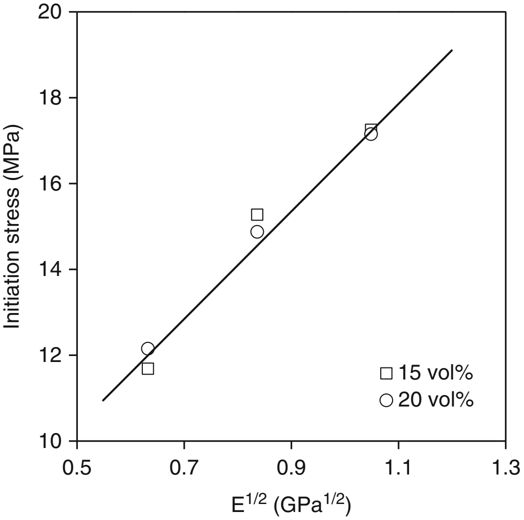


**Fig. 15** Dependence of debonding stress derived from volume strain measurements on the stiffness of the matrix (see Eq. 9)

determined in PP/$CaCO_3$ composites from volume strain measurements is plotted against the stiffness of the matrix in Fig. 15 in the representation predicted by the model (Sudár et al. 2007). The correlation is close and corresponds to the prediction. Similarly, good correlations can be obtained if we plot debonding stress against the reversible work of adhesion (Pukánszky and Vörös 1996) or the particle size of the filler (Pukánszky et al. 1994b) (see Eq. 9).

Micromechanical deformations are competitive processes, and the dominating one depends on material properties and loading conditions. Several fiber-related processes, like fiber breakage, pull out, buckling, etc., may take place in short- and long-fiber-reinforced composites. Quite a few of these can be observed also in wood fiber-reinforced polymers or layered silicate nanocomposites as well. The complexity of deformation and failure in such materials is demonstrated well by the number of processes detected in wood flour-reinforced PP composites (Dányádi et al. 2007b). The stress versus strain correlation of a PP composite containing 20 wt% unmodified wood flour is presented in Fig. 16 together with the acoustic signals detected during deformation. Since the adhesion between wood and PP is poor and the particles are large, the majority of the signals is emitted by the debonding of the wood particles. The cumulative number of acoustic events versus elongation plot clearly indicates that at least two processes occur in this composite shown by the two steps in the correlation. The application of a coupling agent, which improves interfacial adhesion between the components, changes the mechanism of deformation completely; the fracture of the fibers dominates under those conditions. The analysis of a large number of results showed that at least four processes take place during the deformation of PP/wood composites. The PP matrix deforms mainly by shear yielding, debonding, and fiber pull out dominate when the adhesion is poor, while mainly fiber fracture takes place in the presence of MAPP coupling agent, which creates strong bond between the matrix and the wood particles

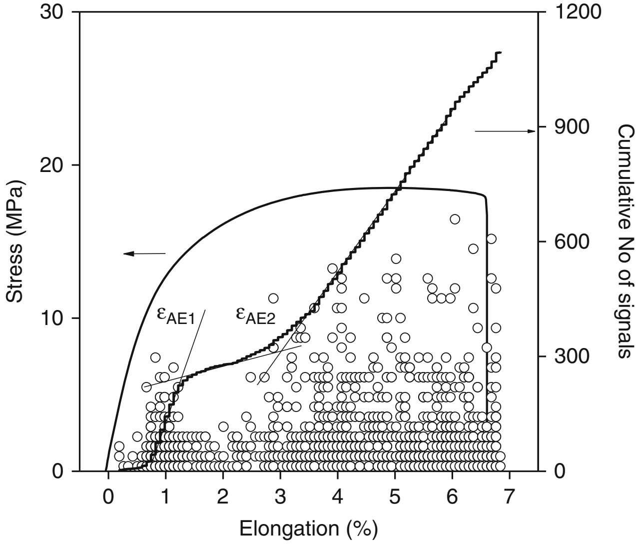


**Fig. 16** Acoustic emission testing of a PP composite containing 20 wt% wood without MAPP (poor adhesion). Small circles indicate individual acoustic events. Stress vs. strain and cumulative number of signal vs. strain traces

(Dányádi et al. 2007b; Renner et al. 2009, 2010). The fracture and the fibrillation of a particle are shown in Fig. 17 in order to support the analysis. The importance of local deformations is strongly supported by Fig. 18 in which composite strength is plotted against the initiation stress of the dominating process of a large number of PP and PLA composites reinforced with wood. It is obvious that micromechanical processes initiated by local stress maxima determine the final properties of particulate-filled and reinforced composites, and only the analysis of the resulting processes can help the development of stronger and better materials.

## Properties

The properties of particulate-filled thermoplastics depend strongly and usually nonlinearly on composition. Models are needed for the prediction of properties in order to produce composites with desired characteristics. Relatively few models exist for the prediction of the effect of filler content on properties, and the majority of these are empirical equations.

### Rheological Properties

The introduction of fillers or reinforcements changes practically all properties of the polymer including its rheological characteristics. Viscosity usually increases with

**Fig. 17** SEM micrograph showing the fracture of a wood particle during the deformation of PP/wood composites. Good adhesion of the components was achieved by the use of functionalized PP

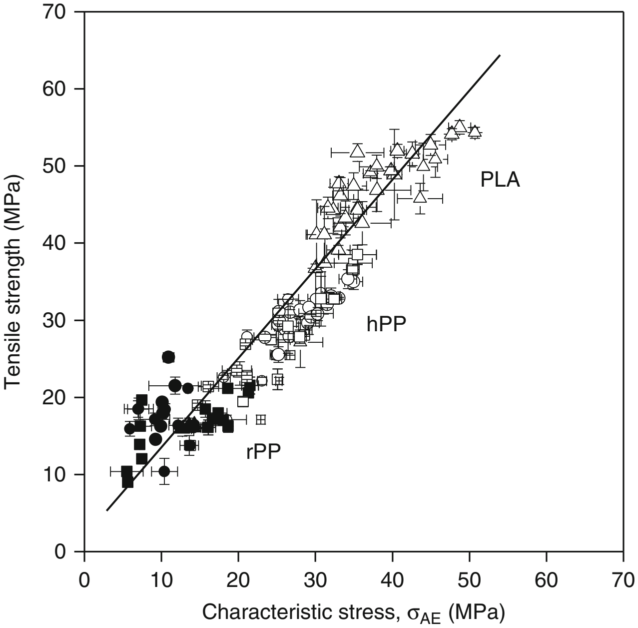


**Fig. 18** Close correlation between the initiation stress of the dominating deformation process and the strength of the composite. Symbols: (□) rPP/wood, (○) hPP/wood, (Δ) PLA/wood. Full symbols: poor adhesion, empty symbols: good adhesion

filler content, while melt elasticity decreases at the same time (Faulkner and Schmidt 1977). These changes depend very much on the particle characteristics of the filler although unambiguous correlations are not known. Matrix/filler interactions lead to the formation of an interphase and have the same effect as increasing filler content (Stamhuis and Loppe 1982).

The composition dependence of rheological properties is modeled only in surprisingly few cases. Quite a few models are derived from Einstein's equation, which predicts the composition dependence of the viscosity of suspensions containing spherical particles. The original equation is valid only at infinite dilution or at least at very small, 1–2%, concentrations (Jeffrey and Acrivos 1976), and in real composites, the equation must be modified. Usually, additional terms and parameters are introduced into the model most often in the form of a power series (Jeffrey and Acrivos 1976). The Mooney equation represents a more practical and useful approach which contains adjustable parameters accommodating both the effect of interaction and particle anisotropy (Jeffrey and Acrivos 1976), i.e.,

$$\ln\frac{\eta}{\eta_0}=\frac{k_E\varphi_f}{1-\varphi_f/\varphi_f^{\max}} \tag{10}$$

where $\eta$ and $\eta_0$ are the viscosity of the composite and the matrix, respectively, $\varphi$ is the volume fraction of the filler, and $k_E$ is an adjustable parameter related to the shape of the particles. $\varphi_f^{\max}$ is the maximum amount of filler, which can be introduced into the composite, i.e., maximum packing fraction, and it is claimed to depend solely on the spatial arrangement of the particles. The study of PP/$CaCO_3$ composites proved that interfacial interactions and the formation of a stiff interface influence its value more than spatial arrangement, and the maximum amount of filler which can be introduced into the polymer decreases with increasing specific surface area of the filler.

## Stiffness

Modulus is one of the basic properties of composites and the goal of using particulate fillers is often to increase it (Bajaj et al. 1987). Modulus is not only the most frequently measured but also the most often modeled composite property. A large number of models exist which predict the composition dependence of stiffness or give at least some bounds for its value. The abundance of models is relatively easy to explain: modulus is determined at very small deformations, and thus the theory of linear viscoelasticity can be used in model equations. The large number of accessible data also helps both the development and the verification of models. Model equations developed for heterogeneous polymer systems can be classified in different ways (McGee and McGullough 1981, Dickie 1978). Ignoring completely empirical correlations, we distinguish four groups here:

1. Phenomenological equations which are similar to the spring and dashpot models used for the description of the viscoelastic properties of polymers (Dickie 1978).
2. Bounds. These are usually exact mathematical solutions which do not contain any or only very limited assumptions about the structure of the composite (Halpin and Kardos 1976).
3. Self-consistent models. The mechanical response of a composite structure is calculated in which the dispersed particle is assumed to be embedded into the continuous phase. A well-known model of this type, frequently used also for particulate-filled composites, is the Kerner equation (Dickie 1978). Although it was much criticized because of the incorrect elastic solution used (Christensen and Lo 1979), the model gained wide use and acceptance.
4. Semiempirical models. In spite of the effort of the self-consistent models to take into account the influence of microstructure, they very often fail to predict correctly the composition dependence of composite modulus; thus, additional, adjustable parameters are introduced in order to improve their performance. The most often applied equation of this type is the Nielsen (also called Lewis-Nielsen or modified Kerner) model (Nielsen 1974).

$$G = G_m \frac{1 - AB\varphi_f}{1 - B\Psi\varphi_f} \tag{11}$$

$$A = \frac{7 - 5\nu_m}{8 - 10\nu_m} \tag{12}$$

$$B = \frac{G_f/G_m - 1}{G_f/G_m + A} \tag{13}$$

$$\Psi = 1 + \left( \frac{1 - \varphi_f^{\max}}{\varphi_f^{\max^2}} \right) \varphi_f \tag{14}$$

where $G$, $G_m$, and $G_f$ are the shear moduli of the composite, the matrix, and the filler, respectively, $\nu_m$ is the Poisson's ratio of the matrix, and $\varphi_f$ is the filler content.

The equation contains two structure-related or adjustable parameters ($A$, $\Psi$). The two parameters, however, are not very well defined. $A$ can be related to filler anisotropy, through the relation $A = k_{\mathrm{E}} - 1$, where $k_{\mathrm{E}}$ is Einstein's coefficient, but the relation has not been thoroughly investigated and verified. $\Psi$ depends on maximum packing fraction. $\varphi_f^{\max}$ is related to anisotropy, but it is influenced also by the formation of an interphase which was not taken into consideration in the original treatment (Nielsen 1974). Its experimental determination is difficult. McGee and McCullough proposed a different form for $\Psi$, which is supposed to be based on a more rigorous treatment (McGee and McGullough 1981).

In spite of these uncertainties, the model is quite frequently used in all kinds of particulate-filled composites for the prediction of the composition dependence of modulus. In some cases, merely the existence of a good fit is established; in others, conclusions are drawn from the results about the structure of the composite. However, the attention must be called here to some problems of the application of these equations or any other theoretical model. The uncertainty of input parameters might bias the results considerably. Poisson's ratios between 0.25 and 0.30, as well as moduli between 19.5 and 50 GPa, have been reported for $CaCO_3$ (Chacko et al. 1982; Vollenberg 1987). Such changes in component properties may lead to differences in the final prediction which exceed the standard deviation of the measurement. Maximum packing fraction influences predicted moduli especially strongly, but its value is usually not known. A certain packing of the particles may be assumed, but this approach neglects the effect of particle size distribution and interactions. At the moment, the best solution is the fitting of the equation to the experimental data and the determination of $A$ and $\varphi\, f max$ . The model is very useful for the estimation of the amount of embedded filler in polymer/elastomer/filler composites, but otherwise its value is limited.

## Properties Measured at Large Deformations

The fact that modulus is determined at very small deformations simplifies both measurements and modeling. On the other hand, yield properties are measured at larger deformations making predictions much more difficult. The composition dependence of yield strain is described assuming that at the considerable deformations (5–10%) of yielding, only the polymer matrix deforms and the rigid filler does not. This strain magnification of the matrix increases with increasing filler content. One of the equations based on this principle was derived by Nielsen (Nielsen 1974). Occasionally, the same approach is used for the prediction of the composition dependence of elongation at break (Nielsen 1974; Maiti and Mahapatro 1991).

More attempts are made to predict and analyze yield stress. The most often applied correlation is attributed to (Nicolais and Narkis 1971), although the equation of (Ishai and Coheno 1968) is practically the same. (Nicolais and Narkis 1971) assumed that the filler decreases the effective cross section of the matrix which carries the load during deformation. Assuming a certain arrangement of the particles, they calculated this cross section and from that the dependence of yield stress on composition, i.e.,

$$\sigma_y = \sigma_{y0}\left(1 - 1.21\,\varphi_f^{2/3}\right) \tag{15}$$

where $\sigma_y$ and $\sigma_{y0}$ are composite and matrix yield stress, respectively. The approach, however, results in a matrix cross section assuming zero value at $\varphi_f < 1$ which is naturally incorrect. The model assumes zero interaction and ignores all other factors influencing yield stress. Because of these simplifications, deviations from the prediction occur very often. As a consequence, the model is frequently modified to accommodate the effect of different arrangements of the particles (Nielsen 1974), interactions, stress concentration (Maiti and Mahapatro 1991), or other effects. Usually, the two constants, i.e., 1.21 and 2/3, are treated as adjustable parameters, but in such cases they lose their physical meaning, and the entire approach becomes invalid.

Another model (Pukánszky 1992) takes into account at least some of the factors neglected by (Nicolais and Narkis 1971). The model applies a different expression for the effective load-bearing cross section (Turcsányi et al. 1988) and takes into account also the influence of interfacial interactions and interphase formation:

$$\sigma_y = \sigma_{y0} \frac{1-\varphi_f}{1+2.5\varphi_f} \exp\left(B\varphi_f\right) \tag{16}$$

where $B$ is related to the relative load-bearing capacity of the components, i.e., to interaction. A detailed analysis has shown that $B$ accounts both for changes in interfacial area and for the strength of interaction through the expression

$$B = \left(1 + A_f \rho_f \ell\right) ln \frac{\sigma_{yi}}{\sigma_{y0}} \tag{17}$$

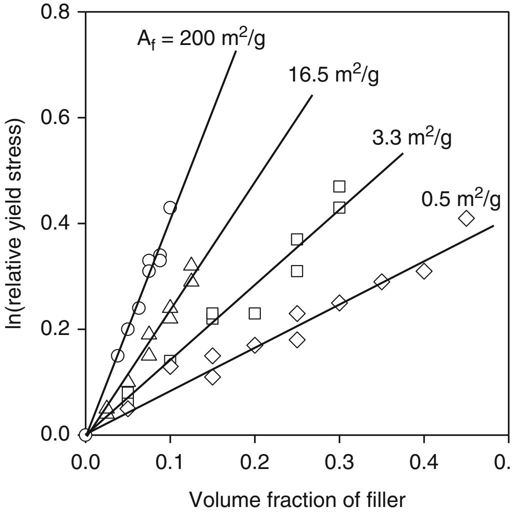
where $A_f$ and $\rho_f$ are the specific surface area and density of the filler, while $\ell$ and $\sigma_{yi}$ are the thickness of the interphase and its yield stress, respectively. The correlation proved to be valid for most particulate-filled systems (Pukánszky et al. 1989; Pukánszky 1990; Dányádi et al. 2007b). The rearrangement of Eq. 16 eliminates the effect of changing matrix cross section, and if the natural logarithm of relative yield stress, i.e., $\sigma_{yrel} = \sigma_y$ $(1 + 2.5\ \varphi_f)/\ \sigma_{y0}(1 - \varphi_f)$, is plotted against the volume fraction of the filler, straight lines should be obtained. The validity of the approach is proved by Fig. 19, in which the relative yield stress of the PP/$CaCO_3$ composites of Fig. 10 is plotted in the linear form. The change in the slope of the straight line indicates the effect of interfacial area ($A_f$), which increases with decreasing particle size, i.e., with increasing amount of interphase formed (see Eq. 17). Parameter $B$ measures quantitatively changes in the strength of interaction achieved by surface modification.

The composition dependence of ultimate tensile properties, i.e., tensile strength and elongation at break, is very similar to that of the yield characteristics. Usually both elongation and strength decrease with increasing filler content, although occasionally some reinforcement can be observed, too. However, changes in elongation with filler content make the prediction of strength difficult; the cross section of the specimen decreases at large elongations, while the orientation of the matrix results in strain hardening. The modification of Eq. 16 successfully copes with these problems, i.e.,

$$\sigma_T = \sigma_{T0} \lambda^n \frac{1-\varphi_f}{1+2.5\,\varphi_f} \exp\left(B\varphi_f\right) \tag{18}$$

where true tensile strength ($\sigma_T = \sigma\lambda$, $\lambda = L/L_0$, relative elongation) accounts for the change in specimen cross section and $\lambda^n$ for strain hardening. $n$ characterizes the

**Fig. 19** Relative tensile yield stress of the PP/$CaCO_3$ composites presented in Fig. 10 plotted against composition in the linear representation of Eq. 16



strain hardening tendency of the polymer and can be determined from matrix properties (Pukánszky 1990). *B* is defined by a correlation similar to Eq. 17, but its value is naturally different from that determined from the composition dependence of yield stress.

Fracture and especially impact resistance are crucial properties of all materials used in engineering applications. Similarly to yield stress, the fracture toughness of particulate-filled polymers is assumed to decrease with filler content, which is not necessarily true. Fracture and impact resistance often increases or goes through a maximum as a function of filler content both in thermoplastic and thermoset matrices (Brown 1980; Vu Khanh et al. 1985). Several micromechanical deformation processes take place during the deformation and fracture of heterogeneous polymer systems. New deformation processes initiated by heterogeneities always consume energy resulting in an increase of fracture resistance. The various deformation mechanisms consume different amount of energy; thus, the change of properties and composition dependence may also vary according to the actual processes taking place during deformation. Deformation mechanisms leading to increased plastic deformation of the matrix are the most efficient in improving fracture and impact resistance. Because of the effect of a large number of factors influencing fracture resistance and due to the increased role of micromechanical deformation processes, the modeling of this property is even more difficult than that of other composite characteristics. Nevertheless, a relatively large number of models have been published up to now (Friedrich and Karsch 1983; Evans et al. 1985; Jancár et al. 1993), but very few of them gained wide acceptance. The semiempirical model applied for the description of the composition dependence of other mechanical properties (see Eqs. 16, 17, and 18) can be extended also to fracture and impact resistance (Pukánszky and Maurer 1995). The model could be used successfully for a large number of composites both with thermoplastic and thermoset matrices.

## Other Properties

Particulate-filled and reinforced polymers are frequently used in structural applications, and the main goal of modification is often the improvement of stiffness. As a consequence, much attention is paid to the study and modeling of mechanical properties, but other characteristics of the composites are investigated much less and relatively few attempts are made to describe their composition dependence by models. *Heat deflection temperature* (HDT) is closely related to stiffness and changes with composition in a similar way. *Cost* is an important attribute of every engineering material, and it usually decreases with increasing filler content. However, decreasing polymer prices and increasing compounding costs make particulate-filled polymers competitive only if their technical benefits are utilized to their full extent. The introduction of fillers may change the *appearance* of the product (color, surface) or influence the *stability* of the compound. *Heat capacity, heat conductivity, shrinkage*, and *dielectric properties* can be described quantitatively by models used for the description of the composition dependence of modulus. Fillers influence the *barrier properties* of polymers; the permeation of gases and vapors decreases with increasing filler content. Models exist for the description of this phenomenon (Yano et al. 1993; Bharadwaj 2001), which take into account the tortuosity of the diffusion path.

The inherent *flammability* of plastics is one of their major drawbacks, and the use of flame retardants is required today in most applications, especially in construction or transportation. Traditional halogen/antimony flame retardants are very efficient, but their use will be banned in the future because of environmental and health considerations. One of the alternatives is the use of hydrated mineral fillers, like aluminum or magnesium hydroxides. These can provide acceptable levels of frame retardancy without the formation of smoke or corrosive and toxic gases. Unfortunately, these minerals must be used in large quantities in order to achieve the necessary effect, which deteriorates other properties, like processability, strength, and especially impact resistance. Appropriate surface modification must be used in order to overcome the negative effect of large filler content.

Polymers are basically insulators with surface resistivity of around $10^{14}$–$10^{18}$ Ωcm. Applications exist which require a certain *conductivity*, like air ducts in mines, pipes for solvent transport, EMI shielding, and some other areas. Conductivity is usually achieved by the introduction of conductive fillers. Traditionally, special conductive carbon blacks or metal fillers, particles, or flakes are used in such applications, but recently, intensive research is going on to use carbon nanofibers or nanotubes for this purpose (Pötschke et al. 2007). Conductivity increases stepwise at a certain additive content, and the percolation threshold is claimed to be much smaller, around several tenth of a weight percent (Pötschke et al. 2007), for nanofillers than for traditional fillers. This claim is strongly supported by the results of (Pötschke et al. 2007) presented in Fig. 20. The percolation threshold of the special conducting carbon black is around 8 wt% in polycarbonate, while that of single walled nanotube is less than one percent in the same

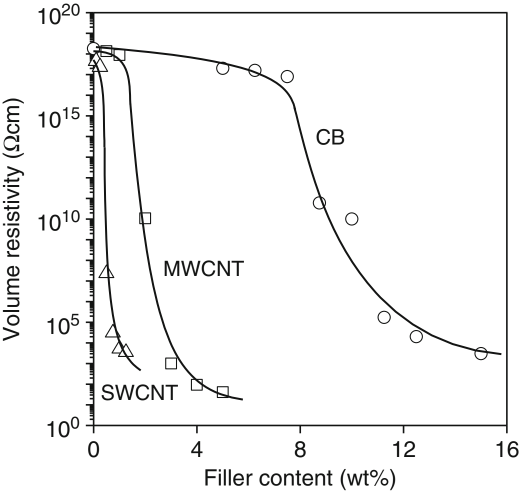


**Fig. 20** Comparison of the effect of carbon black (*CB*), multiwalled (*MWCNT*), and single walled carbon nanotubes (*SWCNT*) on the conductivity of polycarbonate composites

polymer, indeed. Such behavior can be described, and the composition dependence of conductivity can be modeled with percolation theories (Barrau et al. 2003).

## Conclusions

Although particulate-filled polymer composites are mature materials with a long history of application, their structure–property correlations are more complicated than usually assumed. The characteristics of all heterogeneous polymer systems including composites containing micro- or nanofillers are determined by four factors: component properties, composition, structure, and interfacial interactions. Several filler characteristics influence composite properties, but the most important ones are particle size, size distribution, specific surface area, and particle shape. The main matrix property is stiffness. Composite properties usually depend nonlinearly on composition; thus, they must be always determined as a function of filler content. The structure of particulate-filled polymers is often more complicated than expected; segregation, aggregation, and the orientation of anisotropic particles may take place. Interfacial interactions invariably develop in composites; they lead to the formation of a stiff interphase considerably influencing properties. Interactions can be modified by surface treatment, which must be always system specific and selected according to the goal of modification. Particulate-filled polymers are heterogeneous materials in which inhomogeneous stress distribution and stress concentration develop under the effect of external load. These initiate local micromechanical deformation processes, which determine the macroscopic properties of the composites. The dominating deformation mechanism is usually debonding in filled polymers. Although the number of reliable models to predict properties is relatively small, they offer valuable information about structure and interactions in particulate-filled composites.

## Cross-References

- ▶ Calcium Carbonate Fillers
- ▶ Compounding of Particulate-Filled Thermoplastics
- ▶ Particulate Fillers, Selection, and Use in Polymer Composites
- ▶ Surface Modifiers for Use with Particulate Fillers
- ▶ Talcs
- ▶ Wollastonites

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# Compounding of Particulate-Filled Thermoplastics

# 4

Peter Hornsby

## Contents

**Abstract**

The properties of filled thermoplastics critically depend on how the filler is presented in the polymer, especially its degree of interaction with the host matrix and the nature and extent of mixing achieved. Furthermore, the nature of the filler has a profound influence on the compounding methodology employed. Heat- and shear-sensitive fillers need a very different approach to fillers which have a strong tendency to agglomerate. Different technologies will also be required to produce highly loaded filled compounds to those containing small amounts of filler. The method used to combine filler and polymer defines the microstructure developed, principally through exposure to the shear and elongational flow fields encountered during melt compounding. This is influenced by the rheology of the

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formulation and the constructional design and operational parameters used, which, in turn, define the extent and mode of mixing achieved. Additional functional stages may be required, for example, to extract volatiles from the compound or undertake reactive steps in the process. A key aspect in many filled compounding operations is the need for dedicated ancillary equipment, which often includes pre-blending components in the formulation, controlled feeding of filler and polymer into the compounder, and downstream cooling and pelletizing of the ultimate compound. In order to monitor compound consistency, a variety of in-process characterization techniques are being used or are under development. More energy-efficient filled compounding procedures are available which combine the mixing requirements with end product formation by extrusion or injection molding.

This entry will explore these issues, highlighting specific compounding requirements for differing filled polymer combinations, the principles of mixing particulate fillers into thermoplastic melts, and how this knowledge influences the engineering design and effective operation of industrial compounding plant.

**Keywords**

Mixing • Dispersion • Distribution • Rheology • Internal mixer • Ko-kneader • Twin-screw extruder • Mixture characterization

## Definition

The properties of filled thermoplastics strongly depend on how the filler is presented in the polymer, especially its degree of interaction with the host matrix and the nature and extent of mixing achieved. The method used to combine filler and polymer defines the microstructure developed, principally through exposure to the shear and elongational flow fields encountered during melt compounding.

## Scope of Compounding Requirements

The properties of particulate-filled thermoplastic composites critically depend on the mixing procedures used to combine filler and polymer, the end processing techniques used to convert this compound into finished products, and the resulting structure developed in the composite. This entry will consider the former, which is usually undertaken by the judicious use of melt processing technologies, where the aim is to achieve uniform containment of filler in the polymer with the particle size being reduced to the minimum achievable level. There are many factors which can influence this requirement, in particular, the agglomeration tendency of the filler particles and the effectiveness of the melt mixing process in breaking down these interactions and creating a uniform distribution within the polymer matrix. Interparticle attraction is also affected by the surface chemistry of the filler, the presence of modifying surface treatments applied to the filler, and the polarity of the host polymer, including the presence of reactive or polar functional phases blended with the polymer to enhance interaction with the filler.

The importance of optimum mixing between filler and polymer is demonstrated by the effect of filler dispersion on physical properties of the composite. With inorganic fillers, such as calcium carbonate, poorly dispersed particles, evident as agglomerates, can act as stress concentrators causing large reductions in tensile and impact strength. Furthermore, the optical properties of pigments in polymers, including color strength, opacity, and gloss, and the efficiency of UV light stabilizers, strongly depend on the extent of filler dispersion.

Although many additives, such as pigments and heat and light stabilizers, are used in very small amounts (<3% by weight), a large number of fillers are added to thermoplastics at much higher addition levels, even as much as 60–80% by weight. This might be to create a wood effect with the polymer, maximize its resistance to combustion, or impart special magnetic or optical properties. Frequently, polymer masterbatches are prepared containing high concentrations of functional additives, such as pigments, which are subsequently diluted when added to virgin polymer during secondary processing. In some polymer-based formulations used for making injection-molded ceramics, on a volume basis, the inorganic filler level may greatly exceed the amount of polymer present, which is then removed during subsequent burnout. The presence of high loadings of filler poses several additional challenges during compounding in addition to effective dispersion, including the requirement for premixing of filler and polymer before melt compounding or, alternatively, controlled feeding of the filler directly into the melt compounding machine, together with a capability for the machinery to effectively melt and transport the compound through the process, especially when continuous compounding. A further directly related consideration is the dramatic increase in melt viscosity of the polymer, which occurs when significant loadings of filler are present. This results in high processing pressures and power requirements, resulting in the need for specially engineered, robust, and generally costly compounding plant.

In addition to the various material factors highlighted above, the design and operation of the melt compounding machinery is of prime importance in determining particle dispersion, or breakdown of agglomerates, with their subsequent randomization within the matrix. Often this requires development of high levels of shear stress during mixing, where interparticle attractions are strong, with controlled shear strain in the melt to optimize particle distribution and ultimate structure within the composite. However, there are some instances with shear-sensitive additives, such as hollow glass microspheres or carbon or glass fibers, where the application of excessive shear stress can result in significant filler damage with resulting loss of functionality, and a compromise must be achieved to obtain acceptable homogeneity with minimum additive breakdown.

Some fillers are thermally sensitive and can degrade or decompose during the compounding stage, due to both the time and temperature of exposure when melting the polymer. For example, such concerns apply with organic fillers, such as wood flour and alumina trihydrate fire retardant. The viscous dissipation of mechanical energy into shear heat can exacerbate this problem, especially where there is a need to develop high shear stress to effect filler dispersion or where filler loadings are high (causing an increase in polymer melt viscosity) or in high-throughput continuous compounding lines.

Moisture sensitivity is an issue relevant to all polymer melt processing operations. However, the presence of high surface area or hygroscopic fillers may significantly increase the need for pre-drying measures, either before compounding or through design of one or more devolatilization stages during the compounding process, to remove moisture (and/or other volatiles) present in the material, which would otherwise detrimentally affect the quality of the compound. For this purpose, vacuum-assisted venting zones are frequently used during continuous extrusion compounding.

There are many specialist-compounding situations, for example, with multiphase additive combinations involving the use of fillers. In this regard, particulate fillers may be combined with reinforcing fibers to control fiber orientation in the composite. Here there may be a conflict between achieving high levels of shear stress to disperse the filler and minimizing breakage to the shear-sensitive fiber. In order to obtain a balance between modulus increase, due to the presence of rigid fillers in thermoplastics and increased toughness from inclusion of rubbery additives, a combination of these two phases may be used. Whether or not the rubbery phase encapsulates the filler or exists as discrete particles has a direct effect on mechanical properties. This spatial distribution is influenced both by the relative physiochemical affinity of the filler and rubber and by the compounding methodology employed. Imparting electrical conductivity into thermoplastics is equally complex and can be achieved by inclusion of fillers such as graphite, carbon black, or metal powders into the polymer. However, in order to obtain electrical percolation (a conductive pathway) through the material, it requires judicious control of the amount of filler, the particle characteristics (size, shape, and inherent conductivity), and, very importantly, the microstructure developed during primary melt mixing and then after secondary processing to the finished product. Although outside the scope of this review, melt compounding considerations are central to the emerging field of polymer nanocomposites. This includes nanoscale fillers such as silicate layer (or nanoclay) structures, carbon nanotubes, graphene, and cellulose nanofibers. Amounts added to the polymer tend to be very low, sometimes less than 1 wt%, and may require specially modified compounding methods. More relevant to the present discussion, however, is the emerging interest in combining conventional macroscale fillers with nanoparticulates within the same compound, thereby achieving property benefits from each component.

## Principles of Mixing with Filled Polymers

The underlying science behind polymer compounding operations depends not only on the chemical and physical nature of the materials requiring combination but also on the application of specially designed process technology to effect the optimum composition and microstructure required. In the case of introducing fillers into thermoplastics, as mentioned earlier, there are many different factors and situations which can arise, each posing their own challenges and often requiring tailored solutions.

## Agglomerate Breakdown

Of central importance is the need to disperse and distribute the additive without thermal or mechanical damage to either the filler or polymer. The energy required to achieve this depends on the extent of particle agglomeration; the interparticle strength of crystalline aggregates, which generally form the substructure of agglomerates; and the way in which these aggregates combine together to produce the agglomerate. The magnitude of agglomeration forces between powders results from surface interactions and may involve electrostatic, van der Waals, or liquid-bridge forces, of which the latter can be up to four times larger than electrostatic forces due to the presence of moisture. In practice with many mineral fillers, this reinforces the need to ensure that powders are fully dry before compounding. Adhesion forces between particles may also depend on their contact geometry and surface roughness and, in some cases, their ability to undergo plastic deformation. When subjected to powder compaction, rearrangement of the particles may occur, increasing their packing efficiency and hence interparticle adhesion forces. Such a situation can occur on the rotor blades of a high-speed mixer used to pre-blend powders of filler with polymer before melt compounding and during the early stages of extrusion compounding, where powdered filler is compacted prior to, or during, polymer melting.

## Mechanism of Mixing

Different mixing scenarios can be present during polymer compounding operations, broadly classified as extensive or intensive (dispersive). High molecular mass polymers in their molten state tend to be very viscous, and extensive mixing is achieved principally by convection, which may be distributive or laminar. This has the overall aim of achieving compositional uniformity or randomness of the particulate filler phase.

More specifically, distributive mixing is concerned with the rearrangement of the mixture through an ordered or random mixing process. In particular, this is found in a variety of solid-state filler-polymer pre-blending operations, for example, in tumble, Z-blade, and high-speed mixers. Laminar extensive mixing occurs when the polymer is molten, where, through the imposition of shearing, squeezing, or elongational flow patterns, the polymer (and in some cases additive) undergoes permanent deformation. The large strains developed can result in an increase in interfacial area between components in the system, as in the case with pigment particles, such as carbon black.

Intensive or dispersive mixing, however, concerns rupture of filler agglomerates and depends on the localized generation of high shear stress. This involves application of shear to the filler through the polymer melt and is strongly influenced by compounding machinery design, such as clearances between screws or mixing elements; operational conditions, including temperature and mixing element speed; and material composition. For example, the presence of filler in the polymer raises its viscosity (discussed later) which has the effect of raising the level of shear stress developed by the polymer. This must exceed a certain threshold value for agglomerate breakdown to occur. In this regard, extensional (or stretching) flow is far more effective than shear flow in dispersing agglomerates due to the higher levels of hydrodynamic viscous drag force exerted by the polymer with this flow situation. In order for effective dispersion to occur, the molten polymer must first adequately "wet out" the filler by covering surfaces and penetrating between and, if possible, within the agglomerates. Contributory factors influencing filler dispersion through the development of shear (and elongational) stress are shown in Fig. 1, with details of common mixer designs referred to, discussed below.

Once the agglomerates are broken down, distribution of the resulting fragments occurs through randomization within the polymer matrix. This no longer depends on the magnitude of stress but on the overall level of shear strain applied.

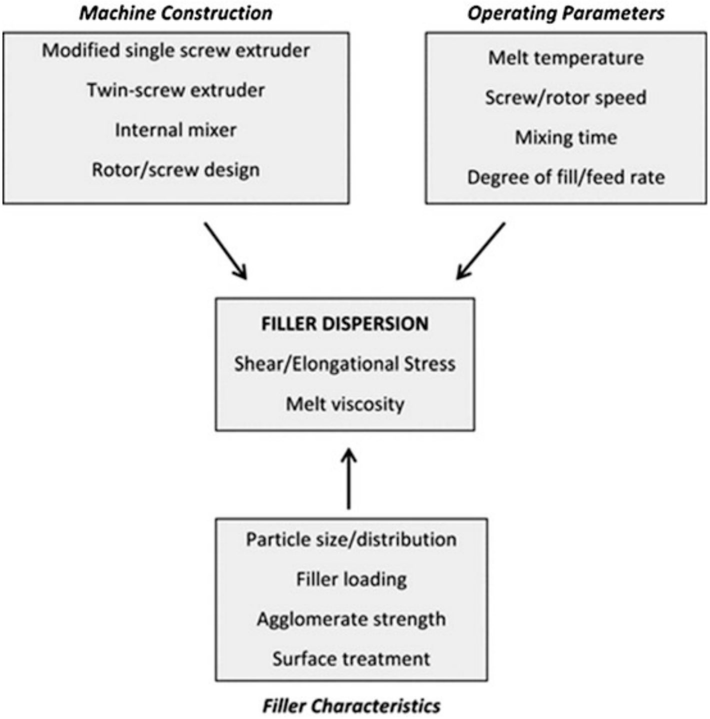

**Fig. 1** Key factors influencing filler dispersion during melt compounding with thermoplastics

## Rheology of Filled Polymers

The flow characteristics (or rheology) of molten polymers have a profound effect on the constructional design and operational performance of most polymer processing machinery influencing levels of shear stress developed (including mixing capability), power consumption, and throughput rate. Other important considerations such as dimensional changes occurring in extrudate (die swell) and flow defects (melt fracture and sharkskin) are also directly related to the rheology of the polymer. Of relevance to the present discussion, however, is the additional effect on flow behavior of introducing fillers to polymer melts and the resulting consequences to compounding machinery design.

In general, the addition of rigid fillers to thermoplastics results in an increase in melt viscosity, which, in common with unfilled polymer, is shear rate dependent. The level of viscosity increase can be very significant depending on the filler loading and the size and shape of the filler particles. In this regard, anisotropic particles, which are fibrous or platelike, may undergo flow-induced orientation and change the shear rate dependency of the filled polymer.

The presence of very high levels of filler commonly results in a critical yield stress, which must be exceeded for flow to occur, due to strong interaction between the filler particles. At stresses below this threshold value, the viscosity of the filled polymer is unbounded, behaving like a solid only deforming elastically, whereas at higher applied stress levels, it undergoes flow.

A phenomenon, commonly found with filler polymers undergoing melt flow, is the wall effect caused by a nonhomogeneous distribution of the disperse phase, resulting in the formation of a melt layer depleted of filler at the wall surface. Having relatively low viscosity, this layer gives rise to lubrication effects, or apparent wall slippage, at the melt boundary.

An important consideration relevant to both compounding and secondary processing of filled polymers is the presence of filler surface treatment. This is generally applied not only to influence interfacial bonding between the filler and matrix to enhance mechanical properties but also to ameliorate the adverse effects of filler on melt viscosity and processability. Coating of fillers with surface modifiers, such as metal stearates and titanates prior to processing, results in a significant reduction in melt viscosity relative to untreated material.

## Constructional Features of Compounding Machinery for Filled Polymers

Combining fillers with thermoplastics is normally undertaken when the polymer is molten. Depending on the physical form of both filler and polymer and the amount of filler present, premixing operations involving these materials in solid form are often undertaken prior to this stage, which creates an initial distribution of the components. Alternatively dosing the filler directly to the melt compounding machine is possible, which, in the case of continuous compounding plant, relies on accurate metering of both filler and polymer. Due to the wide variety of filled compound types with differing mixing requirements, the constructional design of compounding plant must be sufficiently flexible to accommodate differences in the necessary heating and shear requirements, as well as throughput rate. Whether the machinery is batch or continuous in operation, most commonly with filled thermoplastics, the resulting product is a uniform pellet containing well-dispersed filler, suitable for subsequent extrusion die-forming or injection molding secondary processing stages.

Although the melt mixing unit is central to the production of filled plastic compounds, various forms of ancillary equipment are required to ensure consistent commercial production. As mentioned previously, this includes specialized feeding equipment for accurate metering filler and polymer, together with cooling and pelletization operations after mixing has been achieved. Increasingly, means for monitoring the quality and consistency of filled compound are also incorporated. A summary of considerations required for the compounding of fillers into thermoplastics is given in Table 1, with further explanation of these requirements discussed below.

## Functional Stages

Melt mixing technologies can be *batch* operations which involve introducing the required quantities of filler and polymer into the machine, then after a predetermined time when mixing is complete, removing the compound, and then repeating the cycle. More commonly with filled thermoplastics, however, compounding is carried out using a modified form of single- or twin-screw extruder capable of high-intensity mixing. Solid filler and polymer are fed into the machine *continuously* and with the resulting mixture exiting a die producing strands of molten extrudate which are then cooled and pelletized. A principal benefit of this type of compounder is that, in the case of twin-screw extruders, the screw and barrel sections are often modular, allowing the machine design to be reconfigured to suit different filler-polymer combinations.

Melt compounding machinery, whether batch or in particular continuous, relies on most or all of the following discrete, or overlapping, *functional* stages.

Effective *material transport* is essential in continuous compounders. As mentioned earlier, this may start by controlling the flow rate of materials into the extruder, either as a premix or by separate feeding of filler and polymer. Furthermore, these may be introduced into the same feed port at the start of the machine or by split feeding the materials, whereby some or all the filler is introduced through a downstream opening in the barrel after the polymer has melted. This practice is particularly useful with heat- and shear-sensitive fillers. With highly filled systems, feeding some of the material with the polymer and the remainder downstream can be beneficial. Conveyance of polymer through single-screw extruders generally relies on a drag flow mechanism, involving frictional differences between the polymer and metal surfaces within the extruder. However, when fillers are present, especially at high loadings, insufficient friction may result, limiting conveyance, and alternative

**Table 1** Principal considerations for compounding-filled thermoplastics

| Material/process | | Machinery/operating | |
|---|---|---|---|
| Drying of filler and or polymer | Moisture sensitivity of feedstock(s) | Vacuum/oven drying | Single- or multiple-stage venting |
| | | Devolatilization during compounding | |
| Method of combining filler and polymer | Flow properties of filler | Premixing of filler and polymer | Tumble, cone, ribbon blenders, Z-blade mixers, high-speed mixers |
| | Filler loading | Separate metering of filler and polymer | Gravimetric or volumetric feeding |
| | Position and amount of filler addition | Split feeding of filler | Gravimetric or volumetric feeding |
| Batch or continuous compounding | Throughput rate | Two-roll mills | Automatic/manual intervention |
| | Filler loading | Internal mixers | Batch or continuous, rotor design |
| | Shear sensitivity of filler | Single-screw extruders | Enhanced mixing/conveying requirements |
| | Dispersive mixing requirements | Ko-kneaders | Screw and kneading teeth geometry, L/D of screw, location of filler addition |
| | | Twin-screw extruders | Corotating or counterrotating screws, L/D of screws, location of filler addition |
| | | | Mixing/kneading element design, number, position |
| Ancillary equipment | Throughput rate | Pelletizing | Die-face cutting, cooling in air/water |
| | Filler loading | Quality control | Strand pelletization, strand cooling in air/water |
| | Melt strength of filled compound | | Dicing of strip |
| | Moisture sensitivity of filler and/or polymer | | In-line measurements: rheometry, ultrasound, specific energy consumption |
| | | | Off-line measurements: microscopy, X-ray radiography, capillary/parallel plate rheometry, ultrasound, ashing, dissolution |

screw designs are needed, the most important being intermeshing twin screws. These exert a positive mechanical displacement action, being much less dependent on frictional characteristics of the material. In addition to conveyance of solid or semisolid material in the earlier stages of compounding, the mechanism must be sufficiently effective to transport molten polymer containing well-mixed filler out of the machine through a die which imposes a flow restriction, thereby generating high pressure. Due to their effective conveying efficiency and reduced dependency of throughput on die pressure, intermeshing twin-screw extruders are normally starve fed with only partial filling of the screws to prevent electrical power overload, rather than being gravity fed giving fully filled screw channels, as is the case with conventional single-screw extruders.

*Melting* of the polymer is a requirement with all melt mixing operations. This can result in part from thermal conduction from the heated wall of the compounder, but most importantly from the dissipation of mechanical energy applied to the machine, into heat. Since the presence of filler can significantly increase the melt viscosity of the polymer, together with its low thermal conductivity, levels of shear heat generated by this mechanism can potentially lead to the polymer overheating, necessitating introduction of effective cooling measures, particularly in compounding extruders operating at high speeds. Conversely, the presence of highly thermally conducting fillers can be so effective in withdrawing heat from the polymer that enhanced heating may be needed. This can become apparent, for example, when compounding high levels of carbon nanotubes into thermoplastics.

Achieving optimum *mixing* between filler and polymer was discussed earlier through convective and dispersive phenomena. This is the major consideration governing the construction and operation of all compounding equipments. Many different batch and continuous design variants exist for this purpose, which allow control of the exposure time and shear intensity experienced by the polymer and filler. At one extreme, the aim may be to exert high shear stress to break down filler agglomerates, while at another level, gentler mixing may be required, the prime purpose being to randomize the components.

Removal of entrapped air, moisture, and, in some cases, reaction by-products, for example, where chemical modifications are undertaken, is a requirement in most thermoplastic compounding operations involving fillers. This can be achieved by *melt devolatilization* through the design of a low-pressure zone in the process to allow volatiles to be removed at this point, generally under an applied vacuum, through diffusive and convective mass transport mechanisms.

## Premixing Processes

Preliminary processes, which entail pre-blending of polymer and filler, can be characterized as being low or medium intensity. Since their primary aim is to achieve a degree of randomization, the level of applied shear is low, and temperatures are kept below the melting point of the polymer. A wide variety of options are available, such as simple tumble mixers, V blenders, and double-cone blenders, where the particulates are gently moved from end to end through a tumbling action as the mixer rotates. Ribbon blenders achieve a similar result by transporting the components back and forward along single or double horizontal trough-shaped horizontal mixing chambers, as well as creating movement from top to bottom.

More intense blending again without melting of the polymer can be obtained using non-fluxing high-speed mixers. These comprise a revolving impeller, located in the bottom of a jacketed mixing chamber. Rotational speed is much higher than the low-intensity premixers described above (4,000 as compared with 50 rpm or less), causing the material to be forced out radially by the rotor, traveling up the walls of the mixer, and falling down through a central zone forming a vortex. A baffle may also be introduced to create additional turbulence to this fluidlike flow.

These machines are widely used for PVC dry-blend production and are sometimes used to distribute particulate filler with polymer, especially when both components are in powdered form. Since shear intensities are higher, some de-aggregation of loosely bound agglomerates may also result. In the absence of polymer, mixers of this type can also provide a convenient method for application of surface treatments to fillers in order to modify their interfacial properties. Since filler is in a “fluidized” state and may be cold or heated, liquid modifiers can be introduced through an opening on the mixer lid to achieve a uniform coating. Alternatively, fatty acids can be effectively coated onto fillers first preheated to a temperature above the melting temperature of the surface treatment.

## High-Intensity Melt Mixing Technologies

There are a variety of melt mixing options available for combining fillers into thermoplastics, the more important of which are summarized in Table 1. Since their flexible design and operation also makes them suitable for a wide range of alternative compounding situations, which may exclude the use of fillers, only an overview of their construction is presented below. A range of texts providing more detailed information is given at the end of this entry.

Due to their effective mixing action, through the generation of the high shear stresses necessary to break down agglomerates, *two-roll mills* are widely used in laboratories and, to a limited extent, production environments, for combining additives into plastics and more especially rubbers. They comprise two counterrotating temperature-controlled rolls which cause the polymer to melt (in the case of thermoplastics), adhere to, and rotate with one of the rolls. As it passes through the narrow clearance between the rolls, material is subjected to intense shear, which facilitates dispersive mixing. The rolls may run at the same or differential speeds, thereby further influencing the local shear intensity. With this machine design, lateral cross-mixing must also be applied, generally by manual intervention, to impose a degree of convective mixing, ensuring compositional uniformity. A rotating bank of material located at the entrance of the nip gap between the rolls further augments the overall mixing effectiveness. Process variables include the adjustable nip gap between the rolls, the relative rotational speed (and hence friction ratio) of the rolls, and the mixing time.

Since two-roll mills have limitations in terms of scale and generally the need for significant operator involvement, *internal mixers* provide an alternative approach to mixing and are available in both batch and continuous designs. Analysis has shown that both shear and elongational melt flows occur, creating a unique and highly effective mixing action.

The polymer and filler are introduced into a temperature-controlled mixing chamber in the shape of a figure of eight containing two counterrotating specially configured rotors. A vertically mounted hydraulically driven ram is lowered onto the material, creating pressure and intensifying mixing. The rotor designs and their degree of intermesh critically affect the mixing action. This involves generation of high shear stress between the rotors and through the clearances between the rotors and walls of the mixing chamber, combined with convective longitudinal and lateral transfer of material throughout the mixing chamber. The other principal operational variables include the rotor speed, batch temperature, mixing time, ram pressure, and amount of material present in the mixing chamber (fill factor). With some filled compositions, the order and amount of component addition (simultaneous or sequential) can also influence the shear intensity and quality of mixing. Once mixing is completed after a predetermined time, material is discharged through an opening underneath the mixing chamber onto a two-roll mill or extruder for subsequent pelletization. Continuous variants are also available which contain mixing rotors similar in design to batch elements; however, materials to be mixed are continuously fed into the machine using counterrotating twin screws and then, after the mixing stage, are discharged through an exit opening, often into a single-screw extruder to allow for further homogenization, volatile venting, and die forming into strands or strip for pelletization. Some continuous internal mixer designs allow for direct addition of fillers or other additives into molten polymer.

*Extrusion compounding* is a well-established and often preferred method for combining fillers with thermoplastics, since the process is continuous and, with most machinery designs, offers considerable flexibility in terms of screw and barrel configuration to meet the requirements demanded from differing material types. There is a wide range of variants available based on single- and, in particular, twin-screw designs. Standard *single-screw extruders* have limited inherent mixing capability, developing only low levels of shear strain and stress. Their drag flow conveying action is also unsuitable for processing thermoplastics containing high filler levels. Nevertheless, these drawbacks can be partially overcome using modified screw designs, which impart a greater degree of distributive and, to some extent, dispersive mixing capability suitable for simple blending situations. Special grooved barrel designs can also aid conveyance of feedstock in the feed zone of the extruder. Static mixers, positioned between the end of the extruder and die, can be used to aid mixture homogeneity, by repeated passage of molten polymer through a tube containing motionless profiled elements. However, these designs generally only redistribute material and, being without a dispersive capability, are generally unsuitable for highly filled compositions.

For most purposes, specially designed compounding machinery is required of which *ko-kneaders* and *twin-screw extruders* have achieved greatest commercial importance. The ko-kneader is effectively a modified form of single-screw extruder, although its design and mode of operation are unconventional and somewhat distinctive. The screw used is not continuous but contains flights which are interrupted by three gaps per turn, and the barrel has three corresponding rows of stationary teeth projecting from its surface. During operation, the screw simultaneously rotates and reciprocates, causing the screw flights to pass forward and then backward between the teeth. This provides an interchange of material in both axial and radial direction and controllable shear stress between the teeth and screw surfaces, in addition to a forward conveying motion. Despite this apparent complexity, many design and operational variants exist, providing control and flexibility, including changing the screw and kneading teeth geometry, the length to diameter ratio of the screw, provision for downstream additive addition into the polymer, and a melt devolatilization capability. In order to produce pellets, the output from the ko-kneader is discharged into, and passed through, a single-screw extrusion pump.

The workhorse machine for filled thermoplastic compounding, however, is the twin-screw extruder. The two screws are located in a figure of eight-shaped barrel, and may be intermeshing or not, and rotate in the same, or opposite directions. As mentioned earlier, a feature of such machines is that they have effective material conveying characteristics, depending on degree of screw intermesh, which makes them particularly suitable for transporting filled compositions. In addition, most designs incorporate specially designed (kneading) elements within the screw profile to augment and intensify mixing and melting behavior. Their design (e.g., bi- or tri-lobal or segmented), position along the screws, number, and relative stagger can all influence shear intensity developed in the polymer during compounding. Machines are also designed to be multifunctional, incorporating downstream filler addition and melt devolatilization stages. Flexibility in machine configuration is achieved by using a modular screw and barrel assembly, which, in addition to allowing the length to diameter ratio of the machine to be changed, permits different functional tasks to be undertaken within the same machine. This feature gives an additional benefit, since screw and barrel sections in zones which are particularly prone to wear, such as in the feed end, can be easily and economically replaced. Although screws and barrels are normally specially hardened or protected with liners to make them wear resistant, this will inevitably occur when processing polymers with abrasive inorganic fillers, particularly at high loading levels.

Whereas closely intermeshing counterrotating twin-screw designs are in widespread use for processing thermally sensitive UPVC compounds, including filled variants, most general-purpose filled thermoplastic compounding is undertaken with corotating, so-called self-wiping screw machines configured with banks of the kneading elements described above. Some machines are also designed to have split barrels, which can be readily opened to expose the screws to aid cleaning and changes to screw assembly, or with two-stage operation, whereby the output from the twin-screw compounding section is fed into a crosshead single-screw extruder to enable melt pressurization before exiting through a die for pelletization.

## Ancillary Compounding Equipment

It will be evident from the preceding discussion that efficient and reproducible compounding processes strongly depend on various ancillary facilities to achieve consistency. Controlled metering or *feeding* of polymer and filler into continuous melt mixers is normally undertaken through volumetric or gravimetric principles. Powdered fillers have variable flow characteristics, may differ in bulk density, and, as indicated earlier, are incorporated into the polymer at a range of addition levels. Volumetric feeders generally incorporate rotating single or twin screws, which may be solid or designed in the form of an open spiral and are particularly sensitive to variations in powder flow characteristics, such as bulk density. Gravimetric feeders, however, transport material on a mass basis and are capable of much higher accuracy. These use a weighbridge to continuously monitor the material mass being delivered, either by controlling the speed of a weigh belt or, in the case of the loss-in-weight feeder, by regulating the rate of weight change per unit time of feeder and storage hopper against a predetermined set point value.

Since the product from filled thermoplastic compounding lines is a pellet or granule, its shape and geometry must be uniform and controllable to achieve consistent bulk density and flow behavior through the hopper in secondary processing extrusion or injection molding processes. Several methods are available for the conversion of polymer compound from melt to solidified granule, using a *dicer* for material produced as sheet or strip (e.g., from an internal mixer), a *pelletizer* for compound made into continuous strands and then cooled in water, or a *die-face cutter*, where melt extrudate is cut by rapidly rotating knives at the die exit, while the polymer is still molten, then carried away, and rapidly cooled in circulating air or water. Die-face cutting is the preferred means of compound pelletization, when processing polymer compositions with limited melt strength, which can occur at high filler loadings, where there is insufficient strand stability, or in high-throughput extrusion compounding lines. The method of cutting the polymer into pellets and whether or not it is in a solid or molten state have a profound influence on the granule shape and hence its bulk density. After pelletizing, drying of the granules may be required where water cooling has been employed, before bagging.

## In-Process Compound Characterization

Assessing the quality of filled polymer compounds is of considerable importance to ensure acceptable end performance from these materials. Of particular interest is the consistency of filler loading, the uniformity of filler distribution, and the extent of dispersion determined by the presence of agglomerates. While it can be relatively straightforward to determine these measures of quality by batch sampling followed by off-line analysis (some common procedures are listed in Table 1), ideally this should be undertaken continuously during, or immediately following, compound preparation. Although this is very challenging to achieve, a number of approaches can be considered to characterize the mixing effectiveness of compounding machinery and in-line assessment of the compound produced.

These can be based on measurements of pressure and power consumption which are readily monitored during extrusion, and in some instances batch compounding, and can be indirectly related to the state of mixture quality. To this end, the s*pecific* *energy consumption* may be expressed as the ratio of the required power input to the effective material throughput and is expressed in kWh.kg$^{-1}$. For a particular machine design and operating conditions, it is closely related to the melt viscosity of the polymer and hence the amount of filler present. Since mixture uniformity is also sensitive to specific energy input, by knowing what value is required to achieve acceptable product quality, continuous measurement of this parameter can give an overall indication of compound consistency.

Similarly, *rheological* measurements can provide useful information about the influence of filler type, content, and surface treatment on the overall melt viscosity of polymer containing particulate additives. At low shear rates, for example, using a parallel plate rheometer oscillating at low angular frequencies, information about the state of structure formation can also be inferred. Although various capillary and low shear rheometers are available to continuously monitor changes in viscosity during compounding, in practice, melt from compounding extruders tends to generate pressure fluctuations; hence, to provide meaningful information, consistent pressures must be first obtained, for example, by incorporating a gear pump in the line, or more acceptably, by directing a side stream of melt from the compounder for rheological analysis.

A direct and very practical approach for the assessment of additive dispersion is to analyze pressure development in polymer melt flowing through a screen pack of defined restriction. This so-called pressure filter test has been specifically applied to pigment-containing compositions but may have some relevance to compositions containing low concentrations of other fillers. The test involves using a premix of pigment masterbatch and virgin polymer (with total pigment content of 4% by weight) and metering molten material from an extruder through a screen pack, with defined mesh size, ideally using a gear pump. Pressure is developed in front of the screen which is monitored as a function of time. The test is completed either when a pressure of 120 bar is reached or after 90 min.

A promising approach for the continuous evaluation of compositional changes and mixture uniformity in filled thermoplastics is to use *ultrasonic* measurements. The method involves determination of the elastic behavior of solids by measurement of ultrasonic wave velocity and can be undertaken off-line in solid material and, more usefully, directly during melt compounding. By this means, transit times passing through the material can be correlated with compositional changes and, more speculatively, dispersion, in filled compounds. Absolute correlations are complicated by fluctuations in melt temperature and pressure, however.

## Future Perspectives

Compounding technology for combining fillers into thermoplastics has reached a relatively mature level with future developments in machinery hardware likely to be incremental rather than fundamental in nature. The emphasis will be on improving cost-effectiveness of compounding technology through enhancement of machinery performance by increasing output rates, greater reliability, and robustness of equipment design and construction and developments in control systems, for example, closed loop feedback to ensure consistency of compound quality. The operational requirements from machinery will be largely responsive to developments in materials, including innovations in filler technology, such as different combinations of existing filler types and blends with other modifying additives. The widespread interest in combining nanofillers with polymers poses immediate challenges for established filler compounding technology, including the safe handling and accurate feeding at very low dosage levels of nanoparticulates. The unique character of these materials and the strong degree of interparticle attraction will require further optimization of mixing technology and procedures to ensure effective and reproducible dispersion and optimum control of the microstructure required, for example, for the intercalation and exfoliation of nanoclays and introduction of graphene or carbon nanotubes to achieve high electrical conductivity in thermoplastics. Direct compounding and end forming to the final product in a single operation yields only one heat and shear history for the polymer and filler. This approach has been available for many years and practiced to a limited extent, principally through the use of twin-screw extruders in combination with injection molding and conventional extrusion die-forming processes. However, it may become more significant as filler mixing requirements become more demanding, and there is a need to manage ultimate product microstructure through one processing stage.

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# Particulate Fillers in Thermoset Plastics

# 5

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## Contents

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## Abstract

Although thermoset polymers are significant users of particulate fillers, the scientific literature is much scarcer than for other polymer types. This is because they are usually used in combination with glass fibers, which then dominate the properties of the composite.

The processing of thermosets is different to that for the other two polymer types, with the filler being added to a relatively low viscosity, often liquid, phase; where the high shear that helps dispersion in other polymer types is missing. On the other hand, there is less damage to the filler particles, which means that it is easier to use fillers such as mica, wollastonite, and glass fibers. It is also easier to incorporate hard fillers, such as crystalline silicas, and temperature-sensitive ones like cellulosics, than it is with other polymers. Thermoset polymers are also able to tolerate larger particle size fillers. Because they are polymerized during molding, thermosets can also exhibit higher mold shrinkage and controlling this is an important role of particulate fillers. Fillers are also important in reducing polymerization exotherms, which can otherwise cause problems.

The main general purpose filler used in thermosets is calcium carbonate in various forms. This is mainly employed for cost reduction, shrinkage, and exotherm control. Large quantities of aluminum hydroxides are also used for low smoke and fume flame-retardant and aesthetic purposes. Epoxy printed circuit boards use fillers such as alumina to impart high thermal conductivity while retaining low electrical conductivity. Thermosets make more use of hard fillers such as crystalline silicas than other polymer composites. These are used to improve abrasion resistance in flooring and solid surface applications.

Most thermosets are polar, and this means that they can wet and interact well with many types of fillers, especially minerals like carbonates. This reduces the need for surface-modifying species, but dispersants and coupling agents may still be utilized, especially with siliceous fillers. Coupling agents are also often used to help property retention under adverse environmental conditions rather than to improve initial properties.

**Keywords**

Thermosets • Unsaturated polyesters • Polyurethanes, epoxy resins • Calcium carbonate • Aluminum hydroxide

## Definitions

Thermoset plastics are polymers which are produced “in-situ” from relatively low molecular weight precursors, usually in a mold cavity. The final shape is thus set by chemical reaction (curing), as opposed to cooling of a melt, which occurs with thermoplastics. Most elastomers are also thermoset, but start from high molecular weight polymers and have much less cross-linking than thermosets.

Particulate fillers are powdered substances, with low aspect ratio particles usually less than 100 μm in size, which are added to polymers to reduce cost, to improve processing, and/or to modify one or more properties. They can be inorganic or organic in nature and may be of natural origin or synthetic.

Solid surfaces are an important, glass fiber-free, application for fillers in thermoplastics. The term refers to a solid, non-porous surfacing material mainly used in kitchens and homes for counter tops, sinks, and bathroom fittings. They are usually made from highly filled polyester or acrylic resins and, by judicious choice of fillers, can have a very attractive appearance, resembling polished minerals, but much more easily shaped and cut. They also need to be formulated to resist heat, stains, and impact and to either be very scratch resistant or able to be easily resurfaced by polishing. The main fillers used in this application are ATH and crystalline silicas.

## Introduction

In common with other polymers, thermosets are significant users of particulate fillers, often at high addition levels. However, they do differ in the processing methods, reasons for use, and the filler types most often met. As with many particulate filler topics, the bulk of the literature is in trade publications and conference proceedings, rather than in peer-reviewed journals.

The principal thermoset polymers using fillers are unsaturated polyester resins (UPR), polymethyl methacrylates (PMMA), phenolics, epoxies, and polyurethanes. The main fillers used and the reason for their choice are summarized in Table 1. More detail is given in sections "Processing of Thermoset Composites" and "Effect of Particulate Fillers on Properties."

## Processing of Thermoset Composites

Processing of thermosets is completely different to that for the other two polymer types, with the filler having to be added to the pre-polymerized monomer, rather than the polymer itself. This means they are added to a relatively low viscosity, often liquid, phase, where the high shear that helps dispersion in other polymer types is missing. On the other hand, the processing causes less damage to the filler particles, which means that thermosets are more able to use fillers such as mica, wollastonite, and glass fibers. It is also easier to incorporate hard fillers, such as crystalline silicas, and temperature-sensitive ones like cellulosics, than it is with other polymers. Thermoset polymers are also able to tolerate larger particle size fillers and higher addition levels.

In addition, most thermosets are quite polar, which means that they can wet and interact well with many types of fillers, especially minerals like carbonates. This reduces the need for surface-modifying species, but dispersants and coupling agents may still be utilized, especially with siliceous fillers. Coupling agents are also often used to help property retention under adverse environmental conditions rather than to improve initial properties.

The addition of particulates can significantly increase pre-cure resin viscosity making molding difficult and special methods have to be adopted when very high

**Table 1** The main filled thermoset composites in commercial use

| Polymer | Main particulate fillers used in thermosets and primary purpose | Comments |
|---|---|---|
| Unsaturated polyester resin (UPR) | Natural $CaCO_3$ – cost saving and processing<br>Aluminum hydroxide (ATH) – flame retardancy and aesthetics (solid surfaces)<br>Talc – stiffness without glass fiber | Addition levels can be quite high and particulates are often used in conjunction with glass fibers |
| Urea and melamine formaldehyde | Wood flour – cost saving | |
| Epoxies | Alumina, magnesia, natural aluminosilicates – improved thermal conductivity<br>crystalline silicas – abrasion resistance | Thermal conductivity is an important requirement in some applications |
| Phenolics | Wood flour<br>Natural CaCO3 – cost saving and processing<br>ATH – flame retardancy<br>Crystalline silicas – abrasion resistance | |
| PMMA | Aluminum hydroxide – flame retardancy and aesthetics (solid surfaces)<br>Crystalline silicas – abrasion resistance | Where used, this is often at high levels |
| Polyurethanes | Aluminum hydroxide and expandable graphite – flame retardancy | |

loadings are desired. High filler addition levels are often required when using aluminum hydroxide for flame-retardant purposes, with 150–300 phr (parts per hundred resin) often being required. Two approaches are used to control viscosity: use of special dispersing agents and particle size manipulation to maximize packing.

## Effect of Particulate Fillers on Properties

Although thermoset polymers are significant users of particulate fillers, the scientific literature is much scarcer than for other polymer types. This is because they are usually used in combination with glass fibers, which then dominate the properties of the composite. The following concentrates on the effects that are observed in the absence of fibers.

The principal property enhancements of importance that are produced by fillers in thermoset polymers are:

- Cost reduction
- Exotherm control and reduced cure shrinkage
- Increased modulus
- Reduced thermal expansion
- Enhanced thermal conductivity
- Flame retardancy
- Aesthetics
- Abrasion resistance
- Toughness

The main properties which may be negatively affected are:

- Rheology of the pre-cure mix
- Transparency

## Cost Saving

In assessing materials cost savings, one needs to take into account the volume cost of the filler compared with the polymer, not the weight cost. This is because most fillers are significantly denser than polymers and hence proportionally more is needed to fill the same volume. While this consideration weighs heavily on cost saving opportunities in commodity thermoplastics, it is less of an issue for thermosets which are generally more expensive and have a higher specific gravity. Fillers are also easier to incorporate, and all these factors mean that there is a much better case for using them for cost reduction. The most widely used fillers for this are the carbonates, especially calcium carbonates.

## Exotherm Control and Shrinkage Reduction

The polymerization of many thermoset polymer systems is considerably exothermic and accompanied by significant shrinkage; both of which can cause problems in molding operations. The presence of inert fillers is often used to reduce both these problems, although care must be taken not to reduce the exotherm too far. Isotropic fillers are best for reducing shrinkage, as their effect is uniform, while anisotropic ones can lead to uneven effects and warpage. While most inorganic fillers could be used, the less expensive calcium carbonates are usually employed when this is the main concern.

## Stiffness (Modulus)

While particulate fillers do increase stiffness of thermosets, this is frequently not their primary purpose. This is because thermosets are already much stiffer than other polymers and glass fibers (which are outside of the scope of this article), rather than particulate fillers, which are frequently used for this purpose where it is necessary.

Even so, fillers can have a significant effect, which can be well described by semi-empirical models (See Jackson et al. 2003). Typical results for a silica-filled methacrylate polymer are presented in Fig. 1. Increasing aspect ratio also improves modulus, at least up to a limiting value, as shown in Fig. 2. Somewhat surprisingly,

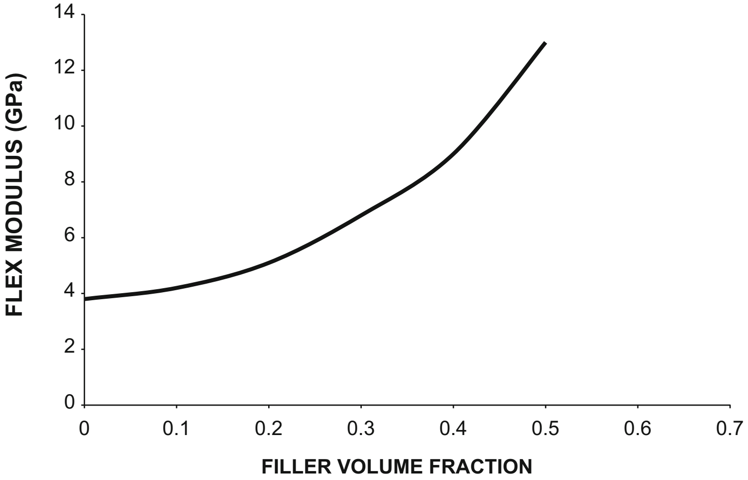

**Fig. 1** Effect of filler volume fraction on the flex modulus of a silica-filled methacrylate polymer (from Jackson et al. 2003, with permission of Smithers Rapra)

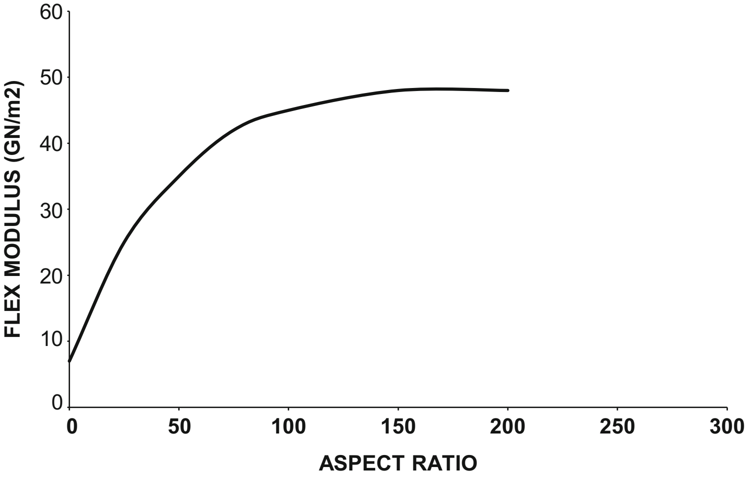

**Fig. 2** The effect of aspect ratio of mica on the modulus of a filled unsaturated polyester resin (adapted from Canova 2000)

adding coupling agents has little effect on the initial modulus, probably due to shrinkage effects during curing and processing which create compressive bonding.

## Thermal Expansion

Polymers generally have higher coefficients of thermal expansion (CTE) than most mineral fillers and so, mineral incorporation can significantly reduce the coefficient of expansion of a composite material. This effect is usually beneficial, reducing shrinkage when a part cools after molding and making it easier to match polymers to other materials such as metals in composite structures.

Isotropic particles are best for this, as they produce a uniform effect. Some specialty fillers have been designed to have very low coefficients of thermal expansion (e.g., some glass ceramics). Negative coefficients are also possible (e.g., zirconium tungstate and some zeolites), and these are used for special applications.

## Thermal Conductivity

There is a separate chapter on thermally conductive additives, so this is only briefly covered here.

Thermal conductivity is an important topic for some thermoset applications, notably printed circuit boards. These are a significant market for thermoset polymers and require high thermal conductivity to remove heat. As shown in Table 2, metals have the highest thermal conductivity among common materials, but they also have high electrical conductivity, which eliminates them for printed circuit boards. Common mineral fillers, such as calcium carbonates, can significantly improve the performance of polymers, but fillers like aluminum oxide are far superior and widely used for this purpose.

Specialty fillers, such as some naturally occurring aluminosilicates, are used when high thermal conductivity is paramount, for example, in heat sinks for laptop

**Table 2** The thermal conductivity of various common materials (the measurement of this property is quite complex and so approximate values only are given here)

| Material | Thermal conductivity W/(m K) at 273 K |
|---|---|
| Common metals | 80–400 |
| Aluminum oxide (Corundum) | 30 |
| Magnesia | 30 |
| Some naturally occurring aluminosilicates | 14 |
| Calcium carbonates | ~5 |
| Glass | ~1 |
| Water | 0.6 |
| Polymers | 0.2–0.4 |
| Air | 0.024 |

computers where enormous amounts of heat must be managed in a confined space. One would imagine that the higher the thermal conductivity of the filler, the more effective it would be at increasing the thermal conductivity of the composite. This, however, turns out not to be the only factor; the elastic modulus of a composite also has a significant effect, and fillers that significantly increase this can perform better than expected (Weidenfeller et al. 2012).

## Flame Retardancy

For the general principles of this topic, see ▶ Chap. 17, "Mineral Filler Fire Retardants".

The use of fillers is one of many approaches to flame-retarding polymers. Their main attraction is the absence of many of the health and safety issues accompanying the more reactive systems, notably halogen/antimony oxide combinations.

Many thermoset applications require good fire safety, and in many cases, this needs to be achieved by systems which do not give rise to significant levels of smoke and fume. Two types of filler are widely used for low smoke and fume, thermoset polymer formulations. The main one is aluminum hydroxide, which functions by endothermic decomposition, releasing water. It is a very effective flame retardant, although requiring high loadings.

Flame-retardant testing is a complex topic, but illustrative results showing the effect of adding aluminum hydroxide (ATH) flame-retardant fillers to a cross-linked PMMA matrix on a widely used test (oxygen index) are presented in Fig. 3. The higher the oxygen index, the more flame retardant a composite is and the results show that

- ATH is an effective flame retardant.
- High levels are needed to achieve a significant effect.
- There is a small particle size effect, with smaller sizes giving better results.

One of the main reasons for using ATH as a flame retardant is that, unlike some other systems (notably halogens) it gives low smoke levels when the composite does

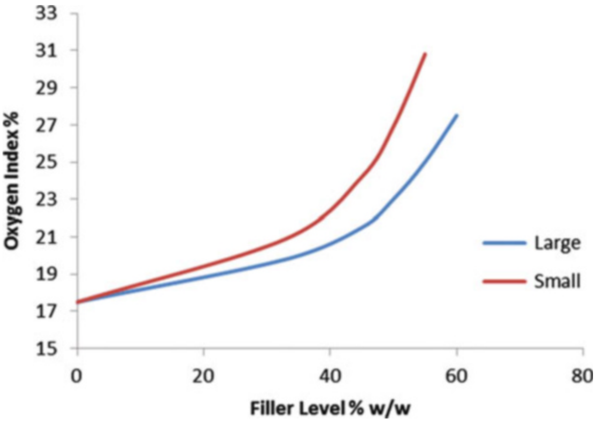

**Fig. 3** Effect of addition level and particle size on the oxygen index of aluminum hydroxide-filled PMMA

**Table 3** The effect of an ATH filler on the smoke generation from a typical SMC unsaturated polyester resin formulation

| ATH addition level (phr) | Maximum specific optical density (NBS smoke chamber test) |
|---|---|
| 0 | 375 |
| 100 | 225 |
| 150 | 200 |
| 200 | 190 |
| 300 | 180 |

burn. This is important in many applications in construction and transport, where smoke can seriously affect escape times. Table 3 shows how the addition of ATH flame-retardant affects the smoke from a burning polyester sheet molding compound (SMC). Note that, in contrast to the reduction seen, a halogen/antimony oxide system would have dramatically increased the smoke level.

The other flame-retardant filler of significance is expandable graphite (EG), which is mainly used in polyurethane foams. This product works by exfoliation of the graphite particles under fire conditions which releases thin graphite sheets that help to produce a stable char layer. The exfoliation is achieved by intercalating a species between the graphite layers which turns to a gas at typical flame temperatures. Shi et al. (2005) have reported on the use of EG in rigid polyurethane foam.

## Aesthetics

Aluminum hydroxides can be used to give desirable translucent effects, similar to marble and onyx in some solid surface applications and are widely used for this. The information on formulations is largely proprietary, but dispersants and coupling agents are widely used to maximize performance.

## Abrasion Resistance

Thermoset polymers such as PMMA are widely used in solid surface applications and, where these need good wear resistance, such as in kitchen sinks and worktops, then hard fillers such as quartz and cristobalite are used. In other instances (e.g., vanity basins), the ability to polish out scratches means that relatively soft fillers, such as aluminum hydroxide, are employed. As described above, these also have aesthetic advantages.

## Toughness

Thermoset polymers are quite brittle materials and this is one reason for the prevalence of glass fibers in their composites. Although not generally one of their main functions, rigid, particulate fillers may also increase fracture toughness. This is a complex topic, well covered by Jackson et al. (2003). In general the improvement is thought to originate from crack pinning by the particles and is most noticeable with smaller particle size and with good particle to matrix adhesion. The strength of the particulate additive also appears to be important in determining whether significant toughening is achievable. Weak particles, especially those that can be readily cleaved, such as talc, aluminum hydroxide and mica, can actually act as the loci for failure.

Fatigue strength can also be important in some thermoset applications (such as the solid surface applications referred to under abrasion resistance). Again it is a complex topic, with both static and dynamic fatigue and environmental factors (e.g., wet or dry) to be considered. It is not frequently addressed in the literature, although the work by Jackson et al. (2003) referred to above gives a good introduction. Environmental factors, especially water, can have a profound effect and lead to accelerated failure, with good interfacial adhesion, such as provided by coupling agents, playing an important stabilizing role.

## Rheology of Pre-Cure Mix

Thermoset resins, unlike most other polymer types, start off as a liquid monomer of oligomer, which flows into a mold for curing. Addition of fillers (and glass fibers) inevitably increases the viscosity of the system and affects its flow properties. To some extent the increased viscosity can be beneficial to filling and molding operations and can be useful in preventing filler settling during storage of the premix. Indeed specialized thixotropic agents are sometimes used to prevent such settling. However, if the viscosity increase goes too far, then it can cause problems. As well as inhibiting mold filling, high viscosity can prevent proper degassing, which is needed to remove air entrapped during filler addition and molding operations. These viscosity effects are most noticeable at high filler addition levels such as employed for maximum flame retardancy when using ATH.

Two tools are at the formulator’s disposal to counteract deleterious viscosity effects. The first is the use of dispersant additives, of which several specialist ranges exist. When choosing these additives, consideration must be given to the stability of the viscosity over time, as this can often change. The second tool is to use fillers with tailored particle size distributions that allow for maximum packing. These distributions can be made up by the formulator (see Ferrigno 1978) or supplied by the filler producer. Oil absorption of a filler is a good guide for this, with a low value giving least effect on viscosity.

An example of the use of a proprietary dispersing agent on the viscosity of an ATH at 275 phr in an unsaturated polyester resin system is given in Fig. 4. The effect of particle size distribution on viscosity of a similar system is given in Table 4.

Particle shape also has an important bearing on resin viscosity and this is particularly relevant to ATH, which can be produced by two different methods, grinding or precipitation. Grinding produces platy particles, while precipitation gives blocky ones with lower oil absorption and less effect on viscosity.

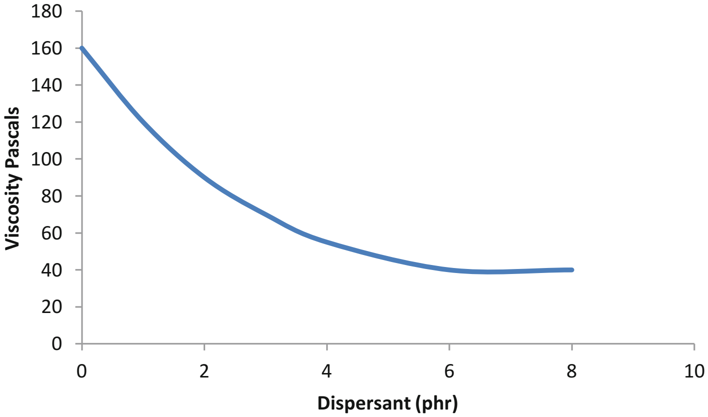

**Fig. 4** Use of a dispersing agent to reduce the viscosity of a highly filled UPR (275 phr ATH)

**Table 4** The effect of optimizing particle size distribution on the viscosity of an unsaturated polyester system containing 150 phr of an ATH filler (all fillers with 12 μm average particle size)

| ATH type | Linseed oil absorption (g/100 g) | Viscosity (cP) |
|---|---|---|
| Standard milled grades | 26 | 25–30,000 |
| Broad particle size distribution | 16 | 10 – 12,000 |
| Highly optimized broad distribution | 13 | Below 10,000 |

### Transparency

Most thermoset resins, being amorphous, are quite transparent. Fillers, such as calcium carbonate and ATH have higher refractive indices than the polymers and so significantly reduce transparency (an effect which varies with particle size). This is not usually an issue in many applications. Where it is, then fillers of lower refractive index, and nearer to the polymer matrix, such as glass and crystalline silicas, are more suitable.

## Particulate Filler Use by Polymer Type

### Unsaturated Polyester Resins (UPR)

Unsaturated polyester resins are used as viscous liquids made by dissolving low molecular weight polymers in vinyl monomers, mainly styrene. This allows easy molding or shaping of the resin into a desired form before curing to the final rigid shape. Cross-linking is achieved by free radical addition polymerization of the styrene monomer.

Typical applications for UPR are in products which are reinforced with fiberglass, such as shower stalls, boat hulls, vehicle panels, and autobody parts and trim. These also usually use mineral fillers in conjunction with the glass fibers. Mineral-filled

UPRs without glass fiber are used in products such as synthetic marble and onyx countertops and in autobody putty.

The main particulate filler used in UPR is natural calcium carbonate. Significant amounts of ATH are also used where halogen-free fire retardancy is required and for some solid surface applications. Talc is also used in products such as automotive body fillers. There is reported to be a significant use of calcium sulfate dihydrate (gypsum) as a filler in the USA, but it is not used to any extent in Europe.

Two of the most important forms of UPR which use mineral fillers are bulk and sheet molding compounds (BMC and SMC). The BMC compounds are the easiest to fabricate, but SMCs have superior properties.

Bulk molding compound (BMC) is a blend of mineral fillers (usually calcium carbonate and/or ATH), glass fiber reinforcement, catalysts, stabilizers, and pigments which are made into the form of a viscous, “puttylike” molding compound. The glass reinforcement is present at between 10% and 30% w/w, and the glass length is typically less than 12.5 mm. Bulk molding compounds have excellent flow characteristics and can be formulated for good mechanical properties, flame and tracking resistance, electrical insulation, corrosion, and stain resistance. As such they are well-suited to a wide variety of applications.

Sheet molding compound (SMC) is similar to BMC in outline, but contains longer glass fibers and higher glass levels and is made for compression molding purposes and larger parts and higher mechanical strength is needed. Glass reinforcement can be up to 60% w/w and glass length up to 25 mm.

SMC is produced in using a continuous in-line process. A paste of all the components except the glass is made first. This is then spread evenly onto a polymer film (usually nylon or polyethylene). Chopped glass fibers are then randomly deposited onto the paste. Another polymer film is introduced to make a sandwich structure which is rolled and allowed to mature. The top and bottom polymer films act to prevent auto-adhesion of the roll. Sheet molding compounds can be molded into complex shapes which, after curing, have excellent mechanical properties and surface appearance, together with good electrical insulation, and are ideal for automotive Class A body panels, high-strength electrical parts, and many other applications.

While the glass fibers are the main contributor to their mechanical properties, particulate fillers also have an effect. Table 5 taken from trade literature shows the effect of an ATH filler on the flexural strength and modulus of a typical SMC

**Table 5** The effect of an ATH filler on flexural properties of a typical SMC formulation (rounded values)

| Filler level (phr on resin) | Flexural strength (MPa) | Flexural modulus (MPa) |
|---|---|---|
| 0 | 90 | 3,000 |
| 100 | 100 | 5,000 |
| 150 | 105 | 7,000 |
| 200 | 110 | 8,000 |
| 250 | 105 | 9,000 |
| 300 | 100 | 10,000 |

formulation and how this varies with filler loading. Note that while the flexural strength starts to decrease at high loadings, it is still above the unfilled, even at 300 phr addition level.

### Polymethylmethacrylate (PMMA)

The PMMA referred to here is a lightly cross-linked form (hence thermoset). PMMA is a relatively expensive polymer and is mainly used for its clarity and transparency. Thus it is mainly used unfilled. Even so, the optical properties can be put to good effect in making highly filled products that simulate the appearance of polished minerals. This is made use of in solid surface applications. In Europe the main fillers used for this application are hard ones such as cristobalite, with relatively small amounts of soft ATH being used. North America and Japan both have a strong liking for what is known as synthetic or cultured marble and onyx for which ATH or calcium carbonate is widely used to obtain the required appearance.

### Phenolic Resins

The phenolic market is a specialized one and mainly uses natural calcium carbonates and hard fillers. Where fire retardancy is important, ATH is often used.

### Epoxy Resins

The main epoxy market making use of particulate fillers is in printed circuit boards, which require fillers that impart high thermal conductivity, while being electrically non-conductive. Alumina, magnesia, and specialized aluminosilicate fillers are used. There is also some use in flooring and solid surface applications which use hard fillers such as quartz.

### Polyurethanes

While large total amounts of thermoset polyurethanes are used, much of this is for foam production where fillers are little used. There is some use of fillers in polyurethanes in footwear, but these are mainly elastomeric types of polyurethane. The main filler use in thermoset polyurethanes is for fire retardance, and this can be achieved by addition of fillers such as ATH or expandable graphite.

## Recycling and Sustainability

In common with other polymer composites, the recycling and sustainability of thermoset composites themselves has received significant attention. Useful reviews can be found by Pickering (2006) and Oliveux et al. (2015).

There have been two main thrusts to this work, mechanical grinding to produce resin particles suitable for incorporation as a filler and thermal resin removal processes such as pyrolysis and solvolysis to recover fillers themselves for reuse.

Most thermoset composites contain glass or carbon fibers in addition to particulates such as calcium carbonate and aluminum hydroxide. Grinding not only reduces particle size but can lead to some fiber removal and various fractions containing different amounts of resin and fiber can often be produced. The particulates are mostly found in the resin rich particles. Some proportion of the recyclate can be used in fresh resin-based composites, depending on the resin, the mechanical processes used, and final application. Most commercial activity has been centered on producing and reusing micronized powder from SMC and BMC materials.

The thermal processes have concentrated on recovery of the higher value glass and carbon fiber reinforcements, rather than particulates. This is outside of the scope of this article and the reviews referred to above should be consulted for this.

## Cross-References

- ► Mineral Filler Fire Retardants
- ► Surface Modifiers for Use with Particulate Fillers
- ► Thermally Conductive Additives

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# Particulate Fillers in Elastomers

# 6

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## Contents

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**Abstract**

Fine particulate fillers are widely used in elastomers (indeed are essential for many applications) and are small hard particles usually of carbon or inorganic origin. The main fillers used in general purpose elastomers are carbon black, precipitated silicas, clays, and natural carbonates. There is also significant use of precipitated calcium carbonates and of synthetic flame retardant fillers such as aluminum hydroxide. Fumed silica plays a key role in silicone elastomers while finely ground crystalline silicas are important in specialist high temperature elastomers.

Filler reinforcing effects depend very much on the type of elastomer. They are most obvious in noncrystallizing elastomers, such as most synthetic types. Here, the fine filler particles are able to act as tiny crystallites and markedly improve the tensile strength, abrasion resistance, and higher extension modulus. In the crystallizing types, such as natural rubber, the elastomer crystallites which develop on stretching often hide filler effects in laboratory tests, but they are still present and important in many applications.

Size, shape, and surface activity are all important factors determining reinforcing ability. Small size, high structure, and high surface activity generally give the best blend of properties. Carbon blacks owe their preeminence to the natural ability of their surface to form strong interaction with hydrocarbon polymers. Other fillers generally require the addition of coupling agents to achieve the same effect.

**Keywords**

Carbon black • Coupling agent • Dynamic properties • Elastomer filler • Fumed silica • Precipitated silica • Reinforcement • Tires

## Definition

Elastomers are a specialized class of polymer made up of long chain, high molecular weight molecules with little crystallinity at rest. These chains are entangled with each other, but are coiled up when unstrained. Uncoiling of the chains allows elastomers to reach high extensions when stressed compared to other polymer types, while the desire of the chains to return to the coiled state allows for rapid recovery when the stress is removed. Cross-linking (often referred to as vulcanization when sulfur is used) introduces a small level of permanent cross-linking and this improves the strength and elasticity.

The polymer coils explain the basic features of elastomers, notably high extensibility and recovery. Some elastomers, such as natural rubber, form tiny crystallites on extension; these naturally reinforce the polymer, giving it high strength. Most synthetic elastomers do not achieve this and are thus of inherently low strength when unfilled.

Particulate fillers are widely used in elastomers (indeed are essential for many applications) and are small hard particles usually of carbon or inorganic origin. Their effects depend very much on the type of elastomer. In the crystallizing types, they cannot increase postcrystallization strength (such as determined in conventional tensile testing) much; although care has to be taken not to interfere with the crystallization and reduce it. In many of the applications of such elastomers, crystallization cannot occur and then fillers show their full potential. Fine fillers can, on the other hand, act as tiny crystallites and markedly improve the tensile strength of noncrystallizing elastomers, providing there is a high degree of surface interaction between the filler and elastomer.

## Introduction

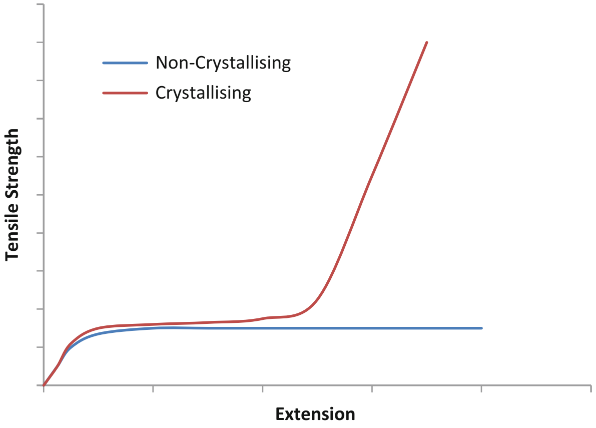
Elastomers (also known as rubbers) are a specialized but widely used class of polymers and can be of natural or synthetic origin. A key feature of elastomers is their ability to undergo repeated deformation cycles (extension or compression) without significant loss in performance, and this makes them ideal for dynamic applications.

Most elastomers require cross-linking to develop useful properties and this is usually achieved chemically, often using sulfur. Sulfur cross-linking is sometimes referred to as vulcanization. These cross-links are largely permanent and thus it is difficult to recover such cross-linked elastomers for reuse. There is a class of elastomers known as thermoplastic elastomers where cross-linking is achieved by phase separation and is reversible. Hence, they are more readily recycled.

The only natural rubber of any significance is that derived from *Hevea brasiliensis* (the rubber tree) and commonly referred to as natural rubber (NR). The principal synthetic elastomer in use today is styrene butadiene rubber (SBR). SBR (and many other synthetic elastomers) can be made by two different routes, solution or emulsion polymerization. Emulsion polymerization is the commonest, as it is less expensive, but will leave significant amounts of emulsifying agents in the final product. As will be discussed under tire applications, this can inhibit filler to elastomer adhesion. Other important rubbers include nitrile (NBR), butyl (BR), and ethylene propylene copolymers (EP and EPDM). There are also several specialized elastomers including silicone and fluorocarbon elastomers. The properties of any class of elastomer vary with molecular weight, branching, microstructure, and ability to crystallize when extended. Natural rubber is the classic example of a crystallizing elastomer, while SBR is noncrystallizing. The difference between the two types is illustrated by the generalized stress–strain curves in Fig. 1. The noncrystallizing elastomer is inherently weak unfilled, while the crystallizing one becomes strong when an extension is reached where the crystallites can form.

Three general classes of elastomer fillers are generally recognized: reinforcing, semireinforcing, and nonreinforcing. These definitions are a little vague as the effects of a given filler can vary from polymer to polymer. One way of differentiating them is by their effect on pure natural rubber (Skelhorn 2003). According to this

**Fig. 1** The different stress–strain curves for crystallizing and noncrystallizing elastomers



approach, a reinforcing filler increases abrasion resistance and tensile and tear strengths, a semireinforcing one increases tensile and tear strengths but not abrasion resistance, while a nonreinforcing one does not enhance any of the properties. The level of reinforcement achievable is largely determined by particle size, increasing with reducing size, provided that a good level of particle to polymer adhesion is maintained. Precise sizes for the different classes are impossible to specify and there is some considerable overlap, but reinforcing fillers are generally regarded as having primary particle sizes of less than 100 nm, with semireinforcing ones being in the range 100–500 nm, while nonreinforcing ones are greater than 500 nm. Some people recognize a further class of fillers called diluent. These have sizes in excess of 5,000 nm and significantly degrade rubber properties.

Another important aspect of the various types of filler is the effect of volume fraction on strength. Reinforcing fillers show a marked peak in performance at relatively low loadings, followed by a significant decline. Semireinforcing ones have a broader peak at higher loading, while nonreinforcing ones have no peak, and a diluent filler shows a steady decline at all loadings.

This is illustrated in Figs. 2 and 3. Figure 2 shows the effect on strength that one can expect to see as a function of filler loading, for the three types of filler in a noncrystallizing elastomer, such as SBR. Figure 3 shows the same effect in a crystallizing elastomer such as NR.

Typical reinforcing fillers include most carbon blacks, fumed and precipitated silicas, nanoclays, and some special minerals such as halloysite. Semireinforcing ones include some clays (often referred to as hard clays), precipitated calcium carbonates, and the thermal blacks. Nonreinforcing ones include other clays (often called soft clays) and natural calcium carbonates.

Both natural and synthetic elastomers are almost always used filled with particulate materials, particularly those of submicron size, such as carbon black and precipitated or fumed silica. This is because such particles are usually required to obtain the required strength.

**Fig. 2** The effect of the three types of filler on the strength of a noncrystallizing elastomer such as SBR

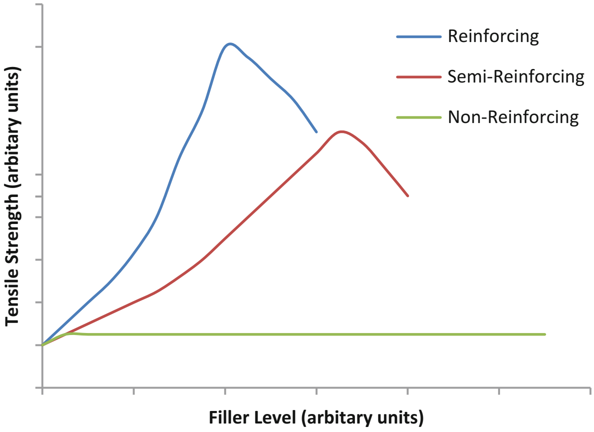
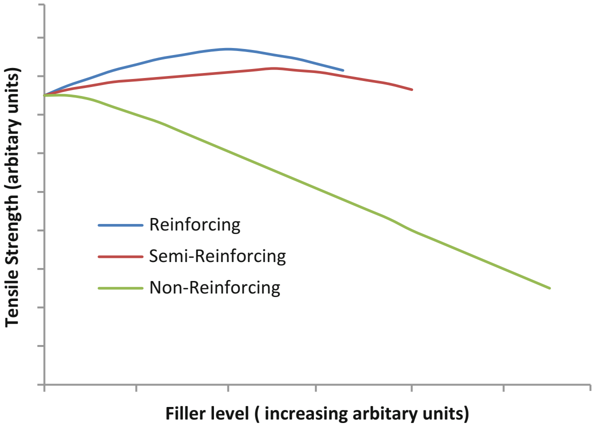


**Fig. 3** The effect of the three types of filler on the strength of a crystallizing elastomer such as NR



## Elastomeric Compounds and Their Important Properties

By their very nature, elastomers are used in relatively sophisticated, often dynamic, applications, with many more properties to consider than is the usual case with other polymer types. In addition to the usual stress–strain properties (tensile strength, elongation at break, and stiffness or modulus), elastomeric compounders have to consider others such as tear strength, abrasion resistance, hysteresis, and gas permeability. Because of the high extensions often encountered, modulus has to be considered over a very wide range and is often quoted at more than one extension. Other issues encountered include the amount of recovery (referred to as permanent set) after deformation, especially at elevated temperatures. This can be a serious issue and usually occurs due to additional cross-linking occurring (for example, due to incomplete cure, leaving unused cross-linking agents in the compound). One should also mention a property known as hardness. This is usually measured by indentation and is widely regarded as a useful way of specifying a compound for a given application. To further complicate matters, a variety of different test methods have been evolved to measure some of the properties, and it is important to specify which one is being used. It must also be remembered that many of the laboratory tests are just that and must be treated with caution, as they do not always relate precisely to the real life service property being modeled. The correlation of laboratory abrasion resistance tests with tire tread wear is a case in point. Finally, one must be aware that the various properties develop at different rates during curing and often go through a maximum and then decline. Because of this, formulation development often requires a study of the effect of cure time.

## The Role of Fillers in Elastomeric Compounds

Fillers, especially the very small sized particulate ones, can significantly affect many of the important elastomeric properties mentioned above, with both positive and negative effects being observed.

The main fillers used in general purpose elastomers are carbon black, precipitated silicas, clays, and natural carbonates. There is also significant use of precipitated calcium carbonates and of synthetic flame retardant fillers such as aluminum hydroxide. Fumed silica plays a key role in silicone elastomers while finely ground crystalline silicas are important in specialist high temperature elastomers.

The principal role of most fillers in elastomer systems is to increase reinforcement; by this is meant improvements in some, or all, of the following:

Tensile strength
Tear strength
Modulus
Abrasion resistance

This usually has to be achieved without detriment to properties such as compression set.

The effect of fillers is most clearly seen in noncrystallizing elastomers, such as SBR, which are inherently weak when no filler is present. This is demonstrated in the stress–strain curves presented in Fig. 2. Crystallizing elastomers (such as natural rubber) appear strong and not so much in need of reinforcement when subjected to simple stress/strain testing, where there is time for the reinforcing crystallites to form, but this is far from the truth. Their apparent strength in these tests derives from the formation of crystallites during deformation, but these are frequently not present or are unable to form, in real life applications, especially under dynamic conditions. Thus filler reinforcement is usually still critical in most applications involving these elastomers.

## Important Filler Properties

Filled elastomer properties are all influenced by different combinations of the following filler properties:

Filler size
Filler shape, including a property known as structure
Filler dispersion
Filler to elastomer adhesion

## Size and Specific Surface Area

While particle size is an easily understood concept for most particulate fillers, some explanation of its meaning is needed for the types of filler most widely used in elastomers, such as carbon black and synthetic silicas. Both of these are made up of very small primary particles, fused together into larger shapes (aggregates). The particle size referred to for these types of filler is normally the primary size, as determined by techniques such as electron microscopy, even though they will not be dispersed down to such particles in elastomer compounds.

Specific surface area is frequently quoted instead of, or as well as, particle size. For those fillers that do not form aggregates this is reasonable, as there is usually a good correspondence between particle size and specific surface area. With aggregating fillers caution is needed, as the level of aggregation will moderate the specific surface area. Nitrogen adsorption is the specific surface area test most commonly used for fine particulate fillers (usually designated as the BET surface area). While this is still used for fine fillers used in elastomers, one will also encounter another method using cetyl trimethylammonium bromide and known as the CTAB method. The logic behind the use of this much larger molecule is that the very fine fillers can contain surface accessible to the small nitrogen molecule, but not to CTAB and the latter gives a truer picture of the surface accessible to elastomer molecules. The CTAB area is usually less than the BET one, with the difference being regarded as an indication of the porosity of the particle.

## Shape and Structure

While conventional filler shape properties such as aspect ratio have some importance, a property referred to as structure has particular importance in fillers used in elastomer applications. The term structure is widely used in elastomer filler technology and can cause considerable confusion. There are two distinctly different types of structure which need to be differentiated and are generally referred to as transient and permanent structure.

## Transient Structure

Both silicas and carbon blacks exhibit a phenomenon known as transient structure when dispersed in liquids or polymers. This is the formation, at rest, of a network of interacting filler particles. This network increases the viscosity of the system, but is readily broken down by shear. This is most noticeable in the thixotropy of some silica dispersions in liquids. It is mentioned here because, as we shall see later, it is of considerable importance in tire technology.

## Permanent (Persistent) Structure

This refers to the particles themselves and has a very distinct meaning and importance in elastomer technology, where it is related strongly to aggregation and shape. In essence, the important factor is the ability of a particle shape to trap or shield polymer. This trapped polymer does not experience the full stress field in the matrix and in some ways this increases the effective volume fraction of the filler. This is a property of many types of filler, but is usually used with reference to carbon black, where it is particularly marked. Permanent structure is usually measured by a simple oil absorption test, with a high value indicating high structure.

A simple schematic view of the concept of structure is presented in Fig. 4. As it is related to the shape of aggregates, structure can be much affected (reduced) by aggregate break down during processing. This is illustrated by the data presented in Fig. 5, where carbon black was recovered from compounds before vulcanization and the oil absorption compared with that of the original black. It can be seen that the high structured black (HAF-HS) suffers a significant loss in oil absorption (i.e., structure) while the low structured one (HAF-LS) shows no loss. Various techniques have been developed to take account of this loss during processing; one such is to compress or crush the carbon black before determining the oil absorption (Dollinger et al. 1967). This is sometimes referred to as the 24 M4 value.

## Dispersion

Filler dispersion is an important issue in most filled polymer applications but is especially important and has received most attention in elastomers. The measurement of dispersion in a filled compound is a complex topic and various techniques

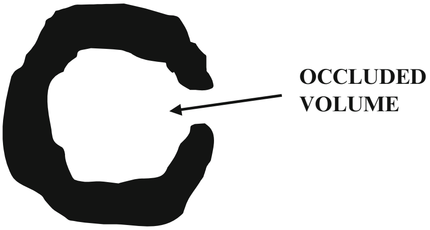


**Fig. 4** Simplified representation of permanent filler structure

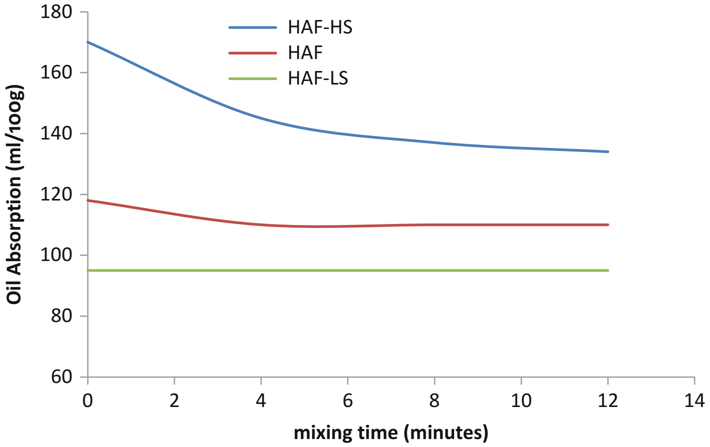


**Fig. 5** The effect of polymer processing on the structure of carbon blacks with differing levels of initial structure (adapted from Blow and Hepburn (2009))

can be used to give relative ratings (Hess 1991). These include electron microscopy, electrical conductivity (for conductive fillers like carbon black), and roughness of a cut surface.

Many elastomers have high viscosities at the relatively low temperatures at which fillers are incorporated and thus high shear forces are generated which considerably aid dispersion. The permanent structure of the filler aggregates referred to above is also an important feature for aiding the dispersion of the very small particle size fillers. This structure prevents very close packing of aggregates and thus more ready penetration by the rubber molecules.

## Filler to Elastomer Adhesion

Because of the high deformations involved, strong adhesion between the filler particles and the polymer chains is essential and should be retained even at high extension. In most elastomers, the natural surface of carbon black gives rise to such adhesion and this is one of the reasons for its dominance in elastomers.

Most other fillers, including the synthetic silicas and calcium carbonates, do not give rise to useful levels of interaction in their natural, unmodified state. This is a serious limitation and is tackled by the use of chemical additives which can react with both the filler surface and the polymer matrix (usually through the cure process), thus tying the two together. These additives are referred to as coupling agents for obvious reasons. Organosilanes are most widely used and are effective with synthetic silicas and most clays. They carry sulfur functionalities when used with sulfur cures and unsaturation (typically vinyl) for peroxide cures. The organosilanes are ineffective on carbon blacks, which have sufficient surface reactivity not to need them, and on calcium carbonates. Carboxylated polymers can be used for coupling carbonates into both sulfur and peroxide cured elastomers (Rothon 2010).

The use of coupling agents has to be carefully carried out if optimum properties are to be achieved. In particular, care has to be taken when other surface active species may be present in the formulation and compete for the filler surface. This type of chemical can be found in significant quantities in natural rubber and emulsion polymerized synthetic elastomers. Some curatives, such as zinc oxide, can also interact with and reduce the effectiveness of the coupling agent. One approach to overcome this is to precoat the filler with the coupling agent rather than adding them separately to the elastomer during the mixing process (often referred to as the “in situ” process). Somewhat surprisingly, the “in situ” process is more widely used than precoating.

## Effect of Filler Properties on Elastomer Performance

The influence of the filler physical properties on reinforcement and other important properties is a very complex subject as they interact with one another. The general trends are summarized in very simple form in Table 1 below. This shows that the best reinforcement is achieved by small particle size, high structure, strong filler/polymer interaction, and good dispersion. Only a few filler types are able to achieve this, notably carbon blacks, synthetic silicas when used with coupling agents such as organosilanes, and precipitated calcium carbonates with unsaturated carboxylated polymer coupling agents.

Some examples of the importance of the various effects follow.

## Some Effects of Particle Size

Table 2 exemplifies how tensile strength and abrasion resistance vary with carbon black primary particle size. This is a based on data in a sulfur cured SBR compound.

## Some Effects of Filler Dispersion

Table 3 shows how various filled elastomer properties develop as a function of dispersion. This study was achieved by measuring dispersion and property profile of a compound as a function of mixing time.

This study did not consider the effect of the actual size or nature of the poorly dispersed material. This was investigated in detail in the classic studies by Boonstra and Medalia (1963) who found that particles become detrimental at a size of about 1 μm. They found little further effect of size above this critical value, but did find that properties deteriorated further as the hardness of the particles increased. The most sensitive property to poor dispersion in both studies was found to be abrasion

**Table 1** The direction and magnitude of the effects of the main filler properties on those of filled elastomers (adapted from (Boonstra 1975))

| | Filler property | | | |
|---|---|---|---|---|
| Elastomer property | Particle size (decreasing) | Structure (increasing) | Dispersion (increasing) | Interaction (increasing) |
| Hardness | ++ | ++ | – | + |
| Tensile strength | ++ | LITTLE | + | + |
| 300% modulus | + | ++ | LITTLE | ++ |
| Elongation at break | – | –– | ++ | – |
| Tear resistance | ++ | LITTLE | LITTLE | LITTLE |
| Hysteresis | ++ | + | – | –– |
| Abrasion resistance | ++ | + | ++ | ++ |

Notes: + and ++ mean increase in that property and – and perty and++ mean increasedo not mean that the change is beneficial or detrimental. This depends very much on the application. For instance, high hysteresis is good for sound damping, but bad where heat build-up has to be avoided

**Table 2** The effect of carbon black primary particle size on tensile sand laboratory abrasion resistance in a sulfur cured SBR compound (adapted from (Boonstra 1975))

| Primary particle size nm | Relative tensile strength | Relative abrasion resistance |
|---|---|---|
| 20 | 1.00 | 1.00 |
| 28 | 0.89 | 0.74 |
| 39 | 0.72 | 0.47 |
| 49 | 0.64 | 0.41 |
| 70 | 0.58 | 0.35 |
| 180 | 0.50 | 0.16 |

**Table 3** Development of dispersion and properties during compound mixing (adapted from (Boonstra 1975))

| | Mixing time (minutes) | | | | |
|---|---|---|---|---|---|
| Elastomer property | 1.5 | 2.5 | 4 | 8 | 16 |
| Dispersion rating% | 24 | 86 | 99 | 100 | 100 |
| Hardness IRHD | 65 | 64 | 61 | 59 | 59 |
| Tensile strength MPa | 16.9 | 24.0 | 25.5 | 26.0 | 25.0 |
| 100% modulus MPa | 3.3 | 2.6 | 1.7 | 1.5 | 1.2 |
| 300% modulus MPa | 12.7 | 13.9 | 12.5 | 12.0 | 11.7 |
| Elongation at break | 380 | 490 | 530 | 540 | 530 |
| Tear strength MPa | 39.2 | 39.2 | 40.1 | 40.1 | 38.2 |
| Abrasion loss (Akron) | 289 | 142 | 136 | – | – |

resistance. Even trace amounts of grit (a few 100 ppm) was found to cause a detectable loss in performance in fatigue tests and are thus important in some critical applications, notably tires.

## The Effects of Filler to Elastomer Adhesion

The effects of filler to elastomer adhesion can be illustrated by comparing the effect of a typical reinforcing carbon black before and after a process known as graphitization. There is a strong natural adhesion between elastomers and the surface of conventional carbon blacks, but this can be removed by the graphitization process, which involves treating the carbon black at high temperature under an inert atmosphere. The results of such a comparison are presented in Table 4. The graphitization procedure used had only a minor effect on the physical properties of the carbon black (specific surface area and oil absorption) and no significant effect on dispersion in the elastomer.

As shown in the table, the main effect was an almost complete removal of bound rubber. Bound rubber is a test carried out on compounded but uncured elastomer and measures the amount of polymer “insolubilized” in a good solvent for the elastomer, after mixing with the filler. This is used as a measure of filler/elastomer interaction and indicates that graphitization has destroyed this. All of the reported compound properties have been changed by the graphitization, but by differing amounts. The biggest effects are seen to be on high extension modulus, abrasion loss, and hysteresis.

## The Effects of Filler Structure

The main effects associated with filler permanent structure are illustrated in Table 5. The carbon blacks used here are of similar specific surface area (and particle size), but differ significantly in oil absorption and hence structure. They both dispersed equally well in the elastomer. Some properties are little affected by the changes in

**Table 4** The effect of carbon black surface activity on compound properties, as demonstrated by graphitization of a reinforcing carbon black (adapted from (Boonstra 1975))

| Elastomer property | Unmodified ISAF black | Graphitized ISAF black |
|---|---|---|
| Bound rubber% | 18 | 1 |
| Hardness IHRD | 68 | 65 |
| Tensile strength MPa | 27.4 | 22.5 |
| 300% modulus MPa | 10.3 | 2.9 |
| Elongation at break% | 630 | 750 |
| Abrasion loss ($cm^3$ per $10^6$ revolutions) | 67 | 142 |
| Hysteresis | 0.204 | 0.297 |

**Table 5** The effect of carbon black structure on elastomer properties (adapted from (Boonstra 1975))

| Property | Normal structure carbon black | High structure carbon black |
|---|---|---|
| Filler specific surface area ($m^2g^{-1}$) | 108 | 116 |
| Filler oil absorption ($cm^3$/100 g.) | 133 | 172 |
| Mooney viscosity [ML(1 + 4)100 °C] | 73 | 83 |
| Extrusion shrinkage% | 40 | 30 |
| Dispersion rating% | 99 | 99 |
| Hardness IHRD | 68 | 73 |
| Tensile strength MPa | 27.4 | 26.5 |
| 300% modulus MPa | 10.3 | 14.7 |
| Elongation at break% | 630 | 450 |
| Abrasion loss ($cm^3$ per $10^6$ revolutions) | 67 | 62 |
| Hysteresis | 0.20 | 0.24 |

structure, notably tensile strength and abrasion loss, but others show significant effects. With respect to processing, compound viscosity increases while extrusion shrinkage decreases; both of these effects are consistent with the concept of occluded rubber mentioned earlier. High extension modulus increases while elongation decreases with increasing structure, again consistent with occluded rubber.

## Dynamic Properties of Filled Elastomers

This subject deserves special treatment as it plays a vital role in many applications, especially in vehicle tires, which account for the majority of elastomer, and hence filled elastomer, applications.

Here, we are dealing with repeated deformations with limited recovery times between them and this can have a marked effect on performance. This is a complex topic and only the simplest treatment will be attempted here. The key feature is the amount of energy lost in the deformation/recovery process, which largely manifests itself as heat and noise.

In tire applications, this lost energy is of considerable significance for the fuel efficiency of a vehicle (through a property known as rolling resistance) and also for road grip and has received considerable attention in the drive to improve efficiency and reduce fuel usage and the associated emissions.

A number of methods of measuring this energy loss are used: ranging from resilience and heat buildup tests to complex dynamic mechanical tests. The former are the easier to understand. Resilience is usually measured by some form of rebound test and low resilience means more energy loss on deformation. Heat build-up is measured during repeated cyclic deformation and a high heat build-up corresponds to higher energy losses.

The dynamic mechanical tests are more informative, if the most difficult to understand, but have a prominence in the important tire applications. Essentially, these tests are carried out using an oscillating sinusoidal stress and allow the sample response to be separated into an elastic and viscous component (storage and loss moduli). From this, one can derive a loss factor, which is commonly referred to as tan delta; the higher this value, the higher the energy losses and heat generation. The loss factor is dependent on energy dissipating processes and is temperature dependent. It is also frequency and rate dependent, with higher frequencies bringing about the same change as reducing temperature. Thus, the change of tan delta with temperature can be used as a guide to how it will change with frequency or rate of deformation. While this may seem academic at this point, it is of great significance in laboratory investigations of tire applications and this is discussed next.

## Tire Applications

Tires are the main user of elastomers and also of the reinforcing fillers such as carbon blacks, which have always played a key role in them. Indeed, it is very unlikely that a useful tire could be made without them. As a result of this, and with the dominance of this market, these fillers have evolved in parallel with tire developments and continue to do so.

Tires are very complex items with the elastomeric components being required to fulfill a number of demanding roles. As a result, one has to consider a number of properties not well known outside of this technology. In the early days, the main concern was with tire life and the use of fillers to reduce tread wear and for some tires (truck and especially off-road ones) to also reduce cutting and chunking. Heat build-up in use was another important consideration and is still a significant factor in failure of truck tires. Grip (also known as traction) is a further important criterion which has to be maintained under a wide range of road, driving, and climatic conditions. Over time, the contribution of the filler to grip began to be understood and developed. Precipitated silica, in particular, was noted for good grip, especially in the wet and under cold, winter conditions. More recently, attention has shifted to minimizing fuel consumption by reducing rolling resistance, while maintaining adequate tire life and grip. This has led to the emergence of what is known as the green or energy tire. Again the filler choice has proved to be a key factor in optimizing this type of tire.

The service conditions and hence requirements of a tire also vary according to the type of vehicle, automotive, van, truck, off-road, etc.

Tires are made up of several parts in order to maximize performance, each optimized for the role that it has to play. The main parts of the tire that can be recognized are tread, side wall, beading, and inner liner. These use different types of elastomer and impose different requirements on the filler. Most interest today is focused on the tread, which is responsible for the grip and for most of the wear issues and requires the highest filler performance. In automotive tires, it is also responsible for most of the rolling resistance. While carbon black has been, and remains, the principal filler used, different grades have evolved to suit the different tire parts. Precipitated silica has long been recognized as giving better tear and chunking resistance and has found a niche in tires requiring this. It has also been recognized that precipitated silicas offer the possibility of achieving lower rolling resistance and they have made great strides in penetrating parts of the tire market over the last 20 years or so. So much so that virtually all new cars in Europe now feature silica-based tread formulations. These tires are often called green or energy tires.

Currently, there is considerable interest in the inner liner. This replaces the inner tube found in old tires, and its primary function is to retain the air added to obtain the desired tire pressure. Thus, gas impermeability is a key requirement. Currently, the impermeability is achieved by using specialized elastomers such as bromobutyl for this purpose. These are much less permeable than more conventional elastomers, but tires still lose pressure at a measurable rate. There are two factors focusing attention on upgrading current inner liners; both are related to the need to reduce fuel consumption. Firstly, the elastomers used are significantly denser than more conventional ones, making the weight of the inner liner a significant factor in the overall weight of the tire. Secondly, running with underinflated tires increases the rolling resistance. Much of the upgrading effort is focused on the filler. All fillers reduce permeability to some degree, but platy ones, such as some clays, can significantly increase this effect. Much of the work is proprietary, but it is confidently expected that significant progress will be made.

## Tire Treads, Green Tire, Precipitated Silica Versus Carbon Black, Payne Effect, Rolling Resistance, etc.

While all the elastomeric components of a tire use fillers, the tread is especially important and has the highest performance requirements. Quite complex properties are involved when one comes to consider the use of reinforcing fillers in tire treads. Notable among these are abrasion resistance, hysteresis and the related properties of heat build-up, grip (traction), noise, and rolling resistance.

Of particular interest is the relationship between rolling resistance, grip, and abrasion resistance. This is commonly referred to as the magic triangle (Fig. 6), with improvements in one of these usually being offset by deterioration in another. As a result, compromises usually have to be made.

Many of the published studies use dynamical mechanical analysis to predict the rolling resistance and grip of filled elastomer compounds. This is done by measuring the energy losses (tan delta) at two temperatures, usually 0 °C and 60 °C or 70 °C. This uses the temperature, strain rate equivalence referred to above, with the lower temperature being considered equivalent to high strain rates (grip), and the high temperature to low strain rates (rolling resistance). While a good approximation in most cases, this analysis is not infallible and must be treated with caution.

One of the major advances in recent years has been the development of effective passenger tire tread compounds based predominately on the use of precipitated silica as the filler rather than carbon black. As will now be explained, this change of filler,

**Fig. 6** The magic triangle concept, showing the interrelationship between grip, tread wear, and rolling resistance

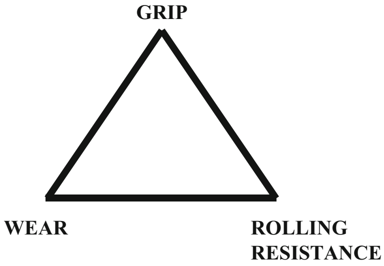


**Table 6** Effect of improving dispersion of precipitated silica on abrasion resistance

| % of undispersed filler | Relative abrasion loss (to 6.6% undispersed filler = 1.00) (DIN test)<br>Lower = better abrasion resistance |
|---|---|
| 6.6 | 1.00 |
| 3.3 | 0.89 |
| 0.5 | 0.87 |

together with the use of specialized coupling agents, allows an expansion of the "magic triangle" referred to above and a better balance to be achieved between tread wear, grip, and rolling resistance (fuel consumption) than was achieved with carbon blacks.

The potential for precipitated silicas to give lower rolling resistance than carbon blacks has been known for some time. The initial block to realizing this was the much poorer tread wear (abrasion resistance) achievable from the silica. This problem was associated with two factors. The first and most important is the relatively weak filler to elastomer bonding that silica achieves compared to carbon blacks. The second was the relatively poor dispersibility associated with the precipitated silicas available at the time. It was only when ways of overcoming these issues were found that the benefits of this filler could start to be fully realized.

The poor dispersibility was tackled by improving the production process, especially the filtration, washing, and drying steps. This led to the emergence of what has become known as easy dispersing (ED) and highly dispersing (HD) grades of precipitated silica. The contribution that improved dispersion can make to abrasion resistance is illustrated in Table 6.

The improvements in interfacial bonding that were required were realized through the development of specialized organosilane chemicals that can react with both the filler surface and, during vulcanization, with the elastomer and so strongly tie (couple) the two together. These chemicals belong to a class known as coupling agents. The first successful coupling agent introduced for this purpose was a polysulphidic tri-ethoxysilane known as TESPT. While other types have been developed since, this continues to be the dominant product today. In order to maximize the improvement in abrasion resistance, and achieve something similar to the tread life associated with carbon blacks, it is necessary to approach complete coverage of the filler surface with the coupling agent. Because of the high specific surface area of the fillers, this translates into quite high addition levels (between 5% and 10% w/w on the filler), making the coupling agent a significant factor in raw material costs.

The effectiveness of the present coupling agents is very much dependent on the type of elastomer they are used in, with solution polymerized synthetic elastomers giving better results than natural rubber or emulsion polymerized synthetics. This may be due to the presence of large amounts of surface active species able to compete with the coupling agent for the filler surface in the latter types.

Once the tread wear issue had been resolved, it was possible to tackle obtaining decreased rolling resistance, while maintaining good grip. For good grip, high hysteresis is required (i.e., the ability to dissipate energy), but the opposite is true for low rolling resistance (fuel consumption). For many years, it was believed that these two properties were inextricably linked and so a compromise had to be made. More recently, it has been established that this does not have to be so, as the conditions prevailing when grip is most required are quite different from normal driving where low rolling resistance is important. Fuel consumption is largely dominated by normal straight line travel, while grip is important when braking or cornering. The deformation conditions in these two cases are significantly different and hence it becomes possible to envisage systems where the hysteresis is maximized under one set of conditions and minimized under the other. It is this realization that has led to the evolution of new, improved tread technologies.

In order to understand how this separation can be achieved, we need to investigate the processes that lead to hysteresis, and how they can be controlled. While still a controversial subject, there are two main potential sources for filler induced hysteresis; these are filler transient structure breakdown and filler/polymer adhesion breakdown. It is now believed that the former (transient structure breakdown) plays the major role in hysteresis, while, as we have seen above, filler to polymer adhesion is mainly responsible for abrasion resistance.

The effects associated with the transient network are well illustrated by a long known phenomenon, which is called the Payne effect, and they manifest themselves as a significant change in energy loss (measured as a property known as tan delta) and elastic modulus with changing low amplitude frequency. The Payne effect can be used to compare fillers and throw some light on how they give different levels of rolling resistance. This is illustrated in Figs. 7 and 8. Figure 7 shows how tan delta (energy loss) changes with dynamic strain for similar elastomer compounds containing carbon black and precipitated silica, while Fig. 8 shows the effect of the same fillers on elastic modulus. It is apparent that the energy loss for the uncoupled precipitated silica is much less than the carbon black at low strains (under 10%) associated with normal driving conditions and peaks much later. This indicates that the precipitated silica has much a stronger filler–filler network. Precipitated silica also has the highest elastic modulus at low strains, indicating considerably more transient network formation than the carbon black. Finally, it is seen that the TESPT coupling agent treated precipitated silica has a broad shallow tan delta trace and low flat elastic modulus trace, indicating little

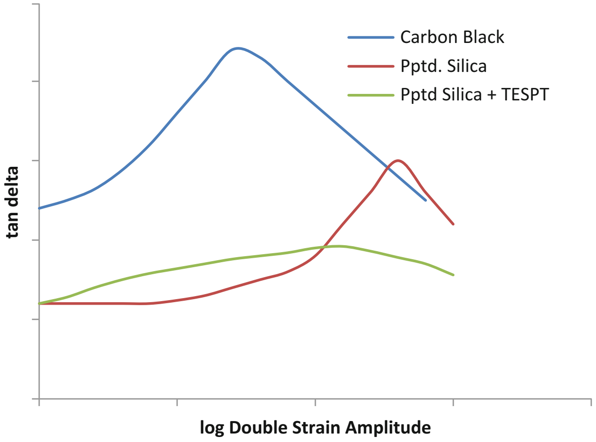


**Fig. 7** Tan delta as a function of double strain amplitude for carbon black and precipitated silica filled tire tread compounds

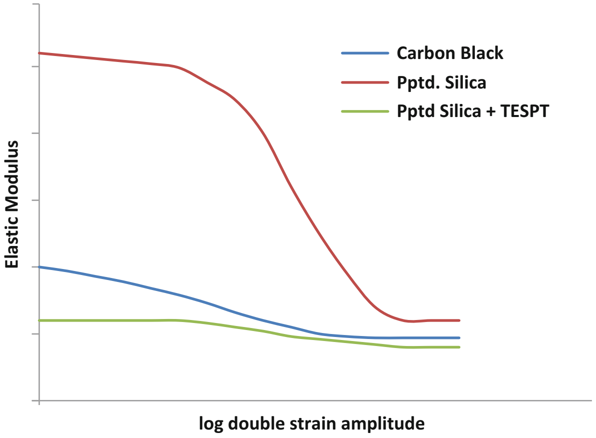


**Fig. 8** Elastic modulus as a function of double strain amplitude for carbon black and precipitated silica filled tire tread compounds

network formation. These features explain how precipitated silica and especially coupling agent treated precipitated silica is able to achieve lower rolling resistance than carbon black.

To summarize, precipitated silica without coupling agent has an extensive network, but this is too strong to cause significant energy losses under normal driving conditions. Carbon black, on the other hand has a less extensive network, but it is much weaker. Paradoxically to some, this means that it gives rise to greater energy losses under normal conditions. These differences explain the lower rolling resistance obtainable from precipitated silicas. Introduction of the coupling agent necessary to improve the lower abrasion resistance with precipitated silicas appears to destroy the strong network, but to form so little in the way of a weak one, that the rolling resistance advantage is maintained, although for a different reason.

## Silica Versus Carbon Black in Tire Treads

The results in Table 7 give a comparison of a carbon black and silica of similar specific surface area in a typical low rolling resistance tread formulation (Solution SBR/BR blend) and provide a good illustration of the effects discussed in the previous section. It is seen that, even without coupling agent, the silica gives lower tan delta at the higher temperature, but markedly worse abrasion resistance. The use of silane coupling agent brings the abrasion resistance close to that of the carbon black, without any loss in the tan delta properties. (NB the laboratory abrasion and tan delta tests are only a guide to actual rolling resistance, grip, and road-wear, which themselves vary according to the severity of the test conditions. It is generally accepted that silica plus silane, while about equal to carbon blacks under modest road-wear conditions, are still inferior at the highest severity).

As expected, the use of TESPT markedly improves tread wear due to the strong coupling and better dispersion. Fortunately, the destruction of the filler network does not have any negative effect on the dynamic properties discussed above, and the rolling resistance and wet grip advantages are retained.

Despite the better balance of properties obtainable, the precipitated silica/silane technology has some significant issues. These are partly around raw material costs, but mostly around processing. Reaction of the coupling agent with the filler is most commonly achieved during the compounding process and as a result it is necessary to control mixing conditions very carefully, if the silane is to react efficiently with the filler surface without the sulfide group entering into premature reaction with the polymer (a process known as scorch). Prereacted fillers are now becoming available, but have made little impact so far. The increased hardness of silica also leads to faster machine wear.

Not unexpectedly, the success of precipitated silica in penetrating the tread market spurred the carbon black producers into upgrading their own products and significant advances have been made, reducing but not eliminating their deficiency in rolling resistance. Typical of these products are nanostructured and inversion carbon blacks. Work is continuing to further upgrade carbon black performance.

As might be expected from the size of the market and the cost of the present system, there is considerable interest in finding alternatives to the silica/silane combination. Most of this is proprietary, but it has been reported that fillers including starch, conventional and nanoclays, and additives like Kevlar are showing promise.

**Table 7** Comparative results for carbon black and silica fillers in a tire tread formulation

| Property | With carbon black | Precipitated silica | Precipitated silica + coupling agent |
|---|---|---|---|
| Abrasion loss (DIN) | 1.00 | 1.54 | 0.97 |
| Tan delta at 0 °C (grip) | 1.00 | 1.05 | 1.05 |
| Tan delta at 60 °C (rolling resistance) | 1.00 | 0.60 | 0.60 |

## Specialist Elastomers

There are a number of specialist elastomers including silicones, polyurethanes, and fluorocarbons. They are more expensive than the volume elastomers and are used where their special properties, usually heat resistance and heat aging resistance, are required. The most important of these are the silicone elastomers, which have a silicon–oxygen–silicon backbone instead of the carbon to carbon one found in conventional elastomers. They have a very wide operating temperature range from well below freezing to over 150 °C. They also have excellent long-term stability at elevated temperatures, outstanding compression set resistance, and some degree of fire resistance.

The silicone elastomers are polysiloxanes with a Si–O–Si backbone and with the silicon atoms also carrying simple organocarbon groups. These side groups are predominately methyl, some phenyl is copolymerized to extend the low temperature range, and vinyl is commonly used in small amounts to increase the rate of cure, which is normally by peroxide, unlike the sulfur curing systems common with the hydrocarbon elastomers.

The silicone elastomers are generally produced from the corresponding dichlorosilane ($R_2SiCl_2$) by a hydrolysis and ring opening polymerization process.

Like most elastomers, silicones are weak, unfilled, and require the use of reinforcing fillers for most applications. Indeed they are one of the weakest elastomer types at room temperature. While the rules for reinforcement are similar to conventional elastomers, carbon blacks do not perform well, especially with regard to heat stability, and so are little used. The filler of choice is usually fumed silica and, because incorporating these is not a straightforward process, most producers sell ready filled stocks. The fumed silica is an expensive product and is often supplemented by less expensive fillers, often a crystalline silica, such as quartz flour. Because of the cost of fumed silica, there is considerable interest in finding alternatives, with the less expensive precipitated silicas being the most investigated alternative. These have proved to be satisfactory in some cases but their inherently high water content causes problems in extrusion applications and the residual salt content is also an issue in electrical insulation. Nevertheless, work continues on improving the performance of the precipitated grades.

## Future Directions

In common with most fields of activity, elastomer applications are experiencing increased interest in environmental issues. Until recently, this has been focused on energy saving in tire applications, through the use of the silica/silane tread technology discussed above. While this is expected to continue to be of major significance, it is now being joined by sustainability issues. These are currently concentrated on the types of elastomers employed, with natural rubber being regarded as more sustainable, and thus preferable, to the synthetic elastomers, especially SBR types. This is expected to lead to the amount of natural rubber in tire applications (already significant) increasing. Currently, there is an issue here for the fillers as the silica/silane system does not perform as well in natural rubber (possibly due to the surface active impurities in NR) and improvements will need to be made. There is also significant interest in finding alternative rubber latex sources to the rubber tree, with the Russian Dandelion and Guayule plants being intensively researched. The rubber from these will not be exactly the same as that from *Hevea brasiliensis* and will again require some modifications to the filler technology. In most regions of the world, tires have to be recycled in some form and this is leading to research into ways of improving this, especially upgrading the applications in which they can be used, with the ultimate goal of reusing them in tires themselves. These pressures are affecting all aspects of tire formulation and will generate new threats and opportunities for fillers.

Sustainability issues are also beginning to affect the fillers directly. Most questions are currently being directed at the carbon blacks, which are mainly produced from oil (nonrenewable). Some precipitate silica is now being made from rice-hull ash, rather than sand, as a way of increasing sustainability.

## Cross-References

► Carbon Black as a Polymer Filler
► Particulate Fillers, Selection, and Use in Polymer Composites
► Precipitated and Fumed Silicas and Related Products
► Surface Modifiers for Use with Particulate Fillers

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# Part II

# Natural Mineral Based Particulate Fillers

# Calcium Carbonate Fillers

# 7

Roger Rothon and Chris Paynter

## Contents

## Abstract

Calcium carbonate fillers have ideal properties for many polymer applications and the world consumption is over ten million tonnes annually. Both natural (ground (natural) calcium carbonates, GCC) and synthetic forms are in use and can be derived from abundant and widely occurring natural deposits. The natural

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forms are available with a wide particle-size range (0.5 to over 100 µm), are less expensive to manufacture, and have the bulk of the market. They are widely used in thermoplastics, thermosets, and elastomers. The synthetic (precipitated) forms used in polymer applications fall into the nano-size range (under 100 nm) and are used where such small particles are beneficial. Their main use is in elastomers and PVC. Fatty acid surface coatings are often added and there are also specialized coupling agents available.

Ground (natural) calcium carbonates (GCC) is a critical and functional mineral for plastics, and there is no doubt that it will continue to be one of the principal fillers used by the polymer industry. While GCC fillers are long established, they continue to evolve. Developments in grinding are likely to result in even finer forms and increased opportunities. Examples of recent developments include an innovative mineral additive for fibers and nonwovens from Imerys known as FiberLink®. FiberLink increases softness, reduces luster, improves opacity, and improves tensile strength of the fabric/web.

**Keywords**
Calcium carbonate • Elastomers • Filler • Ground calcium carbonate • Ploymers • Precipitated calcium carbonate • Thermoplastics • Thermosets

## Definition

Calcium carbonate is the chemical compound $CaCO_3$ and occurs widely in nature. Calcium carbonate fillers are finely divided forms of this chemical and are derived from various mineral sources. As such they usually contain significant levels of other materials, especially magnesium carbonate ($MgCO_3$) and dolomite ($CaCO_3.MgCO_3$). They are one of the most widely used fillers in all types of polymer and can be either natural or synthetic in origin. The natural forms are often referred to by the acronym GCC (ground (natural) calcium carbonates) and the synthetic ones as PCC (precipitated calcium carbonate).

## Introduction

Calcium carbonate is one of the principal mineral fillers used in polymer applications, with the world consumption being over ten million tonnes annually. It is an abundant natural material; with ideal properties for use as a filler in all types of polymer. It occurs in large, relatively pure, deposits, close to the surface and easily mined. It is nontoxic, with good color, and also relatively soft and easily milled down to a fine size.

There are three different crystal modifications of calcium carbonate, as well as an amorphous form. The crystalline forms are calcite, aragonite, and vaterite, with calcite being the most commonly used form for filler applications.

Two types of calcium carbonate filler can be recognized, natural and synthetic (precipitated).

## Basic Properties Relevant to Filler Applications

The specific gravity of pure calcite is 2.7, while that of aragonite is slightly higher at 2.8–2.9. Calcite and aragonite are both birefringent with refractive indices sufficiently different from most common polymers for them to give some white pigmentation. The two crystal forms are relatively soft. Calcite has a Mohs hardness of three, while that of aragonite is slightly higher at 3.5–4. Calcite usually occurs as rhombohedral crystals, while aragonite frequently occurs in acicular or needlelike form. Vaterite is a relatively rare crystal form and not met with as a polymer additive.

## Ground (Natural) Calcium Carbonates (GCC)

The majority of the filler market is taken by the natural forms of calcium carbonate, with calcite being the main crystal form encountered. Most natural deposits of calcium carbonate are largely derived from sediments made up of the accumulation of minute calcite crystals derived from marine microorganisms. These deposits come in three distinct forms: chalk, limestone, and marble. All three forms are readily converted into useful polymer fillers, usually by grinding and some purification (often referred to as beneficiation). Poor color and the presence of other mineral phases are the main limitations of many potential deposits. Drying is almost always necessary to create a useful polymer filler, and simple surface treatments, notably fatty acids, are frequently also applied to hydrophobize the surface and to make the finely milled particles dispersible in, and compatible with, particular polymer systems.

Chalks are the softest and least altered form of the original sediment and still contain the recognizable remains of the original marine microorganisms, with the individual calcite crystallites easily distinguished (see Fig. 1). These deposits are

**Fig. 1** An SEM image of a coccolith microfossil from a UK chalk deposit – each individual calcite crystallite making up the spherical body is around 3 μm in dimension

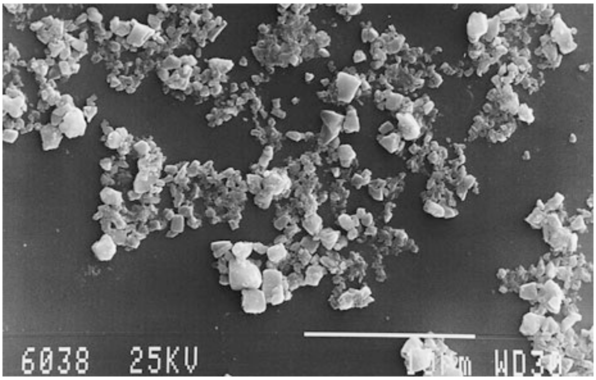

**Fig. 2** Fine chalk-based filler formed by breaking apart the calcite crystallites in a wet-grinding process

readily ground to release the basic crystals which, being only a few microns in size, are ideal for most polymer applications without needing to be further broken down (see Fig. 2). Chalk-derived powders are frequently referred to as whitings.

Limestones have undergone significant densification, as a result of geological processes. They are thus much more compact, harder to grind to fine size, and with no recognizable marine organisms present.

Marble is a metamorphic rock and has undergone the severest geological transformation. Marbles vary markedly in color and find many decorative uses in bulk form. Filler grade marble is usually produced from industrial mines tailored for industrial mineral applications but can also be sourced from the fine dust from cutting marble for architectural use – in this case it usually comes from processing of the whiter grades.

## GCC Production

After mining, the main processes are crushing, grinding to reduce particle size, removal of undesirable impurities (beneficiation), and, where required, coating and drying. Grinding is carried out in either the dry or wet state. Dry grinding is less expensive for the coarser grades, but wet grinding becomes more economic at the finer end, even though the water has to be removed by a combination of filtration and drying. A variety of grinding aids may be employed and can remain in the final product. Various beneficiation processes are used, depending on the quality of the deposit and the applications for the final product. These can include froth flotation, chemical bleaching, magnetic separation, sedimentation, and classification.

The most widely used surface treatments are fatty acid types, especially those based on stearic acid (C18) known as stearates (see Rothon 2010). They are usually applied on the final finished product but can be applied at various stages of the processing. For example, they may be added during size reduction, as they can act as grinding aids. The fatty acid treatments are intended to react with the calcium carbonate surface to produce bound monoacid salts; but this is difficult to achieve in practice. Recent studies have shown that the treatment can result in the presence of various other forms of fatty acid, including the full salt and free acid (Khanna and Xanthos 2010). In some applications even small amounts of these other forms can be detrimental, and where this is so, the coating process has to be carefully controlled to minimize them.

## GCC Specification

The main properties, with usual ranges given for commercial grades of GCC, are presented in Table 1.

## Polymer Applications of GCCs

GCC is an ideal, low cost, and easily used filler for many polymer applications. The low cost makes it possible to reduce raw material costs by replacing polymer by GCC, although the savings are not as great as it appears possible on first sight, as the higher specific gravity means that 2.5–3 times as much weight of filler is needed to replace polymer on a volumetric basis, and additional cost is often incurred to incorporate and efficiently disperse the particulate GCC.

**Table 1** The main properties usually given for GCC fillers and the normal ranges encountered

| Property | Normal range | Comments |
|---|---|---|
| Calcium carbonate content% | 90–98 | Best products are >96%. Main impurity is magnesium carbonate |
| Color brightness (e.g., ISO R 457)<br>Yellowness | 70–95<br>1.4–7.0 | Importance varies according to application<br>Good color usually attracts a premium |
| Particle size<br>Average ($D_{50}$, microns)<br>Top cut ($D_{98}$, microns) | 0.5–10.0<br><10–100 | The two values give an indication of the width of the particle-size distribution. Premium products are at the bottom end of the size range and the lower end of the “top-cut” range. Some applications require a narrow distribution, while others require special distributions to maximize packing |
| Specific surface area (BET, $m^2.g^{-1}$) | <1–10 | |
| Oil absorption (ml/100 g) | 15–25 | This is an important indication of how much of the filler can be incorporated into the polymer. The lower the oil absorption, the higher the obtainable loading, which is important where the filler is being used for pure cost reduction |
| Powder density<br>(aerated) $kg.m^{-3}$<br>(tapped) $kg.m^{-3}$ | 400–900<br>800–1,700 | |

**Table 2** Estimated use of GCC fillers by the various polymer types and application (world basis)

| Polymer type | % of total tonnage | Comments |
|---|---|---|
| Thermosets | 20 | Mainly used in uncoated form<br>Unsaturated polyester resin formulations<br>(Sheet molding and bulk molding compounds) |
| Elastomers | 20 | Widespread use, especially in carpet backing<br>Mixture of coated and uncoated |
| Thermoplastics | 60 | Flexible PVC is the largest market (especially cable insulation and flooring). Significant use also in rigid PVC (pipes and extrusions), polypropylene (garden furniture, household appliances, and automotive), and polyethylene (microporous film and cables). Again, both coated and uncoated forms are used |

The world market for GCCs in polymer applications is over ten million tonnes, and Table 2 gives the estimated breakdown by polymer type and application.

The more important applications of GCC in the different polymer types are outlined below.

## Thermoplastics

GCC is widely used in thermoplastics, especially PVC and polyolefins. The biggest use is in plasticized PVC applications, especially in cable insulation, carpet backing, and floor tiles. Cost is a major consideration together with low oil absorption. Plasticized PVC can accept high levels of filler and loadings can be as high as 400 parts per hundred of resin (phr) in some applications. In cable insulation, very low levels of conductive soluble impurities are required.

Rigid PVC (unplasticized or u-PVC) can only accept lower filler loadings, and GCC levels are typically 2–40 phr, although low-grade products containing up to 100 phr can be found. The main applications are in extrusions, such as pipes, cable management systems, vinyl sidings and window, and other building profiles.

Processing of u-PVC is a complex operation. Due to the thermal instability of PVC, the polymer granules need to be fused together rather than melted as is the case with other thermoplastics, and the speed and completeness of this process are critical. Fillers have a significant effect on this fusion process, and this has to be taken into account. The finer particle sizes usually give the most rapid and complete fusion. Fatty acid treatments also help. The finer particle-size grades also give the best physical and mechanical properties in u-PVC, especially when fatty acid is coated. Although u-PVC used to be a significant market for the very fine PCC, advances in milling technologies have led to this largely being displaced by GCC today.

GCCs are the main filler used in polypropylene (PP) compounds. Apart from cost, their main role is to increase stiffness without too much detriment to other properties, especially impact resistance. Higher aspect ratio fillers, such as talc and wollastonite,

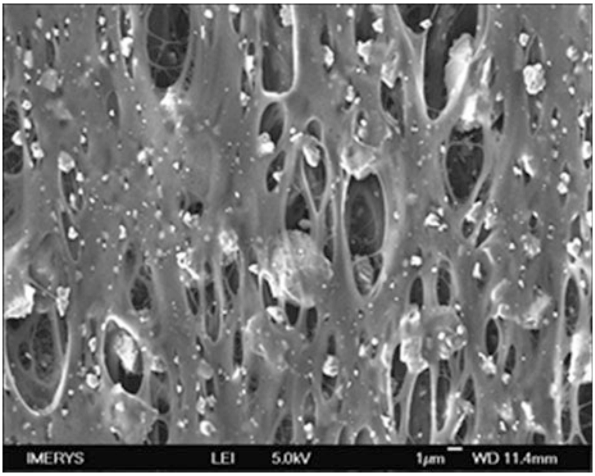

**Fig. 3** An SEM image of a breathable film showing the polymer debonding from the GCC surface

are more effective at increasing stiffness, but have a greater detrimental effect on impact strength. Fatty acid coating aids processing and properties and is frequently used. The finer grades also give the best mechanical properties.

Microporous film is a special application for GCC in both PP and polyethylene (PE). The GCC particles are used to generate the micropores by debonding from the film when it is being stretched during production (see Fig. 3). In order to achieve the best results, a fatty acid-coated GCC with 1–2 μm particle size and a narrow particle-size distribution are required, and special grades are offered for this application. One of the major uses for microporous film is in disposable diapers.

## Thermosets

GCC is also widely used in bulk thermoset applications, especially in unsaturated polyester (UPR) formulations such as sheet and bulk molding compounds. In many of these applications, it is used in conjunction with glass fiber. The main requirements of the GCCs used in these applications are low cost, low moisture content, absence of troublesome impurities, and low oil absorption. The latter is particularly important as high filler loadings are usually required. UPR polymers contain high levels of polar groups which can interact strongly with the filler, and so surface treatments of the fatty acid type are not usually used, although the formulation may contain dispersants to reduce viscosity.

## Elastomers

GCC is also frequently used in commodity elastomer applications, especially carpet backing based on lattices such as styrene butadiene rubber (SBR) and in general

**Table 3** Effect of calcium carbonate particle size (as indicated by specific surface area) on the properties of a sulfur-cured SBR compound

| Property of cured elastomer | With 100 phr of GCC specific surface area 1.8 $m^2g^{-1}$ | With 100 phr of GCC specific surface area 6.0 $m^2g^{-1}$ | PCC (stearate coated) specific surface area 20.5 $m^2g^{-1}$ |
|---|---|---|---|
| Hardness (IRHD) | 59 | 59 | 65 |
| Tensile strength MPa | 4.4 | 11.7 | 13.2 |
| Modulus at 300% MPa | 2.1 | 2.4 | 1.7 |
| Elongation at break% | 610 | 730 | 784 |
| Tear strength (BS) N/2 mm | 30 | 46 | 74 |

rubber goods (GRG). It is little used in tire applications. Most elastomers are inherently weak unfilled and require small particle-size fillers to provide sufficient strength for most applications. Because of their size, only the finest GCCs are able to provide much reinforcement, and so they are commonly used in conjunction with more reinforcing fillers, such as carbon black or precipitated silica. Both uncoated and fatty acid-coated GCCs are used, and fatty acids are also frequently present in the formulation and able to coat the filler surface “in situ.” The effect of calcium carbonate particle size on reinforcement of an SBR rubber is illustrated in Table 3. It can be seen how reducing the particle size of the GCC brings its performance closer to that of PCC, although the magnitude of the effect varies with the property being measured.

## Precipitated Calcium Carbonates (PCCs)

Although generally more expensive to carry out than grinding of the natural minerals, precipitation has several advantages. The main ones are:

Ability to produce various crystal forms and shapes
Ability to carry out significant levels of purification
Ability to produce very small particles, which would be prohibitively expensive using the GCC approach

Today these advantages, especially manipulation of crystal form, size, and shape, are most utilized in making products for paper applications, which is outside of the scope of this article. Even so, significant amounts of PCC are used in polymers, although this is declining, as enhanced grinding methods allow GCCs to compete more successfully.

Several processes can be used to precipitate calcium carbonate from solution. The two main ones are double decomposition and carbonation.

Double decomposition is carried out by adding a solution of sodium carbonate to one of a calcium salt, most commonly calcium chloride. This precipitates calcium carbonate, leaving sodium chloride in the solution. The calcium carbonate is separated by filtration, washing, and drying. The washing has to be very thorough to remove the coproduct salt. Optionally a surface treatment can be applied to the product at some stage.

While originally quite popular, the double decomposition process has largely been superseded by carbonation. In this process, a form of natural calcium carbonate, usually limestone, is heated (calcined) to decompose it, producing lime (calcium oxide) and carbon dioxide. The lime is reacted with water (slaked) to produce a slurry of calcium hydroxide (milk of lime) which is then reacted (carbonated) with the carbon dioxide driven off in the first-stage calcination. This leads to the precipitation of calcium carbonate. As with the double decomposition, the product is separated by filtration and drying; but unlike the double decomposition, there is no need for washing as no coproduct salt is involved. This is a very significant advantage. A surface treatment is nearly always applied for polymer applications and is usually done before filtration, as it aids both this stage and the drying stage. By far the most common surface treatment used is a fatty acid, although carboxylated polymers can be used for specialist elastomer applications.

The crystal form, size, and shape can be manipulated by careful attention to the precipitation conditions in both processes, and the patent literature abounds with examples of different forms including vaterite. Polymer grade PCCs are almost exclusively produced as calcite, with crystals in the range 0.02–0.1 μm. A typical elastomer grade PCC is shown in Fig. 4.

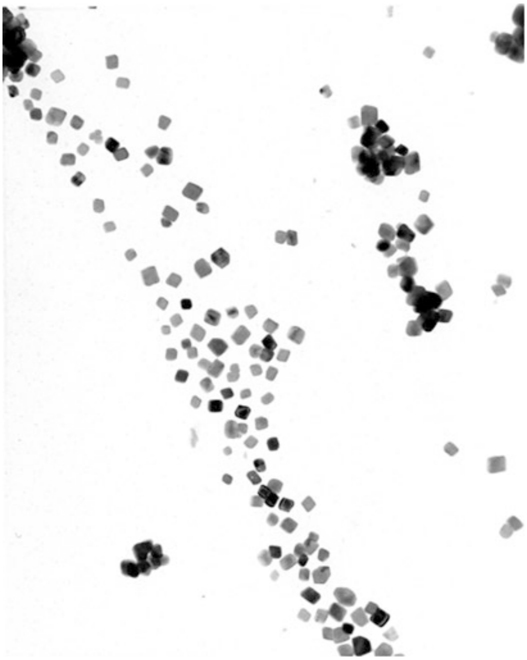

**Fig. 4** A typical precipitated calcium carbonate used in polymers

**Table 4** An illustration of the effectiveness of MPBD coating on the performance of PCC in a sulfur-cured EPDM elastomer (PCC 20 $m^2g^{-1}$ at 150 phr loading)

| Property | Uncoated | MPBD coated |
|---|---|---|
| Hardness IRHD | 56 | 57 |
| Tensile strength MPa | 7.8 | 10.8 |
| Modulus at 300% MPa | 2.0 | 3.8 |
| Elongation at break% | 600 | 685 |
| Tear strength $Nmm^{-1}$ | 14.2 | 25.5 |

PCC is relatively expensive to produce compared to GCCs and, as is illustrated in Table 3, is frequently under threat from improved forms of the latter.

## PCC in Polymers

PCC has a long and varied history in polymer applications, having frequently been forced to reinvent itself, due to improvements in the production of GCCs. It was first introduced as a filler for use in elastomers, especially natural rubber, a market which has now largely been lost. Next it became very important in PVC, especially rigid (unplasticized) PVC, where its small size aids fusion and processing and can give improvements in important properties such as impact resistance, but again this market has been significantly eroded by competition from GCC. Most recently, PCC has found significant application as a rheology control agent in sealant applications, especially in plasticized PVC, where it competes with products such as fumed silicas. So far this market has resisted erosion by GCC.

The reinforcing ability of PCC in elastomers has already been exemplified and compared with GCCs in Table 3. While it is significantly better than all but the finest GCCs, it still falls well short of many other fillers. Part of the reason for this is the poor interaction between the filler and the elastomer. This low interaction is partly due to the fatty acid coatings usually employed. The weak interaction is common for many minerals and usually remedied by the use of a coupling agent able to react with both the filler surface and the polymer and so couple the two together. Organosilanes are the state-of-the-art products for this, but unfortunately they are not effective with calcium carbonates. In the 1980s an effective coupling agent system was discovered (maleinized polybutadiene, MPBD), the effectiveness of which is exemplified in Table 4. Despite this breakthrough the use of PCC remains a relatively expensive option compared to other white fillers, and so MPBD-coated PCCs only occupy a niche position today.

## Environmental Impact and Sustainability of GCC and PCC Production

While it is inescapable that calcium carbonate filler production depletes resources and consumes energy, it must be looked at in a more holistic way. The fillers replace polymers in the final products, and life cycle analysis has shown that in most cases production of the filler is less detrimental to the environment than that of the polymer it is replacing.

## Future Direction

Ground (natural) calcium carbonates (GCC) is a critical and functional mineral for plastics, and there is no doubt that it will continue to be one of the principal fillers used by the polymer industry. Developments in grinding are likely to result in even finer forms and increased opportunities. As an example, it has recently expanded into a new market, fibers and nonwovens, and this opens up a large potential market in polyolefins. Imerys has engineered an innovative mineral additive for fibers and nonwovens based on GCC known as FiberLink®. This new technology is incorporated into the polymer during extrusion and is dispersed in the fiber. It can be added directly to powdered polymer or as a masterbatch with pelletized resins for fiber, spunlace, spunmelt (SMS), and meltblown applications. FiberLink increases softness, reduces luster, improves opacity, and improves tensile strength of the fabric/web. For example, in diaper and hygiene products, adding FiberLink to the spunbond layers of SMS increases the strength in core wrap and leg cuffs. In addition to the optical and mechanical property benefits, FiberLink enables faster throughput or reduced processing temperatures leading to increased productivity or energy savings. An image of a polypropylene nonwoven fiber containing a FibreLink surface-treated GCC is given in Fig. 5.

The picture for PCC is less clear. While it will remain a major filler in paper applications, where the ability to manipulate shape and crystal form and the possibility to introduce satellite production installations utilizing the waste $CO_2$ from the papermaking process protect it from encroachment by GCC to some extent, the use in polymers is expected to remain relatively minor.

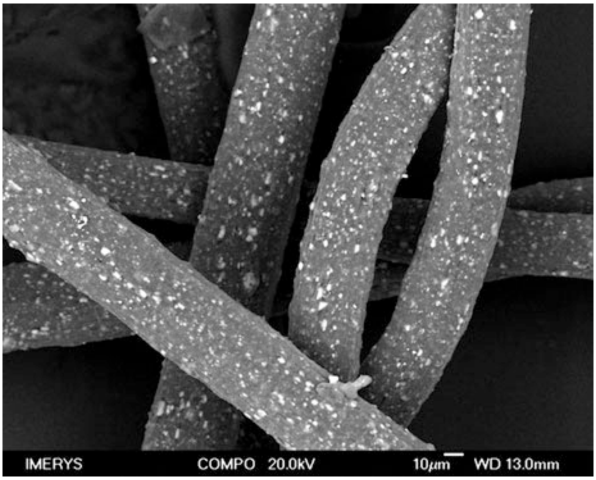

**Fig. 5** Polypropylene nonwoven fibers containing a surface-treated GCC

## Cross-References

- ► Particulate Fillers, Selection, and Use in Polymer Composites
- ► Surface Modifiers for Use with Particulate Fillers

## References

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# China Clay or Kaolin

# 8

Roger Rothon

## Contents

## Abstract

Clays of various sorts are widely available throughout the world and have been used in polymer composites, especially those based on elastomers, since the early days of their industrial application. While there are a large number of clay materials, the main ones used in polymers are based on the mineral kaolinite and are often referred to as kaolin or china clay.

The china clays themselves have limited application in thermoplastic and thermoset applications. This is due to a number of factors, such as poor color and heat aging, especially in polypropylene. The water of crystallization is also an issue for water-sensitive polymers such as nylon and thermoplastic polyesters, as

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it can be released during processing. Many of the problems are overcome by calcination, and calcined forms are more widely used for these polymers.

On the other hand, china clay is a widely used white filler in the rubber industry. Depending on particle size, it can be used as a semi-reinforcing filler (hard clay) or a non-reinforcing filler (soft clay). Common elastomer applications include chemical liners, bicycle tires, conveyor belts, shoe soles, gaskets, and flooring.

**Keywords**
China clay • Kaolin • Metakaolin • Calcined clay • Thermoplastics • Elastomers

## Definitions

**Clay** Although broadly distributed and well known, clays are difficult to define precisely. The term is applied to finely grained natural materials which are plastic when wet and hard and brittle when dried, especially after firing. They are usually complex mixtures of various minerals, with the main component being a platy aluminosilicate.

**Clay mineral** A group of important hydrous aluminum silicates with a layer structure and very small particle size. They may also contain significant amounts of iron, alkali metals, or alkaline earths.

**Kaolinite** A specific clay mineral with the formula of $Al_2O_3 .2SiO_2 .2H_2O$.

**Kaolin** A clay where the principal clay mineral is kaolinite, but significant amounts of other minerals can be present.

**China clay** Another term for kaolin.

**Calcined clay** A clay which has been heated to high temperature, bringing about chemical and structural changes.

**Metakaolin** A dehydroxylated kaolinite produced by partial calcination.

## Introduction

Despite their ubiquitous nature and familiarity, clays are complex mixtures of variable composition and not at all easy to fully define.

Clays are just one form of metal silicate, which is called a phyllosilicate. Silicates can have many structures, depending on how the silica lattice is organized. In the phyllosilicates there are infinite sheets of silica tetrahedra with three of the four oxygens of each sharing with other tetrahedra. The basic structural unit is thus $Si_2O_5^{-2}$. The sheets are then connected to each other by layers of cations, which balance the charge. These cations are often accompanied by water molecules and other neutral atoms or molecules trapped between the sheets. The nature of this interlayer is the principal differentiating factor between phyllosilicates and has a significant effect on their final structure and properties. The phyllosilicates themselves can be subdivided into various types such as micas, talcs, asbestos (serpentine), chlorites, and clays, many of which have important polymer applications.

The clay minerals are a general group within the phyllosilicates in which the balancing cations are predominately aluminum (in the form of oxide or hydroxide), but which also contain large percentages of water trapped between their silicate sheets. Thus, they are described as hydrous aluminum phyllosilicates. While there are a large number of clay minerals, the most important ones for general polymer applications are based on the kaolinite subgroup; this has three members (kaolinite, dickite, and nacrite) all with the formula of $Al_2O_3$ $.2SiO_2$ $.2H_2O$. These three minerals are polymorphs, meaning that they have the same chemistry but different structures. The general structure of the kaolinite group is composed of silicate sheets ($Si_2O_5$) bonded on one side to the outside of aluminum oxide/hydroxide layers ($Al_2(OH)_4$) called gibbsite layers. As a result, a kaolin particle has two different faces, one with surface oxygens linked to silicon and the other surface hydroxyls linked to aluminum. These particles can stack together into “books” by hydrogen bonding between these two faces. This hydrogen bonding is significantly stronger than the van der Waals forces between layers in talc and thus kaolin is a harder mineral.

The remainder of this chapter will focus on kaolinite-based clays (often also referred to just as kaolin). Clays which are rich in kaolinite are frequently referred to as china clays. Ball clays are a subset sometimes met, especially in Europe and some parts of the USA. They are formed from the weathering and transportation by water of parent rocks which are deposited in ancient river basins from where they are extracted. They are still kaolinitic, sedimentary, clays and can contain 20–80% kaolinite, with mica (10–25%) and quartz (6–65%) as major other components. Ball clays are fine-grained and plastic in nature. Ball clays occur in relatively scarce deposits due to the combination of geological factors needed for their formation and preservation. They are mainly mined in parts of the Eastern USA and from sites in South West (SW) England. While they are mainly used for ceramics production, they are also found as fillers for rubber. Ball clays give significantly finer, higher specific surface area, polymer products than do the other kaolin clays.

One of the characteristics of clays is that the bond between the fundamental metal silicate sandwich layers is relatively weak, allowing some cleavage, or exfoliation, to generate plates of varying aspect ratios. Some clay types more readily exfoliate than others, with one type, the montmorillonites, being particularly easily treated in this way. These are the basis of nano-clay technology which has received considerable scientific and commercial interest over the last two decades. This is covered in ▶ Chap. 23, “Nanofillers”.

## Kaolin Occurrence and Extraction

Clay deposits which are rich in kaolinite are widely distributed as hydrothermal, residual, and sedimentary deposits around the world, with the most important resources being in Cornwall in SW England and in South Carolina and Georgia in the USA. Large deposits are also found, and are being exploited, in Russia, Ukraine, Brazil, Spain, Australia, Bavaria, and Bohemia.

Kaolins are formed by the hydrothermal alteration and weathering of feldspathic igneous and metamorphic rocks (especially granite) under relatively low temperatures and pressures. The most common parent minerals are feldspars and muscovite micas. Kaolins can be found as primary deposits (i.e., in the same place as where the alteration took place) or as secondary deposits, such as sedimentary layers which have been transported by water to another location. Because of their relatively complex geological origins, no two deposits are exactly the same, and the type of deposit determines the impurities present and also influences the production process. Extraction and processing of clays for polymer applications is a complex subject much influenced by the nature and location of the deposit and is only covered in outline here. More details can be found in Hancock (2003) and Duca (2010).

Primary deposits will usually be mixed with unaltered granite, mica, feldspar, and quartz. Secondary deposits are usually found in “layered qualities” with very variable purity. The main primary deposits in SW England and Brazil are exploited by hydraulic mining, in which the clay is washed out of the granite matrix using high-pressure jets of water or by dry mining, where the kaolinitic rock is extracted at source and stockpiled into grades of different physical characteristics. The dry-mined rock is crushed and the quartz-containing fraction separated before the remainder is diluted into a slurry with water for further beneficiation. Refining into different particle size fractions is carried out by sedimentation of this aqueous slurry, using the principle of Stokes law to select the required particle size. To achieve good separation, the particles must be deflocculated (separated from each other); this is usually achieved at a neutral pH and by treatment with a polyanion, which can often carry over into the final product. Mineralogical separation is also achieved in the refining step, with ancillary minerals (mostly feldspar, quartz, and mica) remaining in the coarse fractions. During aqueous processing, products may also be reductively or oxidatively bleached to reduce or remove colored inorganic impurities (usually hydrated iron oxides) and organic matter (humus type materials) which are often present as coatings on the particle surface. The clays are then filtered, dried, and, for the polymer industries, pulverized to break down agglomerates, which form during drying.

The sedimentary deposits are mined by a variety of techniques depending on the nature and extent of the impurities. The simplest and cheapest production route involves dry mining, crushing, and milling. More sophistication is used for air-floated products, where the clay after crushing and grinding passes into an air stream of constant velocity and grit and coarse particles remain behind.

More controlled, purer products are produced by wet refining with the dry-mined clay being dispersed in water, degritted and refined using hydrocyclones or centrifuges.

Aspect ratio of the particles in any given product is determined by the degree to which the individual plates are separated from the stacks. For some deposits and products, special grinding is carried out to maximize this. The aim is to separate the stacks as much as possible without too much fracturing of the plates, as this would reduce the aspect ratio.

A stack of kaolinite crystals is shown in Fig. 1 and typical platy particles obtained after processing are shown in Fig. 2.

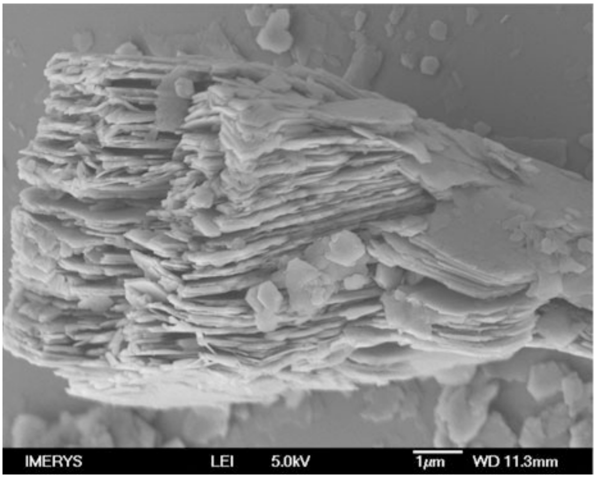

**Fig. 1** A stack of kaolinite crystals (reproduced with kind permission from Imerys)

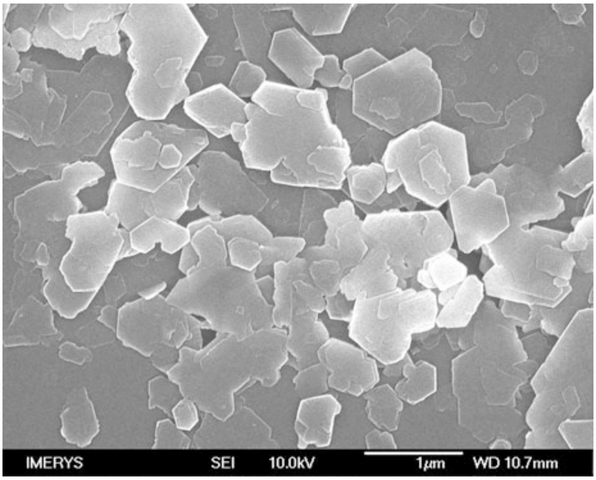

**Fig. 2** Typical kaolinite plates (reproduced with kind permission from Imerys)

## Properties

Pure kaolinite has the idealized chemical composition $Al_2O_3.2SiO_2.2H_2O$. It is a crystalline material with a triclinic form found in microscopic pseudohexagonal plates, which fairly readily undergo cleavage. As a consequence, it has a low Mohs hardness, between 2.5 and 3, depending on the ancillary minerals present. The specific gravity is 2.6 and refractive index is 1.56. As described above, its structure can be regarded as a gibbsite, $Al(OH)_{3,}$ layer bonded to a siloxane ($Si_2O_5$) layer. The idealized structure described above is rarely found in nature, with isomorphous substitution of both Si and Al ions by transition metals and particularly by iron, often occurring. This leads to electrical charges on the plates; with edges being positively charged and faces negatively charged. These charges are countered by ions, which surround the particles in a double layer. (See Jepson (1984) and references therein for a more complete discussion of the properties of clay and kaolinite.)

Because of the isomorphous substitution and also because of the occurrence of broken bonds at the edges, there are both Lewis and Bronsted acid sites on the surface of a kaolinite particle. These sites can be very reactive.

One of the important particle properties of clays used in polymer applications is the platiness or aspect ratio of the particles. This has a number of consequences. It raises viscosity, making processing more difficult, but increases stiffness and gas barrier properties. The aspect ratio achieved varies considerably from product to product. While the bonding of the silicate and gibbsite layers is strong, that between the adjacent silicate layers is weak and readily disrupted, allowing thin, hexagonal, plates to be produced. These plates have aspect ratios in the range 5:1 to 50:1 (but very fine clays can have even higher aspect ratios), which are dependent on particle size. Aspect ratios of the plates are dependent on the nature of the clay deposit with, for example, US clays being blockier than clays from SW England; but they are dependent also on the processing used, because kaolinite stacks or “booklets” readily cleave during processing.

Kaolinite reacts only with very strong acids and bases, is not affected by organic solvents, and undergoes ion exchange reactions; but from most points of view, it is an inert mineral. It does undergo a complex series of reactions when heated, which are of commercial importance and will be discussed fully below (section “Uses in Polymers”).

The commercial products sold as kaolin or china clay (and even clay) can vary in actual composition very significantly and, while the main mineral present is usually kaolinite, this is not always the case. Some “china clays” in fact are sold that contain only 25% kaolinite, but normally kaolins will contain 70–99% kaolinite, with the main impurities being mica, quartz, and feldspar. Other silicates, metal oxides and organic matter, are usually found in trace amounts. Ball clays already discussed above are an example of this.

Particle-size distributions (expressed as equivalent spherical diameter, esd) of clays depend on the inherent particle size of the deposit and the amount of refining that has been carried out during production. In primary deposits, the kaolin plates are usually bound together in a book-type structure (Fig. 1), and refining will separate them to a certain extent. Most commercial products for the polymer industries will be degritted at 300 mesh, so the normal top cut is at least 75 μm. More commonly, clays will have been refined to 20 or 10 μm for a range of applications, and speciality products will have a top cut of 5 μm or finer.

Secondary clays are usually very much finer than primary clays and products that are approximately 100% finer than 5 μm can be obtained by a fairly simple air-float or degritting procedure. Air-floated clays are fairly common in some regions of the world, including the USA.

Although kaolin can be regarded as chemically inert, it does have a complicated surface chemistry. Surface hydroxyls either from the gibbsite layer, or from adsorbed gels, readily react with commercial bifunctional coupling agents such as silanes and titanates. (See ▶ Chap. 2, "Surface Modifiers for Use with Particulate Fillers" for a discussion of coupling agents.) Kaolinite plates have negatively charged faces and positively charged edges and adsorption of both positive and negative ions are of great commercial importance. For example, small amounts of polyanions adsorb on to edges, deflocculating or flocculating the clay depending on the molecular weight of the polymer, and are an essential feature of its use in aqueous media (the paper and paint industries especially).

The presence of Lewis and Bronsted acid sites gives rise to a variety of chemical reactions. Amines, or other Lewis bases, readily adsorb and the use of fatty amines to render the clay organophilic has been applied for many years to modify properties in a number of applications]. Because of these reactive sites, kaolin will enter into organic reactions and, of particular interest for plastics, will catalyze the polymerization of certain monomers. Sometimes depolymerization can occur and they can promote the dehydrochlorination reaction of polyvinyl chloride (PVC).

## Uses in Polymers

China and ball clays have limited application in thermoplastic and thermoset applications compared to calcium carbonates and talcs. This is due to a number of factors such as poorer color and heat aging, especially in polypropylene. Dehydrochlorination of PVC is another issue which has already been mentioned. The water of crystallization is an important issue for water-sensitive polymers such as nylon and thermoplastic polyesters, as it can be released during processing. As described later, many of the problems are overcome with the calcined grades, which do find significant applications in many types of polymer. The reactivity of clays is also exploited in biopolymers, where they act as a pro-degradant, speeding up the breakdown of packaging during composting.

On the other hand, china and ball clays are widely used non-black fillers in the rubber industry. In practice there are a wide range of products covering a spectrum of performance; but two distinct types known as hard and soft clays are often referred to, especially in older literature. This terminology is based on their effect on the hardness of the rubber composite, not on the properties of the clays themselves.

Today, it is more common to talk in terms of the effect of fillers on the reinforcement of elastomers, with four levels being recognized: reinforcing, semi-reinforcing, non-reinforcing, and diluent (Skelhorn 2003). In this context, reinforcement is determined by the increases produced in the tensile and tear strengths of non-crystallizing elastomers such as styrene-butadiene rubber (SBR). Reinforcing fillers show a marked peak in performance at relatively low loadings and an improvement in abrasion resistance, followed by a significant decline. Semi-reinforcing ones have a broader peak at higher loading and little effect on abrasion resistance, while non-reinforcing ones have no peak and diluent fillers show a steady decline at all loadings.

Clays used in rubber generally range from non-reinforcing through to semi-reinforcing, with these classes loosely equalling the old hard and soft types. The main difference between them is in particle size, not mineralogy. Hard or semi-reinforcing clays typically have specific surface areas (a useful indication of size for anisotropic particles) in the range 10–30 $m^2/g$, while the soft (non-reinforcing) ones are in the range 5–7 $m^2/g$. In practice there is no clear-cut distinction with a continuous range of sizes, and hence reinforcement, available.

The use of just two parameters to quantify reinforcement is a great oversimplification, and rubber applications involve many more considerations. These include the following properties, all of which can be affected by a filler:

Processing ease, including viscosity, mill sticking, and mold release
Cure rate: completeness and nature of the cross-links
Hardness
Tensile and tear strengths
Stiffness (modulus) at various strains
Elongation to break
Resilience and heat buildup (energy losses on deformation)
Stability of cross-links, as measured by permanent set under various conditions
Abrasion resistance under a variety of conditions

Cure effects are important for clays which can absorb and partly deactivate accelerators and curatives. This is especially true for the higher surface area products, with more reinforcing potential. Various approaches are used to overcome this, including using additives such as glycols to block the clay surface.

Table 1 shows how a typical semi-reinforcing clay filler affects some rubber composite properties, compared to a non-reinforcing chalk. From this, it can be seen that the clay is clearly superior in terms of tensile and tear strengths and high extension modulus, but is no better than the chalk for abrasion resistance and compression set. Table 2 shows how properties vary with specific surface area for clays of similar mineralogy. The lowest specific area clay would be classed as non-reinforcing.

As mentioned above, organo-silanes can be used to boost the performance of clays in rubber. They achieve this mainly through increasing the adhesion between the filler surface and the elastomer matrix. The main properties to benefit from this are high extension modulus, tear strength, and abrasion resistance. This is demonstrated in Table 3.

**Table 1** A comparison between a fine chalk filler and a semi-reinforcing clay in a sulfur-cured SBR formulation (100 phr filler)

| Property | Chalk | Semi-reinforcing clay |
|---|---|---|
| Hardness (IHRD) | 59 | 66 |
| Tensile strength MPa | 4.4 | 18.5 |
| Elongation% | 610 | 670 |
| Modulus at 300% MPa | 2.1 | 4.2 |
| Tear strength N/mm | 30 | 61 |
| Abrasion loss $mm^3$ | 290 | 282 |
| Compression set% | 37 | 37 |

**Table 2** The effect of particle size, as expressed by specific surface area, on some of the important properties of a sulfur-cured SBR elastomer (100 phr Filler)

| Property | Specific surface area 5 $m^2/g$ | Specific surface area 11 $m^2/g$ | Specific surface area 25 $m^2/g$ |
|---|---|---|---|
| Hardness (IHRD) | 65 | 66 | 69 |
| Tensile strength MPa | 10.7 | 18.5 | 20.5 |
| Elongation% | 600 | 680 | 700 |
| Modulus at 300% MPa | 3.8 | 4.2 | 4.0 |
| Tear strength N/mm | 45 | 56 | 65 |
| Abrasion loss $mm^3$ | 330 | 280 | 287 |
| Compression set% | 35 | 37 | 36 |

**Table 3** The benefit of using an organo-silane on the properties of a sulfur-cured clay-filled SBR compound

| Property | No silane | With mercapto-silane (maximum level and amount of silane required to achieve it, expressed as% on clay) |
|---|---|---|
| Hardness (IHRD) | 73 | 77 (1.5%) |
| Tensile strength MPa | 13 | 14 (1.0%) |
| Modulus at 300% MPa | 4.5 | 9.0 (1.0%) |
| Tear strength $KNm^{-1}$ | 62 | 90 (1.0%) |
| Elongation% | 620 | Steady decrease |

The platiness of some clays results in increased gas barrier properties when properly dispersed and aligned in elastomers, and this effect can be put to good use in products where this property is important, such as tire inner tubes and liners.

## Calcined Clays

As mentioned above, kaolin clays have a number of limitations for thermoplastic and thermoset applications. These can be reduced or eliminated by careful heat treatment (calcination). Among the benefits of this process are a significant reduction in water content and dielectric constant, better whiteness, and much reduced tendency to cause cure interference in elastomer formulations.

A number of products are produced in this way depending on the calcination conditions, especially temperature. Often these products are all called calcined clays, but there are two important types of calcined product for polymer applications, metakaolin and an amorphous product generally referred to just as calcined clay or calcined kaolin. In this article the use of the term calcined clay is restricted to the higher temperature amorphous product.

Metakaolin can be regarded as a partly calcined product and is produced by endothermic dehydroxylation which removes the water of crystallization. Above 500 °C kaolinite starts to lose its water of crystallization, and, by 650 °C, approximately 90% of this dehydroxylation is complete, leaving residual hydroxyl groups randomly distributed but isolated so that further condensation will not readily occur. This product is known as metakaolin, it still retains some crystalline structure, but X-ray diffraction patterns are very diffuse and weak. The aluminum, which was originally in sixfold octahedral sites, now occupies four- and fivefold sites almost equally.

Due to the structural changes, metakaolin is much more chemically reactive than the kaolinite from which it was formed (and also has a very reactive surface (Newman 1987). This reactivity is exploited for its pozzolanic activity in building materials, such as high-strength cements and mortars.

Metakaolin is stable up to 980 °C, when a defect spinel structure, which is virtually amorphous, forms exothermically. Products produced between 980 and 1100 C are known as calcined clays. Above 1100 °C there is a slow transformation of the defect spinel with mullite forming in an amorphous silica matrix. This extremely hard and inert refractory material only has minor use in polymer applications.

During calcination, kaolinite plates tend to fuse face-to-face and so calcined clays are coarser than the feed clays from which they are produced and also have significantly lower aspect ratios, approximately 3:1. (Compare Fig. 3 with Fig. 2.)

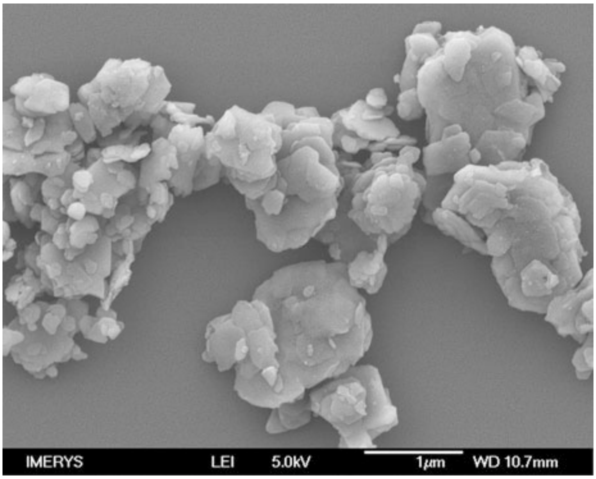

**Fig. 3** A typical calcined clay (reproduced with kind permission from Imerys)

**Table 4** Important properties of calcined products compared with uncalcined kaolin

| Property | Fine kaolin | Metakaolin | Calcined (amorphous) |
|---|---|---|---|
| Specific surface area ($m^2/g$) BET | 16–30 | 12 | 7–12 |
| Surface hydroxyl concentration ($nm^{-2}$) | 8 | 1 | 1 |
| Moisture content (at equilibrium%) | 1.5–2.0 | 0.3 | 0.2 |
| Accelerator and peroxide adsorption | High | Low | Very low |
| Dielectric constant | 2.6[a] | 1.3 | 1.3 |

[a] Note that this is for pure, thoroughly dried kaolinite; most kaolin clays will be higher

**Table 5** Dielectric constant (relative permittivity) for clays and some other common fillers (note some impurities can significantly affect these values)

| Filler | Dielectric constant |
|---|---|
| Kaolin | 2.6 |
| Metakaolin | 1.3 |
| Calcined kaolin | 1.3 |
| Calcium carbonate | 6.1 |
| Talcs | 5.5–7.5 |
| Micas | 2.0–2.6 |
| Wollastonite | 6.0 |
| Aluminum hydroxide | 7.0 |
| Crystalline silicas | 3.8 |

Metakaolin and the amorphous aluminosilicate produced at 980–1100 °C have approximately the same Mohs hardness of 4.0, specific gravity 2.6, and refractive index 1.6. Other important characteristics of typical products compared with kaolinite clay are given in Table 4. One of the principal attractions of kaolin fillers over other common types is that they have a much lower dielectric constant (more correctly referred to as relative permittivity). This is demonstrated in Table 5. The dielectric constant is important for applications such as cable insulation, as it controls energy losses and heat buildup in the insulation. Low values give the least losses. Such effects are negligible in low voltage applications, but become increasingly important as voltage increases.

The residual hydroxyls on the surface of calcined clays make them very receptive to organo-silane coupling agents with which they are widely used in polymer composites. These silanes are chosen to suit the polymer matrix, with vinyl, amino, and sulfur functional silanes being most often used. Some manufacturers offer calcined clays pretreated with silane, but the "in situ" method of adding the silane during composite production is also employed.

## Flash Calcined Clays

If the heating of kaolinite clays is carried out very rapidly, then the outside of the clay particles can fuse, forming a glass, before dehydroxylation occurs. The water formed cannot escape and forms closed pores, giving a lighter weight aluminosilicate, which still has a defect spinel structure (see Fig. 4).

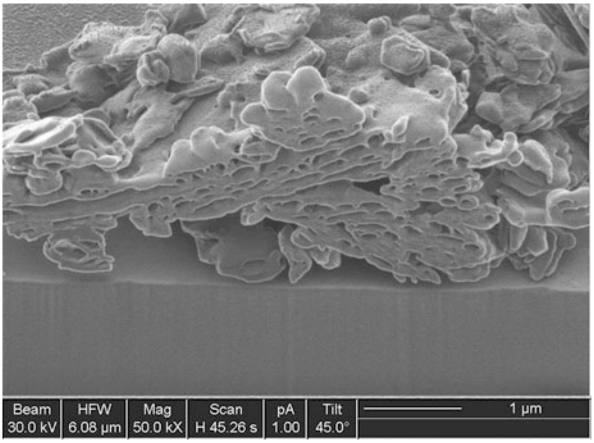

**Fig. 4** Flash calcined kaolin (Opacilite™) (reproduced with kind permission from Imerys)

## Uses of Calcined Clays in Polymers

The low dielectric constant of metakaolin and calcined clays makes them particularly useful for medium- and high-voltage cable insulation use. Their low water content and absorption further help in this regard. While there is some overlap in the performance and applications of metakaolinite and calcined clays, there are significant differences between them which lead to separate use patterns.

### Metakaolin

Metakaolin is mainly used in PVC cable insulation where, in addition to the low dielectric constant, it also improves the electrical resistivity of plasticized PVC. This effect is unique to metakaolin and is thought to be due to its active surface deactivating ionic impurities. This special effect of metakaolin is absent in most other polymers, where calcined clays are then often preferred.

### Conventional Calcined Clays

Calcined clays are used principally in elastomeric cable insulation and in engineering thermoplastics, such as polyamides. The low water content is particularly beneficial in the latter. As described earlier, their use in cable insulation is a consequence of their low dielectric constant.

In elastomeric cable compounds, organo-silane coupling agents can be used to further improve the electrical performance, especially after water immersion. This is demonstrated in Table 6.

The calcined products are also more suited than the uncalcined ones to non-cable uses in thermoplastics, due to a number of factors. These include improved color, much reduced effects on polymer heat stability, and low water content. The extra cost involved makes them relatively expensive and most suited to use in engineering thermoplastics, rather than commodity ones, such as the polyolefins and PVC.

**Table 6** Illustrative values for the performance of an organo-silane coupling agent on the properties of a peroxide-cured, EPDM-based, cable formulation

| | No silane | Vinyl silane 1% on filler |
|---|---|---|
| Hardness (shore A) | 58 | 61 |
| Tensile strength MPa | 6.9 | 7.9 |
| 300% modulus MPa | 1.9 | 6.1 |
| Elongation% | 800 | 510 |
| Tear strength die C KN/mm | 20.5 | 34.5 |
| Specific inductive capacitance at 1 KHz | 2.9 | 2.8 |
| Specific inductive capacitance at 1 KHz after 30 days in water at 75 C | 3.6 | 3.0 |
| Power factor% at 1 KHz | 0.003 | 0.003 |
| Power factor% at 1 KHz after 30 days in water at 75 C | 0.025 | 0.005 |

**Table 7** A comparison of fillers in nylon 6,6 (40% w/w filler level)

| | Unfilled | Calcined clay | Silane-treated calcined clay | Chalk filler | Talc filler |
|---|---|---|---|---|---|
| Flexural modulus MPa | 16 | 50 | 54 | 45 | 45 |
| Impact strength Joules | 16 | 2 | 10 | 2 | 2 |

A significant use of calcined clays is in polyamides, where they are surface treated with an organo-silane (such as an amino-silane) in glass fiber and fiber-free composites. Glass fiber is excellent for increasing stiffness and maintaining impact strength, but gives problems in processing, including variable warpage and mold shrinking. To combat some of these effects, wollastonite may be used instead of short glass fiber. Although platy or anisotropic minerals, such as talc, can provide adequate stiffness, they may have unacceptable effects on toughness. This includes calcined clay alone, but use of the silane restores a good level of impact strength for this filler, an effect that has not been found for the other types. This situation is exemplified in Table 7 compiled from manufacturers' literature.

Another important use is as antiblocking agents in polymer film. Several types of minerals are used as antiblocking additives in thermoplastics films, most notably those of LDPE and LLDPE for packaging. They are added at concentrations of 1000 to 4000 ppm to prevent the adhesion of each layer to the next and thereby assist in their separation. One example would be in grocery bags which are notoriously hard to open. The material works by protruding from the film surface and reducing the area available for surface-to-surface interaction. The antiblocking properties are influenced by particle size, with coarser calcined clays giving better antiblocking performance but, generally, poorer film clarity and transparency. (See separate ▶ Chap. 21, "Antiblock Additives".)

A more novel use of calcined clay is derived from its strong infrared adsorption. The agricultural industry uses polyethylene films to a significant extent as coverage for polytunnels and cloches. As polyethylene is almost transparent to infrared, heat energy readily escapes from it once the heat source (e.g., the sun's rays) is removed. One method to improve the thermal barrier properties is by the addition of up to 10 wt% of calcined clay, which can result in an increased thermal opacity of 70% (Whiteman 2006). This maintains the heat within the enclosed area for longer and is used to extend the growing season of fruits and vegetables.

## Flash Calcined Clays

Internal porosity is the main differentiating feature of flash calcined clays. This results in a lower specific gravity and refractive index than standard calcination. The amount of porosity varies according to the flash calcination conditions, but typical results are given in Table 8.

The low refractive index of the flash calcined clay (FCC) can be utilized as extender pigments for the expensive titanium dioxide pigment, Fig. 5. This application has been described in detail by Whiteman et al (2007), Agra et al. (2009). The voids within the particles appear to lead to light scattering properties in polymers in excess of that expected from the refractive index alone. This is due to multiple reflections within the pores. The effect is particularly apparent in thin films, becoming less obvious with thicker moldings.

**Table 8** A comparison of flash and conventional calcined clays

| | Conventional calcination | Flash calcination |
|---|---|---|
| Specific gravity | 2.6 | 2.1 |
| Refractive index | 1.62 | 1.39 |

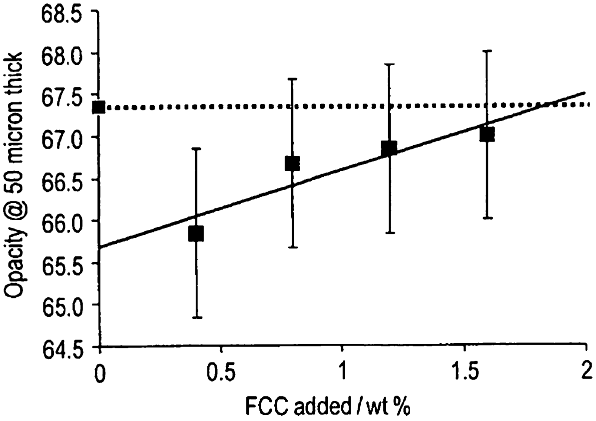

**Fig. 5** Opacity data for the partial replacement of titanium dioxide with flash calcined clay (FCC) in LDPE film (reproduced with kind permission from Imerys)

## Cross-References

- ▶ Antiblock Additives
- ▶ Nanofillers
- ▶ Particulate Fillers in Elastomers
- ▶ Particulate Fillers in Thermoplastics
- ▶ Surface Modifiers for Use with Particulate Fillers

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# Micas

# 9

Joerg Ulrich Zilles

## Contents

## Abstract

Mica (i.e., muscovite and phlogopit) are platelet-shaped reinforcing fillers used for increasing heat deflection temperature and reducing warpage in polymers. Mineralogically the mica group consists of phyllosilicates all with monoclinic crystal structure and perfect basal cleavage. Micas are muscovite (typically white to gray color), phlogopite (brownish depending on iron concentration), biotite (dark brown to black), lepidolite (lithium-mica, white to gray), and others. Industrially in general and especially in polymers, the most commonly used are muscovite, phlogopite, and to some extent also biotite.

Main use is in polyamide for under the bonnet applications in automotive industry. They are truly versatile functional fillers. Whereas sheet and scrap mica minerals are used for larger thermal and electrical insulating shields, ground mica minerals (mostly muscovite) are used as fillers in lacquers, exterior and interior paints, plasterboards, joint compounds, adhesives, and sealants as well as in

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polymers. Most of the properties conveyed to the matrix are due to the crystal structure, chemical composition, fracture and cleavage behavior, as well as processing parameters used to produce the products. As functional fillers, mica mineral flours are making a crucial contribution to improve the properties of modern plastics.

In polypropylene muscovite mica is commonly used for reinforcing purposes due to the good equilibrium between modulus and IZOD strength as well as good HDT. Due to the brownish color, phlogopite mica is not that common in polypropylene although the reinforcing properties due to the good equilibrium between modulus and IZOD strength as well as a high HDT reveal the benefits for the compound even more than muscovite mica.

Muscovite and phlogopite mica are commonly used in polyamide 6 because of their equilibrated mechanical behavior but even more due to their ability to reduce isotropically the shrinkage of the compound and increase the HDT both resulting in extremely low warping materials. This is one of the prerequisites for using PA6 compounds as functional parts in environments being subjected to high temperature changes.

**Keywords**
Mica • Reinforcement • Platelets • Muscovite • Phlogopite • Surface treatment • PA • TPU • PP

## Definition

Micas (i.e., muscovite and phlogopite) are platelet-shaped reinforcing fillers used for increasing heat deflection temperature and reducing warpage in polymers. Main use is in polyamide for under the bonnet applications in automotive industry.

## Introduction

The mica phyllosilicates muscovite and phlogopite are truly versatile functional fillers. Whereas sheet and scrap mica minerals are used for larger thermal and electrical insulating shields, ground mica minerals (mostly muscovite) are used as fillers in lacquers, exterior and interior paints, plasterboards, joint compounds, adhesives, and sealants as well as in polymers. Most of the properties conveyed to the matrix are due to the crystal structure, chemical composition, fracture, and cleavage behavior as well as processing parameters used to produce the products. As functional fillers, mica mineral flours – produced by sophisticated iron-free grinding and subsequent air separation and optional surface modification – are making a crucial contribution to improve the properties of modern plastics.

## Mineralogy

Mineralogically the mica group consists of phyllosilicates all with monoclinic crystal structure and perfect basal cleavage.

Micas are muscovite (typically white to gray color), phlogopite (brownish depending on iron concentration), biotite (dark brown to black), lepidolite (lithium-mica, white to gray), and others (in total 42 species according to the Dana classification). Industrially in general and especially in polymers, the most commonly used are muscovite, phlogopite, and biotite.

Table 1 summarizes typical data for muscovite and phlogopite mica minerals.

The most characteristic feature of the micas is their perfect cleavage behavior due to their six-membered ring structure with a 2:1 layer structure. Due to their geometry, they form three-dimensional house-of-cards structures in a compound and lead to isotropic reinforcement and reduction of shrinkage. In lacquers and paints, the platelet-shaped particles form effective diffusion barriers by the tortuous path mechanism. Historically the perfect cleavage behavior and thin-layered structure was used to form window panes and later on high temperature-resistant peepholes for ovens and furnaces.

Figure 1 shows a SEM (scanning electron microscopy), Fig. 2 a typical microphotograph of a muscovite mica.

USGS (2012) states that in 2011 world production of mica products was about 1.09 million tons. Biggest producing countries were China, Russia, Finland, the USA, and Republic of Korea.

Main consumption of ground mica is in the joint compound and gypsum board business where it prevents cracking and gives reinforcement and resistance to wet environment.

Due to a lack of large pure talc deposits, consumption in North America is the biggest worldwide with 44% of the world production, and Europe consumes only approx. 18%.

In 2004 94,000 metric tons of ground mica products has been used in the USA. In the main fields of application, there were joint compounds (joint cements, putties 60,000 metric tons/a), paints (14,000 metric tons/a), polymers (5,000 metric tons/a), and others (like molded electrical insulation, textiles, decorative coatings, rubbers, welding rods, and roofing, 21,000 metric tons/a) (Fig. 3).

## Applications

Non-surface-treated mica minerals for polypropylene (Nolte-Ernsting 2007).

## Phlogopite Mica

Due to the brownish color, phlogopite mica is not that common in polypropylene, although the reinforcing properties which are in a good equilibrium between modulus and IZOD strength (impact strength) as well as a high HDT (heat distortion temperature) reveal the benefits for the compound.

**Table 1** Composition and properties of muscovite and phlogopite mica minerals

| Property | Muscovite | Phlogopite |
|---|---|---|
| **Chemical analysis** | | |
| **SiO 2 [wt%]** | 52 | 42 |
| **Al 2 O 3 [wt%]** | 27 | 11 |
| **K 2 O [wt%]** | 10 | 11 |
| **Fe 2 O 3 [wt%]** | 3 | 7 |
| **MgO [wt%]** | 3 | 26 |
| **LOI [wt%]** | 5 | 3 |
| **Structural formula** | $KAl_2\ ^{[6]}[Si_3Al^{[4]}O_{10}/(OH,F)_2]$ | $KMg_3\ ^{[6]}[Si_3Al^{[4]}O_{10}/(OH,F)_2]$ |
| **Crystal system** | Monoclinic prismatic | Monoclinic prismatic |
| **Color** | White to light gray | Beige to brownish |
| **Diaphaneity** | Transparent to translucent | Transparent to translucent |
| **Cleavage** | [001] perfect | [001] perfect |
| **Fracture habit** | Fracture rare (brittle) mostly cleavage | Fracture rare (brittle) mostly cleavage |
| **Mohs hardness** | 2–2.5 | 2.5–3 |
| **Density [g/cm 3]** | 2.8–2.9 | 2.8–2.9 |
| **Streak** | White | White |
| **Refractive index** | 1.55–1.62 | 1.53–1.62 |
| **pH** | 9–10 | 9–10 |
| **Chemical resistance** | Excellent against water, most acids, bases, oil, solvents; weak against fluoric acid | Excellent against water, most acids, bases, oil, solvents; weak against fluoric and sulfuric acid |
| **Thermal resistance [°C]** | Up to 900 | Up to 900 |
| **Dielectric constant [ at104Hz]** | 2.0–2.6 | 5–8 |
| **Linear thermal expansion coeff. [1/K*10-6]** | 7.1–12.5 | 21–34 |
| **Thermal conductivity parallel* [W/m*K]** | 30 °C: 3.89 | 33 °C: 3.14 |
| **Thermal conductivity normal* [W/m*K]** | 32–45 °C: 0.62 | 32 °C: 0.52 |

Table 2 summarizes the behavior of a series of non-surface-treated phlogopite mica products in polypropylene at 20% filler load.

Advantages of using phlogopite mica of the TREFIL™ type at 20% load compared to the unfilled polymer are:

- An increase of up to 10% in tensile strength
- An increase of up to 126% in elastic modulus
- Moderate to no decrease in IZOD strength
- An increase up to 49% of HDT
- Reduction of the absolute shrinkage up to 31% in all dimensions
- Isotropic behavior (reduction of warpage)

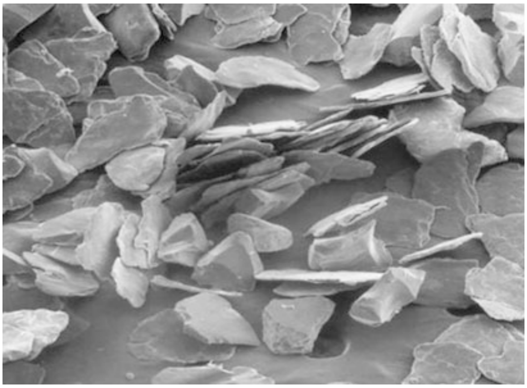

**Fig. 1** SEM of a typical muscovite mica

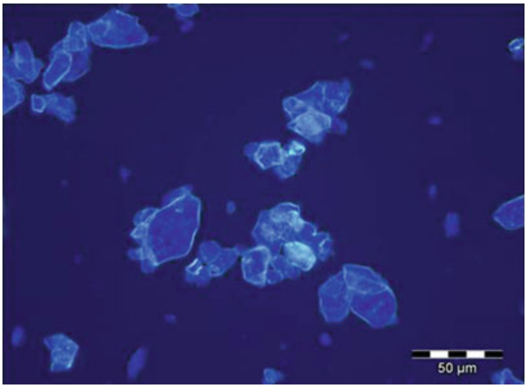

**Fig. 2** Microphotograph of a typical muscovite mica (500× polarized reflected light). Market data of mica minerals

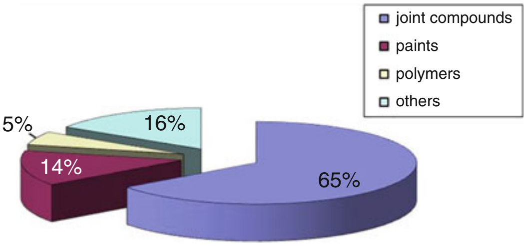

**Fig. 3** Split of ground mica use in the USA in % in 2004 (94,000 metric tons total)

**Table 2** Properties of phlogopite mica products at 20% filler load in PP copolymer Daplen KSR 4525

| Mica functional filler | d 50 sedigraph [um] | BET [m$^2$/g] | Tensile strength [MPa] | Elongation at max. [%] | Elastic modulus [GPa] | IZOD strength | | HDT-B [°C] | Shrinkage | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Unnotched | Notched | | Parallel | Normal | Delta |
| | | | | | | [J/m$^2$] | | | [%] | | |
| TREFIL™ 1232-400 | 12 | 2.3 | 18.3 | 3.4 | 1.79 | 56.8 | 21.5 | 103 | 1.39 | 1.45 | 0.06 |
| TREFIL™ 1232-04333 | 10 | 3.3 | 18.3 | 3.5 | 1.69 | 76.2 | 22.7 | 101 | 1.48 | 1.56 | 0.08 |
| TREFIL™ 1232-04155 | 6 | 5.9 | 18.1 | 4.1 | 1.51 | NB | 30.5 | 96 | 1.52 | 1.61 | 0.09 |
| Unfilled PP | – | – | 16.7 | 7.2 | 0.79 | NB | 55.2 | 69 | 2.03 | 2.1 | 0.07 |
| Talc | 10 | 3.1 | 18 | 4.5 | 1.47 | NB | 22.4 | 98 | 1.53 | 1.66 | 0.13 |

The properties of the filled compound clearly correlate with the average particle size and BET of the TREFIL™ products and give a nice structure–property relationship.

Advantages over typically used talcum type used in this polymer at the same filler load are:

- Up to 22% higher elastic modulus
- Depending on the particle size comparable to better IZOD strength
- Up to 5% higher HDT
- Up to 12% reduction in shrinkage (perpendicular, up to 9% parallel)
- Fifty-three percent better isotropic behavior (reduction of warpage)
- Better scratch resistance in dark compounds due to higher Mohs hardness

## Muscovite Mica

Muscovite mica is commonly used in polypropylene for reinforcing purposes due to the good equilibrium between modulus and IZOD strength as well as good HDT. The analyzed mica products are special compared to other muscovite mica minerals because the deposit contains unusual finely distributed, delaminated mica particles.

Table 3 summarizes the behavior of a series of non-surface-treated muscovite mica products in polypropylene at 20% filler load.

Advantages of using Aspanger muscovite mica at 20% load compared to the unfilled polymer are:

- An increase of up to 9% in tensile strength
- An increase of up to 94% in elastic modulus
- Moderate to no decrease in IZOD strength
- An increase up to 41% of HDT
- Reduction of the absolute shrinkage up to 36% in all dimensions
- Better isotropic behavior (reduction of warpage)

Different production methods lead to materials tailor-made to increase properties depending on the needs of the compound user. Therefore average particle size and BET do not necessarily correlate directly with the compound properties.

Advantages over typically used talcum type at the same filler load used in this polymer are:

- Depending on the particle size comparable to much better IZOD strength
- Up to 19% reduction in shrinkage (perpendicular, up to 15% parallel)
- Up to 77% better isotropic behavior (reduction of warpage)
- Better scratch resistance due to higher Mohs hardness

**Table 3** Properties of Aspanger mica products at 20% filler load in PP copolymer Daplen KSR 4525

| Mica functional filler | d 50 sedigraph [um] | BET [m$^2$/g] | Tensile strength [MPa] | Elongation at max. [%] | Elastic modulus [GPa] | IZOD strength | | HDT-B [°C] | Shrinkage | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Unnotched | Notched | | Parallel | Normal | Delta |
| | | | | | | [J/m$^2$] | | | [%] | | |
| MICA S | 13 | 1.74 | 16.9 | 4.6 | 1.33 | 69.1 | 19.5 | 88 | 1.62 | 1.71 | 0.09 |
| MICA GS | 5.4 | 8 | 17.4 | 4.5 | 1.36 | NB | 26.3 | 97 | 1.37 | 1.4 | 0.03 |
| MICA N | 4.4 | 11 | 18.2 | 4.0 | 1.53 | NB | 37.5 | 96 | 1.42 | 1.50 | 0.08 |
| MICA FS | 3.9 | 12 | 17.2 | 4.5 | 1.32 | NB | 33.9 | 95 | 1.3 | 1.34 | 0.04 |
| MICA SFG 70 | 1 | 21 | 17.3 | 4.1 | 1.31 | NB | 52.7 | 88 | 1.62 | 1.71 | 0.09 |
| Unfilled PP | – | – | 16.7 | 7.2 | 0.79 | NB | 55.2 | 69 | 2.03 | 2.1 | 0.07 |
| Talc | 10 | 3.1 | 18 | 4.5 | 1.47 | NB | 22.4 | 98 | 1.53 | 1.66 | 0.13 |

## Surface-Treated Mica Minerals for Polyamide 6

Muscovite and phlogopite micas are commonly used in polyamide 6 because of their equilibrated mechanical behavior but even more due to their ability to reduce isotropically the shrinkage of the compound as well as increasing the HDT – both resulting in extremely low warping materials (Zilles 2006). This is one of the prerequisites for using PA6 compounds as functional parts in environments being subjected to high temperature changes. HDT As typically are in the region of 120–140 °C at 20% filler load (65 °C on the unfilled PA6). Tables 4 and 5 summarize the behavior of a series of surface-treated Aspanger mica and TREFIL™ phlogopite mica products in polyamide 6 at 20% filler load. All results were obtained on the “dry” injection mold parts.

Advantages of using phlogopite mica of the TREFIL™ type at 20% filler load compared to the unfilled polymer are:

An increase of up to 4% in tensile strength

- An increase of up to 92% in elastic modulus
- Increase in notched IZOD strength
- A typical increase of 90% in HDT A
- Reduction of the absolute shrinkage up to 35% in all dimensions
- Better isotropic behavior (reduction of warpage)

Advantages of using Aspanger muscovite mica at 20% filler load compared in polyamide to the unfilled polymer are:

- An increase of up to 8% in tensile strength
- An increase of up to 83% in elastic modulus
- Increase in notched IZOD strength
- Reduction of the absolute shrinkage up to 32% in all dimensions
- The same isotropic behavior (reduction of warpage)

Muscovite and phlogopite show clear increase of mechanical and thermal properties of polypropylene copolymers and polyamide 6. Whenever equilibrated mechanical behavior (stiffness/brittleness ratio) and isotropic behavior resulting in low warpage are a concern, they show clear advantages in comparison to, e.g., talc or to some extent even glass fibers. Especially in car industry, these mica types will make polymer compounds of PA and PBT available being used in thermal shock environment and high temperature ranges. Whenever scratch resistance and low warpage are a concern, mica shows clear advantages over talc or non-isotropic fillers in polypropylene.

**Table 4** Properties of phlogopite mica products at 20% filler load in PA6

| Mica functional filler | Surface treatment | d 50 sedigraph [um] | BET [$m^2/g$] | Tensile strength [MPa] | Elongation at max. [%] | Elastic modulus [GPa] | IZOD strength | | shrinkage | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | Unnotched | Notched | Parallel | Normal | Delta |
| | | | | | | | [$J/m^2$] | | [%] | | |
| TREFIL™ VP 1232-04347-3 | Mod. siloxane | 12 | 2.30 | 86.2 | 2.8 | 6.22 | 38.6 | 4.6 | 1.25 | 1.32 | 0.07 |
| TREFIL™ 1232-500-059 | Mod. amino silane | 11 | 2.48 | 89.6 | 2.8 | 6.33 | 39.1 | 4.1 | 1.32 | 1.42 | 0.10 |
| Unfilled PA6 | – | – | – | 86.4 | 3.8 | 3.28 | 97.4 | 3.4 | 1.92 | 2 | 0.08 |

**Table 5** Properties of surface-treated Aspanger mica products at 20% filler load in PA6

| Mica functional filler | Surface treatment | d 50 sedigraph [um] | BET [$m^2/g$] | Tensile strength [MPa] | Elongation at max. [%] | Elastic modulus [GPa] | IZOD strength | | Shrinkage | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | Unnotched | Notched | Parallel | Normal | Delta |
| | | | | | | | [$J/m^2$] | | [%] | | |
| MICA TG | Amino silane | 40 | 4 | 89.2 | 2.6 | 6.01 | 29.9 | 4.1 | 1.31 | 1.39 | 0.08 |
| MICA SG | Amino silane | 7.4 | 7 | 93.5 | 3.3 | 5.32 | 50.8 | 4.4 | 1.41 | 1.49 | 0.08 |
| MICA TF | Amino silane | 4.8 | 9.5 | 89.4 | 3.4 | 4.95 | 44.1 | 4.2 | 1.43 | 1.51 | 0.08 |
| MICA SFG20 | Amino silane | 4.2 | 12 | 92.8 | 3.4 | 5.17 | 53.5 | 4.2 | 1.29 | 1.44 | 0.15 |
| Unfilled PA6 | – | – | – | 86.4 | 3.8 | 3.28 | 97.4 | 3.4 | 1.92 | 2 | 0.08 |

## Surface Treatment of Mica

During processing of siliceous products, molecular bonds are broken. The unsaturated terminal silicon and oxygen atoms react with water molecules to form hydroxyl groups. Whereas other water molecules can be absorbed, these water molecules cannot be fully removed by compounding, even under vacuum conditions at high temperature over a long treatment time. Typically (except talc) minerals have high polarity and surface tension (i.e., surface-free energy). On the other hand, typical polymers are lower in surface tension and less polar. Mixing the two is – simplified expressed – like mixing water (the mineral) with oil (the polymer) resulting in a high interfacial tension (due to the mismatch of polar and dispersive parts of surface tensions) and finally in a separation into two phases with minimized surface area. The resulting effects – taking into account that the mineral is a solid and the polymer (when being processed/compounded) is more or less a liquid – are agglomeration of the mineral particles leading to an uneven distribution of the latter and high interfacial tension resulting in easy cleavage of the interface between the two phases (after solidification) being the weakest part in the compound. Even worse, sometimes entrapment of air between mineral and polymer can be observed. Those voids are the nuclei for stress propagation.

By surface treatment of mineral fillers with silanes or silane-based compounds, those interfering effects at the interfaces between the polymer and the filler system can be minimized by – at least – adjusting the surface tensions and polarities of the surfaces.

Silanes are bifunctional chemicals that consist of stable organofunctional and hydrolyzable reactive terminal groups. The hydrolyzable group combines with the inorganic filler surface, while the organofunctional groups harmonize with the organic binder (polymer) system.

An important advantage of this method of incorporating already surface-treated fillers directly into a polymer system over "in situ" treatment is that the condensation by-products already escape during coating of the filler and do not get into and remain in the polymer system, as they do in the case of in situ post-silane treatment. Those condensation by-products (usually humidity and alcohols) typically weaken the polymer matrix. Additionally pre-coated fillers are easier dispersed into a polymer than uncoated ones tending to show much less agglomeration. To achieve an optimum chemical bond between the polymer and the functional filler, a silane specially adjusted to the polymer system must be applied to the surface of the filler.

Comparing the tough fracture of neat mica compounded in a polyamide with a surface-treated mica void can be identified between the mica platelets and the polymer matrix when using the neat mineral. Figures 4 and 5 show tough fracture SEMs of the two compounds.

Another comprehensive comparison of surface-treated and non-surface-treated mineral reinforcing fillers in polyamide is given by Hilgers and Mohr (Thorsten Hilgers 2010). Table 6 shows the reinforcing mineral fillers in comparison.

Tables 7 and 8 show the mechanical and thermal data at 20% (by weight) filler load in polyamide 6.

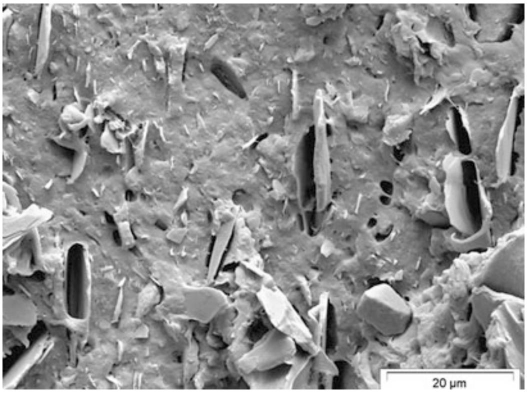

**Fig. 4** Scanning electron micrograph; micronized muscovite mica *without* surface treatment in polyamide after a tough fracture

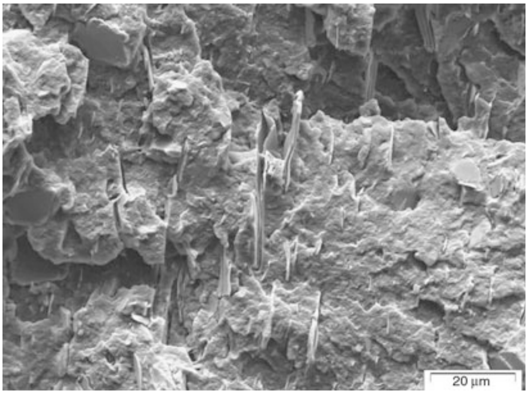

**Fig. 5** Scanning electron micrograph; micronized muscovite mica *with* surface treatment in polyamide after a tough fracture

They conclude for mica:

The thermal and mechanical properties of polyamide compounds can be considerably improved by using platelet-shaped muscovite and phlogopite micas. In this way the following properties can be achieved:

- Improved isotropic shrinkage
- A clear reduction in the shrinkage
- An improvement in the distortion sensitivity
- An increase in tensile strength and in the module of elasticity
- An increase in the rigidity with retention of the tenacity

Coated fillers are more easily incorporated into a polymer in comparison to uncoated ones.

An optimal effect between a polymer and the high-performance filler is achieved by a coating agent that is matched to the polymer system.

**Table 6** Summary of the filler modifications of wollastonite, mica, and kaolin tested in polyamide 6

| Description of the filler | Product name | Date sheet values |  | Method |
|---|---|---|---|---|
|  |  | d50 [µm] | d90 [µm] |  |
| Phlogopite medium | **TREFIL 1232-400** | 11 | 26 | Sedigraph |
| Phlogopite medium silanized | **TREFIL 1232–400 AST** | 11 | 26 | Sedigraph |
| Phlogopite fine | **TREFIL 1232-500** | 11 | 18 | Sedigraph |
| Phlogopite fine silanized | **TREFIL 1232–500 AST/1** | 11 | 18 | Sedigraph |
| Muscovite coarse | **MICA TG** | 40 | 90 | Air jet screen |
| Muscovite coarse silanized | **TREMICA 1305–003 AST** | 40 | 90 | Air jet screen |
| Muscovite medium | **MICA SG** | 7.5 | 15 | Sedigraph |
| Muscovite medium silanized | **TREMICA 1155–006 AST** | 7.5 | 15 | Sedigraph |
| Muscovite fine | **MICA SFG 20** | 5 | 10 | Sedigraph |
| Muscovite fine silanized | **TREMICA 1155–010 AST** | 5 | 10 | Sedigraph |
| Wollastonite, short-needled, medium | **TREMIN 283-400** | 6 | 16 | Cilas laser granulometer |
| Wollastonite, short-needled, medium, silanized | **TREMIN 283–400 AST** | 6 | 16 | Cilas laser granulometer |
| Wollastonite, short-needled, fine | **TREMIN 283-600** | 3.5 | 9 | Cilas laser granulometer |
| Wollastonite, short-needled, fine, silanized | **TREMIN 283–600 AST** | 3.5 | 9 | Cilas laser granulometer |
| Wollastonite, long-needled, medium | **TREMIN 939-400** | 25 | 67 | Needle length/ image analysis |
| Wollastonite, long-needled, medium, silanized | **TREMIN 939–300 AST** | 30 | 69 | Needle length/ image analysis |
| Kaolin, pronounced platelet shape, fine | **Kaolin TEC 110** | 1.1 | 3.5 | Sedigraph |
| Kaolin, pronounced platelet shape, fine, silanized | **Kaolin TEC 110 AST** | 1.1 | 3.5 | Sedigraph |
| Glass fiber | **Glass fiber 4 mm d10µm** | – | – | – |
| Kaolin, calcinated, silanized | **Calcinated kaolin sil.** | 1.1 | 5.2 | Sedigraph |

**Table 7** Mechanical data of different reinforcing mineral fillers at around 20% (by weight) filler load in polyamide 6

| | | Tensile test | | | Pendulum impact tests IZOD | |
|---|---|---|---|---|---|---|
| | | DIN EN ISO 527-1 | | | ISO 180 IZOD | |
| | | | | | Impact | Notched impact |
| Filler | Concentration of filler [%] | Tensile strength [MPa] | Elongation at break [%] | Modulus [MPa] | Resistance [kJ/m$^2$] | Resistance [kJ/m$^2$] |
| **TREFIL 1232-400** | 20.2 | 90 | 4.3 | 6,330 | 29 | 2.9 |
| **TREFIL 1232–400 AST** | 20.3 | 92 | 4.5 | 6,270 | 30 | 2.8 |
| **TREFIL 1232-500** | 20.2 | 88 | 3.2 | 5,930 | 33 | 3.6 |
| **TREFIL 1232–500 AST/1** | 19.0 | 89 | 4.4 | 5,930 | 34 | 3.7 |
| **MICA TG** | 20.3 | 86 | 3.9 | 6,550 | 24 | 2.9 |
| **TREMICA 1305–003 AST** | 19.7 | 89 | 2.6 | 6,010 | 30 | 3.3 |
| **MICA SG** | 19.5 | 90 | 4.9 | 5,580 | 38 | 3.5 |
| **TREMICA 1155–006 AST** | 19.4 | 94 | 4.5 | 5,320 | 51 | 3.6 |
| **MICA SFG 20** | 19.6 | 91 | 5.5 | 5,390 | 47 | 3.4 |
| **TREMICA 1155–010 AST** | 19.9 | 93 | 4.7 | 5,170 | 54 | 3.7 |
| **TREMIN 283-400** | 20.0 | 81 | 3.9 | 4,190 | 47 | 3.6 |
| **TREMIN 283-400 AST** | 19.9 | 84 | 5.2 | 4,170 | 58 | 4.0 |
| **TREMIN 283-600** | 19.3 | 82 | 4.5 | 4,170 | 55 | 3.8 |
| **TREMIN 283-600 AST** | 19.8 | 85 | 3.9 | 4,000 | 65 | 3.9 |
| **TREMIN 939-400** | 19.8 | 96 | 4.6 | 6,130 | 42 | 3.1 |
| **TREMIN 939-300 AST** | 19.3 | 93 | 7.0 | 5,290 | 56 | 3.1 |
| **Kaolin TEC 110** | 19.7 | 92 | 4.3 | 5,780 | 40 | 3.2 |
| **Kaolin TEC 110 AST** | 19.1 | 90 | 5.0 | 5,410 | 51 | 3.4 |
| **Glass fiber 4 mm, d10µm** | 20.0 | 144 | 5.7 | 7,110 | 39 | 6.3 |
| **Calcinated kaolin, silanized** | 18.5 | 88 | 9.3 | 4,280 | N.B. | 3.9 |
| **Polyamide** | 0.0 | 86 | 8.4 | 3,210 | 107 | 2.5 |

**Table 8** HDT and shrinkage data of different reinforcing mineral fillers at around 20% (by weight) filler load in polyamide 6

| Filler | Concentration of filler [%] | Heat distortion temperature | Shrinkage | | |
|---|---|---|---|---|---|
| | | ISO 75 | ISO 294-4 | | |
| | | HDT A [°C] | Parallel [%] | Perpendicular [%] | Delta [%] |
| **TREFIL 1232-400** | 20.2 | 135 | 0.9 | 1.0 | 0.09 |
| **TREFIL 1232-400 AST** | 20.3 | 136 | 0.9 | 1.0 | 0.09 |
| **TREFIL 1232-500** | 20.2 | 123 | 0.9 | 1.0 | 0.07 |
| **TREFIL 1232-500 AST/1** | 19.0 | 122 | 0.9 | 1.0 | 0.07 |
| **MICA TG** | 20.3 | 146 | 0.9 | 1.0 | 0.08 |
| **TREMICA 1305-003 AST** | 19.7 | 140 | 0.9 | 1.0 | 0.08 |
| **MICA SG** | 19.5 | 110 | 0.9 | 1.0 | 0.06 |
| **TREMICA 1155-006 AST** | 19.4 | 108 | 0.9 | 1.0 | 0.06 |
| **MICA SFG 20** | 19.6 | 107 | 1.0 | 1.1 | 0.09 |
| **TREMICA 1155-010 AST** | 19.9 | 104 | 1.0 | 1.1 | 0.09 |
| **TREMIN 283-400** | 20.0 | 88 | 1.3 | 1.3 | 0.02 |
| **TREMIN 283-400 AST** | 19.9 | 86 | 1.3 | 1.3 | 0.03 |
| **TREMIN 283-600** | 19.3 | 85 | 1.3 | 1.4 | 0.01 |
| **TREMIN 283-600 AST** | 19.8 | 84 | 1.3 | 1.4 | 0.02 |
| **TREMIN 939-400** | 19.8 | 129 | 0.9 | 1.1 | 0.20 |
| **TREMIN 939-300 AST** | 19.3 | 114 | 0.9 | 1.1 | 0.20 |
| **Kaolin TEC 110** | 19.7 | 132 | 1.0 | 1.2 | 0.20 |
| **Kaolin TEC 110 AST** | 19.1 | 128 | 1.1 | 1.3 | 0.21 |
| **Glass fiber 4 mm, d10µm** | 20.0 | 198 | 0.4 | 1.0 | 0.55 |
| **Calcinated kaolin silanized** | 18.5 | 79 | 1.4 | 1.4 | 0.06 |
| **Polyamide** | 0.0 | 72 | 1.6 | 1.6 | 0.06 |

Due to this the system, improving properties of the filler are optimally utilized in most cases. In particular tenacity can be improved by the use of silanized fillers.

## Micas in Other Polymers

Sreekanth et al. measured the mechanical, thermal, and morphological influence of muscovite mica on the properties of PBT (Sreekanth 2009).

Inorganic fillers, viz., mica, added to the polymer improved its rigidity, strength, and thermal stability, but dramatically decreased the elongation at break. There is a significant increment in the flexural strength and modulus with an increase in the filler concentration. The impact strength decreases with concentration of filler due to the reduction of elasticity of material due to filler addition and thereby reducing the deformability of matrix. There is a significant increase in the dielectric strength with filler addition. Addition of mica improved the thermal properties of the composites due to small and uniform crystallite size distribution. Morphological studies showed that there is a better interaction between filler and the matrix at lower filler concentration and platelets are aligned parallel to each other. The mechanical properties of the composite were found to be a function of the particle size, aspect ratio, the dispersion, the particle orientation, the interfacial interaction between the minerals, and the polymer matrix. Platy structured filler such as mica gave significant improvement in stiffness. It is concluded that the composite showed improved mechanical (flexural), thermal, and electrical properties on addition of filler.

Thomas et al. (2013) described the influence of compatibilizers and mica on the properties of the completely immiscible polymers TPUs (thermoplastic polyurethanes) and POs (thermoplastic polyolefins); the effects of incorporation of polypropylene copolymer (PPCP), TPU-g-MA (maleic anhydride-grafted TPU), and TPU-g-AA (acrylic acid-grafted TPU) as compatibilizer on the miscibility of the blends and effect of mica filler to enhance the mechanical properties were studied.

Compatibilizers such as polypropylene copolymer (PPCP), TPU-g-MA, and TPU-g-AA were found to be good compatibilizers for the TPU/PO blends. Addition of mica as filler into the blends with compatibilizer increased the mechanical properties such as tensile strength, hardness, and elongation and decreases the impact strength. SEM images show good dispersion of mica filler into the blend matrix.

Busigin et al. (Polypropylenes 1984) measured the influence of aspect ratio of specially prepared phlogopite mica model fillers (wet ground, narrowly classified) on the mechanical properties of polypropylene compounds. The higher the aspect ratio, the higher the modulus of the compound, but tensile strength was only little influenced. Tensile strength was to a greater extent depending on particle size as such with the smallest particle sizes resulting in the highest tensile strength. HDT and notched impact strength were mostly dependent on the filler concentration used than on other parameters. The finer the phlogopite, the more often reprocessing could be performed without deterioration of mechanical properties.

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# Talcs

# 10

Roger Rothon

## Contents

## Abstract

Talc is a naturally occurring magnesium silicate mineral, widely used as a polymer filler. Its main differentiating features in this context are its softness (it is the softest mineral known) and lamellarity (platiness). Useful deposits are widespread and processed by conventional mining operations to produce filler grade material. The platiness depends on the source and manufacturing methods. The main use for talc is in thermoplastics, such as polypropylene, where it gives a useful balance of strength and stiffness, together with increased heat distortion temperature and creep resistance. The platy nature also provides better gas barrier properties than blocky fillers like calcium carbonate. Significant issues with talcs in composites are the limited response to coupling agents such as organo-silanes and accelerated heat aging due to impurities which varies with the origin of the deposit.

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**Keywords**
Talc • Occurrence • Extraction • Processing • Purity • Color • Lamellarity • Aspect ratio • Particle size • Surface treatments • Thermoplastics • Modulus • Heat distortion temperature • Creep • Permeability • Impact strength • Recycling

## Definition

Talc is a natural mineral, which has the chemical composition $Mg_3(Si_4O_{10})(OH)_2$.

This entry is concerned with commercial talcs, which, because of their natural origin, can contain significant and variable levels of other minerals. These impurities are often not revealed in the literature, although nearly all dilute the special properties of the pure mineral, and a few may even be deleterious.

## Occurrence

Talc is a secondary mineral and is found in metamorphic rocks from the degradation of minerals such as olivine, pyroxene, and amphibole and also along faults in magnesium-rich rock.

The metamorphic changes that gave rise to talc also produced other magnesium-containing minerals, and commercial talcs are usually a mixture of natural products. Common impurities include magnesite (magnesium carbonate), chlorite (a mixed magnesium silicate-magnesium hydroxide in which $Fe^{2+}$, $Fe^{3+}$, and $Al^{3+}$ may substitute for $Mg^{2+}$ and $Al^{3+}$ for $Si^{4+}$), and tremolite (calcium magnesium silicate). Indeed, some commercial talc may contain the actual mineral only as a minor constituent or, in some cases (all chlorite), not at all.

Processable talc deposits are widespread, although not as extensive as those of calcium carbonate or clay, with main production coming from the USA, Norway, France, Italy, India, China, and Australia. Some massive forms known as steatite or soapstone (after the characteristic soapy feel of talc) occur, but most of the talc is found in veins.

## Extraction and Processing

Talc is produced by conventional selective opencast mining or by underground mining followed by crushing, grinding, beneficiation, and classification. After the crude rock is crushed, it is often subjected to a manual selection process, although automated techniques are now being introduced. It is then ground in a variety of ball mills, hammer mills, and fluid mills with air classification systems included in a closed-loop system to produce products with a range of particle-size distributions but with the majority having top cuts of 100, 200, and 300 mesh, 20 and 10 μm.

Some talcs may also be subjected to beneficiation by froth flotation. In this case, the talc is ground and dispersed in water, before being subjected to froth flotation using the appropriate surfactant to achieve a separation. The talc may then be subjected to grinding, classification, or both to achieve the desired particle-size distribution.

## Properties of Talc

Pure talc is the softest known mineral with a hardness of 1 on the Mohs' hardness scale; its specific gravity is 2.8, and it has three indices of refraction, 1.539, 1.589, and 1.589, according to crystal direction.

Pure talc has a trioctahedral crystal structure in which an octahedral brucite [Mg $(OH)_2$] sheet is sandwiched between two tetrahedral siloxane $S_2O_5$ sheets. This structure is electrically neutral and will bond to an adjacent layer only through van der Waals forces. Thus, talc undergoes cleavage very readily, is very soft, and has a soapy feel. Faces of the layers consist of oxygen atoms, and reactive hydroxyl groups are only found at broken edges, and so talc is fairly hydrophobic.

## Grades of Talc

Many commercial talcs are available, with the main differences between talc grades being:

Purity
Color
Lamellarity
Particle size
Surface treatments

Two types of impurity can be distinguished: external and structural. External refers to the nontalc matter mixed with the talc. Structural refers to impurities in the talc crystals themselves. The first type is mainly minerals such as magnesite, chlorite, and tremolite, referred to earlier, and these vary with the ore origin and processing. They mainly dilute the special effects of talc. Structural impurities are substitution of silicon in the structure by metals such as aluminum and iron. Such substitutions don't usually have much effect on the primary effects of talc in composites but can have profound effects on important secondary properties, such as color and stability.

While pure talc is white, commercial talcs can vary markedly and can even be brown or black. This is usually due to structural impurities as outlined above.

Lamellarity refers to the platiness of the particles. This can also be described as their aspect ratio and is the plate diameter divided by plate thickness. This can vary significantly and is a main differentiating feature between talcs. The ultimate thickness is fixed by the crystal structure, and so the aspect ratio is determined by the plate size and how well the particles are delaminated during processing (both during powder manufacture and mixing with the polymer).

The plate size (diameter) is a function of the geological deposit, the processing involved in separating and finishing the product for filler applications and lastly by the polymer processing conditions. The latter should not be ignored as much of the delamination often occurs during this stage.

Two extreme types of talc deposit can be recognized: microcrystalline and macrocrystalline. The microcrystalline type has the smallest diameter plates and will give rise to low aspect ratio particles. The macrocrystalline type has the potential to give much higher aspect ratios if properly processed.

Particle size mainly refers to plate diameter and is a function of the ore source and the processing conditions. Plate sizes in talc deposits can be as low as 1 μm and as high as 100 μm. While the largest size plates give the highest aspect ratio, they can have deleterious effects on other composite properties, and a top size of no more than about 12 μm with an average size of less than 5 μm is generally preferred.

Talcs for polymer use have aspect ratios in the range 5–20 in the powder form. The balance between particle size and aspect ratio is tailored to meet different applications.

Some talcs are also offered with added surface treatments. These range from stearate salts through to organo-silanes but currently have limited utility, and a true coupling agent does not seem to have been found. This is due to two factors. The first is the inertness of the plate faces, relegating chemical coupling to the more reactive edges. The second is the weak nature of the crystal stacks. Unless complete delamination and reaction occurs, these can fail in the composite.

The smallest size, high lamellarity talcs have low bulk densities (often less than 0.3), leading to difficulties in polymer compounding operations. Densified talcs (up to 0.9 bulk density) have been developed to overcome this.

## Polymer Uses of Talc

The best talcs are significantly more expensive than fillers such as calcium carbonates and have to bring extra benefits to justify their use. The main benefits of talc are a greater increase in stiffness and heat distortion temperature than observed with the same amount of a blocky (low aspect ratio) filler like calcium carbonate. These effects are particularly noticeable in semicrystalline thermoplastics, such as polyolefins, and, as a result, these polymers are the main markets for talcs. In particular, they are used in polypropylenes for various automotive applications and in household appliances. In some applications, they are used in conjunction with lower-cost fillers, such as calcium carbonates. The extreme softness is a benefit as it means that machine wear is less than with other fillers (although this can be compromised by the presence of hard impurities, notably quartz).

As described earlier, there are many grades of talc, with variations in particle size and aspect ratio being two key variables. Unfortunately, much of the published literature isn’t very specific about these properties, often just referring to low, medium, or high lamellarity and particle size. The difference in effect on stiffness between a calcium carbonate and two different aspect ratio talcs in a polypropylene matrix is demonstrated in Fig. 1.

Heat distortion (deflection) temperature is another key property of semicrystalline thermoplastics which benefits from the use of lamellar fillers like talc. This is illustrated in Table 1.

While it is generally held that their enhanced effect on stiffness and HDT is due to their platy nature, other factors also contribute, notably the relatively high stiffness of the plates themselves and their effect on polymer crystallinity.

Creep is an important limitation of thermoplastics but receives little attention in the general literature. One of the advantages of platy fillers like talc is a significant reduction in creep compared to blocky fillers. This is illustrated by values presented in Table 2.

The lamellar nature means that talc can significantly lower the permeability of polymers, especially if the particles are aligned to provide maximum effect, as in polymer film. This is illustrated by the data in Table 3, which compares the oxygen and water vapor transmission rate of polypropylene film containing talc with one containing a calcium carbonate.

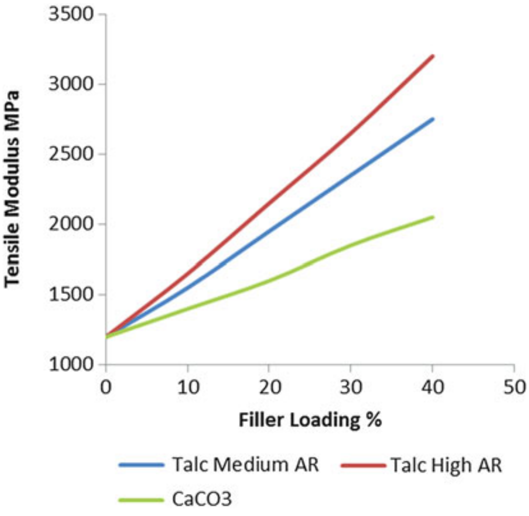

**Fig. 1** A comparison of calcium carbonate and two talc fillers of different aspect ratio on the tensile modulus of a homopolymer polypropylene compound

**Table 1** The effect of talc lamellarity on the heat deflection temperature (HDT) of polypropylene

| Talc type and level | HDT (centigrade) |
|---|---|
| None | 97 |
| 20% w/w low aspect ratio talc | 109 |
| 20% w/w high aspect ratio talc | 121 |

**Table 2** A comparison of the effect of talc on the creep of a polypropylene composite

| Filler type and level | Creep (expressed as % change in strain after 2 years) |
|---|---|
| None | 1.2 |
| 20% w/w calcium carbonate | 0.95 |
| 20% w/w high aspect ratio talc | 0.65 |

**Table 3** A comparison of the effect of a lamellar talc on the permeability of homopolymer polypropylene film

| Filler type and level % w/w | Oxygen transmission rate $cm^3/m^2$ in 24 h | Water vapor transmission rate $g/m^2$ in 24 h |
|---|---|---|
| None | 430 | 0.50 |
| 30% calcium carbonate | 325 | 0.41 |
| 30% talc | 190 | 0.31 |

Impact resistance is always an important property for thermoplastics but is a complicated property to describe. The failure mechanism and the effect of fillers and filler surface treatments vary considerably with the type of thermoplastic matrix involved. Glassy, amorphous polymers, such as polystyrene, behave much differently to semicrystalline polymers where the amorphous phase is ductile. Here, we only discuss the semicrystalline types, as they are the major market.

Impact resistance in these semicrystalline polymers can be affected by many talc properties, especially particle size, dispersion, and lamellarity, and these are not often sufficiently described in the literature on talc compounds to allow the different factors to be unambiguously quantified. It does seem that talcs in general reduce the impact strength of both homo- and copolymer polypropylene when used at levels above 10% w/w. What is clear is that the smaller size talcs give the best impact resistance, as shown in Fig. 2. (Note: this is a simplification for illustrative purposes only. It uses the average particle size; the largest size is as important and is assumed constant within the series used here.)

There is some evidence that very fine talcs actually increase impact resistance at loadings below 10% w/w, an effect that is believed to arise from polymer nucleation. This is illustrated in Fig. 3.

Deleterious effects on aging performance can be an issue for some talcs, especially in polypropylene which is particularly susceptible to such problems. These effects vary markedly from talc to talc and are mainly due to structural impurities such as aluminum and iron which can promote polymer degradation. It should be noted that the reactivity of these impurities can vary markedly, depending on their chemical environment, and so metal level alone is not a sufficient guide to performance. In some cases, surface treatments are used to deactivate these troublesome sites. This is illustrated in Fig. 4.

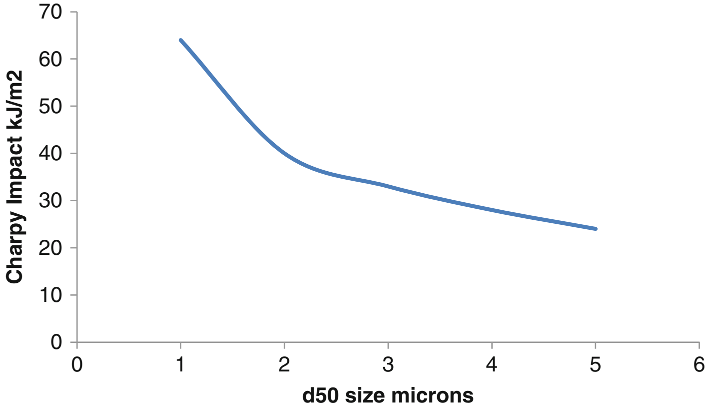

**Fig. 2** The effect of talc particle size (d50) on Charpy impact resistance of a polypropylene copolymer (20% w/w talc loading)

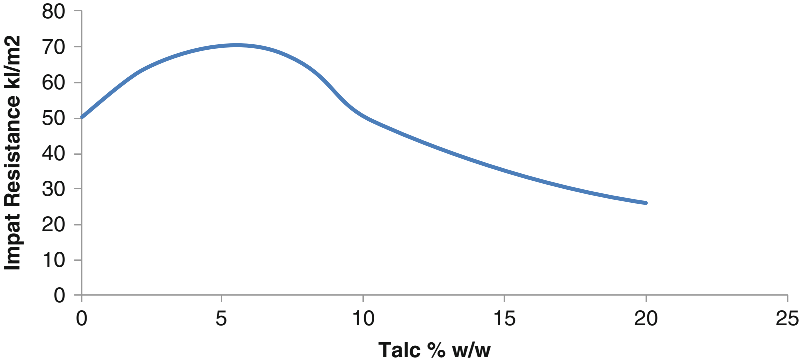

**Fig. 3** The effect of fine talc addition level on the impact resistance of a high impact grade of polypropylene

## Recycling Issues

The main polymer use for talc fillers is in thermoplastic compounds for the automotive industry, and it is believed that these compounds have a high recycling rate. Many of the major automotive markets have stringent environment targets which encourage recycling. Thus, in the EU, the End of Life Vehicle Directive requires that a minimum of 95% of a vehicle's weight must be reused or recycled. Talc-filled thermoplastics are recovered and reused for a variety of automotive applications, mainly in under bonnet parts, body arch liners, and cable harness parts. There is also downcycling into nonautomotive parts, such as water and sewage pipes, furniture feet, etc. According to the Industrial Minerals Association (ima-europe.eu), about 95% of the talc used in automotive applications in Europe is recycled in some way.

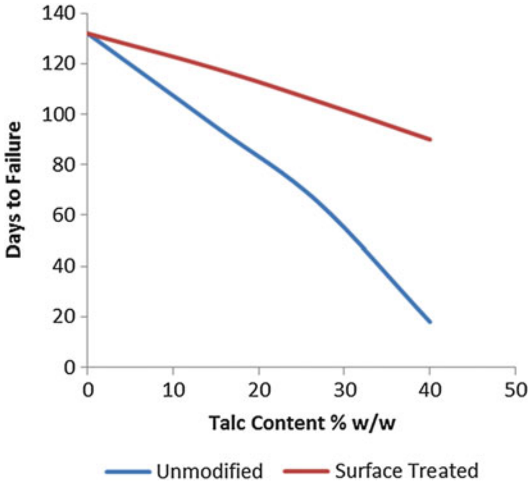

**Fig. 4** Effect of talc surface modification on thermal stability of homopolymer polypropylene (days to failure at 150 °C)

## Future Prospects

Talc is expected to remain an important filler, as long as suitable deposits are available. It is expected that there will be growth in the use of compacted and densified forms to improve processing rates. It is also believed that there is a scope for more exploitation of the ease in delamination and the reaching of higher aspect ratios than currently exploited. There is said to be good growth prospects in barrier film for food packaging. Really effective surface treatments remain a “Holy Grail,” and true coupling agents have long been sought. This remains a difficult target.

## Cross-References

- ▶ Particulate Fillers in Thermoplastics
- ▶ Particulate Fillers, Selection, and Use in Polymer Composites
- ▶ Surface Modifiers for Use with Particulate Fillers

## Further Reading

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# Wollastonites

# 11

Joerg Ulrich Zilles

## Contents

## Abstract

Wollastonite is a metasilicate having an inosilicate (chain silicate) structure. It belongs to the pyroxenoid group of minerals. It is the only white acicular mineral and became famous and widely used in the industry in the 1970s 1980s as a nonhazardous replacement for asbestos fibers. During crushing and grinding, it forms acicular particles having an aspect ratio (length vs. diameter ratio) in the range of 1:3 up to 1:15. The structure of the wollastonite particles depends partly on geological conditions of genesis but also to a large extent on the

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grinding technology. The applications are widely spread reaching from additive in metallurgy (protective slag, welding electrodes) over ceramics and ceramic boards to reinforcement in thermoplastics and thermosets (car interiors, fenders, trims) and corrosion inhibitor as well as reinforcement in paints and coatings.

Especially in cost-efficient PP systems, high-aspect-ratio (HAR) wollastonite can confer the compound properties necessary to replace other high-price polymeric systems, e.g., in automotive industry. Properties asked for by automotive applications are low thermal expansion (CLTE), zero-gap bumpers, painting ability, high flow, mold in color, high stiffness, reduced shrinkage, and improved resistance to UV and petrol. Besides the fibrous structure of the mineral and its size distribution, the surface treatment plays a major role when looking at dispersing ability, scratch resistance, and mechanical properties.

LAR, aminosilane-coated wollastonite flours have been successfully used for many years as functional fillers for polyamides. With HAR wollastonite the rigidity of the compound is even higher than with LAR wollastonites. Polyamides reinforced in this way offer a range of different possibilities for the design of low warpage, rigid moldings/parts. They are used in, e.g., wheel covers, air filter housings, and electrical appliance parts.

Polyurethane for reaction injection molding (PUR RIM) is a microcellular (integral) hard foam for thin-walled moldings exposed to compressive and flexural stress. The PUR R-RIM-reinforced variants with HAR wollastonite are used when a higher elastic memory is required.

In comparison to other fillers in mid-voltage insulation applications based on epoxy resin molding materials, wollastonite is used due to its reinforcing properties when wall thickness in technical parts shall be reduced or resistance toward cracking – i.e., better flexural modulus – should be improved. The coefficient of linear thermal expansion is comparably low.

In recent years the development of brake pads/linings based on phenolic resins has led to the use of environmentally friendly raw materials like wollastonite, which is critical to health.

LAR, silane-coated wollastonite flours are successfully used for many years as functional fillers in shaft seals based on fluoroelastomers in order to adjust the hardness. Apart from the good reinforcement in fluoroelastomers, LAR wollastonite (due to its bright and neutral color) provides also the advantage of colored bright mixtures. These optimized fluoroelastomers are ideally suited for the applications under special conditions, e.g., when high mechanical load and high temperatures apply and whenever chemical resistance is crucial.

## Abbreviations

| | |
|---|---|
| PA | Polyamide |
| PP | Polypropylene |
| PUR R-RIM | Polyurethane for reinforced reaction injection molding |

## Definitions

Wollastonite is a naturally occurring calcium silicate mineral with an acicular (needlelike) particle shape when carefully processed. The acicular shape allows it to give useful properties in many polymers, especially polypropylene, polyamides, and thermosets such as epoxies and phenolics.

## Introduction

Wollastonite is named after William Hyde Wollaston (1766–1828), an English chemist and physicist who discovered the chemical elements rhodium and palladium. The mineral was named after Wollaston because he rendered outstanding services to crystallography and mineralogy.

Wollastonite is a metasilicate having an inosilicate (chain silicate) structure. It belongs to the pyroxenoid group of minerals. It is the only white acicular mineral and became famous and widely used in the industry in the 1970s–1980s as a nonhazardous replacement for asbestos fibers. The applications are widely spread reaching from additive in metallurgy (protective slag, welding electrodes) over ceramics and ceramic boards to reinforcement in thermoplastics and thermosets (car interiors, fenders, trims) and corrosion.

## Wollastonite Mineralogy

The theoretical stoichiometric formula of wollastonite is $CaSiO_3$. $SiO_4$-tetrahedrons form chains so the mineral belongs to the inosilicate structure type of silicates.

The genesis of wollastonite can be metamorphic or magmatic. Depending on the genesis, the deposits are defined as carbonatites if formed in a magmatic process or skarn if formed by metamorphosis.

Metamorphosis is the change of one mineral into another mineral. In the case of wollastonite, it is the precipitation from hydrothermal siliceous solutions intruding into calcium carbonates.

In magmatic deposits, wollastonite was generated by intrusion of silica-rich magma into a calcite or dolomite host rock forming local mineralization in contact zones.

Having an inosilicate structure and two perfect cleavage planes being nearly perpendicular to each other (84°), the mineral forms needle-shaped particles upon grinding.

Table 1 shows some mineralogical properties of wollastonite.

Wollastonite shows a low coefficient of thermal expansion ($7 \times 10^{-6}$ 1/K 20–800 °C). The pH is about 9 and the refractive index 1.63.

Depending on the genesis, commercially available wollastonite is associated with other minerals like diopside, quartz, garnet, calcite, and dolomite.

Figure 1 shows two lumps of wollastonite of Indian origin.

**Table 1** Mineralogical/physical properties of wollastonite (Carr 1994)

| Crystal system | Triclinic |
|---|---|
| Form and habit | Bladed crystal masses, acicular |
| Color | White, sometimes cream, gray, or very pale green |
| Hardness | 4.5–5 on the Mohs scale |
| Luster | Vitreous to pearly |
| Streak | White |
| Cleavage | Two perfect at 84° and one good |
| Specific gravity | 2.87–3.09 |
| Melting point | 1,540 °C |
| Inversion temperature | Pseudowollastonite (high-temperature polymorph) at 1,120 ± 10 °C |

**Fig. 1** Lumps of wollastonite

## Availability

Total world production of wollastonite except the USA is in the 600 Ttpa range. China accounted for approx. 300 Ttpa and India for 210 Ttpa. The USA is the third biggest producer of wollastonite; data of production are not published (Virta 2013).

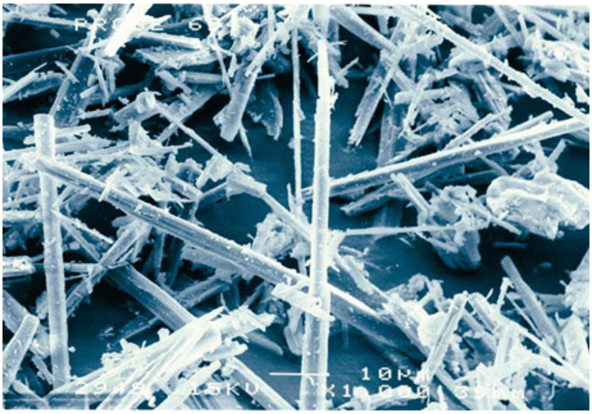
Wollastonite is available in lumps and flours down to an average particle size of approx. 2 μm. Neat grades as well as surface-treated grades are used depending on the application.

## Properties

Wollastonite is unique in being the only white and acicular, nonmetallic mineral. During crushing and grinding, it forms acicular particles having an aspect ratio (length vs. diameter ratio) in the range of 1:3 up to 1:15. The structure of the wollastonite particles depends partly on geological conditions of genesis but also to a large extent on the grinding technology. With specific processing technologies, powders with exceptional acicular structure can be achieved. Figures 2 and 3 show two wollastonite products prepared by different methods. A nearly blocklike wollastonite (TREMIN 283-product series by HPF – The Mineral Engineers) with an average aspect ratio of approx. 3:1 is shown in Fig. 2. These are the so-called low-aspect-ratio (LAR) wollastonites. A wollastonite product with an exceptional acicular structure (TREMIN 939-product series by HPF – The Mineral Engineers) – including

**Fig. 2** Scanning electron micrograph: micronized LAR wollastonite flour (magnification 1:1,000)

**Fig. 3** Scanning electron micrograph: micronized HAR wollastonite flour (magnification 1:1,000)



fractions with aspect ratio of up to 30:1 – is displayed in Fig. 3. This type is called high-aspect-ratio (HAR) wollastonite.

Because of the particle shape and – frequently also for special applications – surface treatment with silanes or silane-based compounds, wollastonite powders have excellent reinforcing properties. The mineral fiber itself is said to have a tensile strength of approx. 2,700–4,100 MPa.

Usual brightness of the processed mineral flour is about 90 (Y), so the neutral color and high brightness make it applicable in most polymer systems.

## Modern Analytical Description of HAR and LAR Wollastonite Particle-Size Distributions

Particle-size distributions measured by light-scattering techniques are close to reality if the particles somehow are spherical in shape (Zilles and Nolte-Ernsting 2005). Light-scattering techniques only give a steady result at least for acicular particles, if the flow conditions are absolutely constant in such apparatus.

Especially HAR wollastonite is acicular (a fiber) which renders the compound good mechanical properties. These are governed by the average aspect ratio (L/D50) of the mineral, the average length (L50), and the length distribution, as well as the distribution of aspect ratio.

If – as usual for mineral fillers – only the diameter is taken into account, which is the standard measure to describe the filler by sieves (mostly for the top cut), the materials HAR wollastonite and LAR wollastonite do not show much difference in particle-size distribution as Fig. 4 reveals. Only the general difference in d50

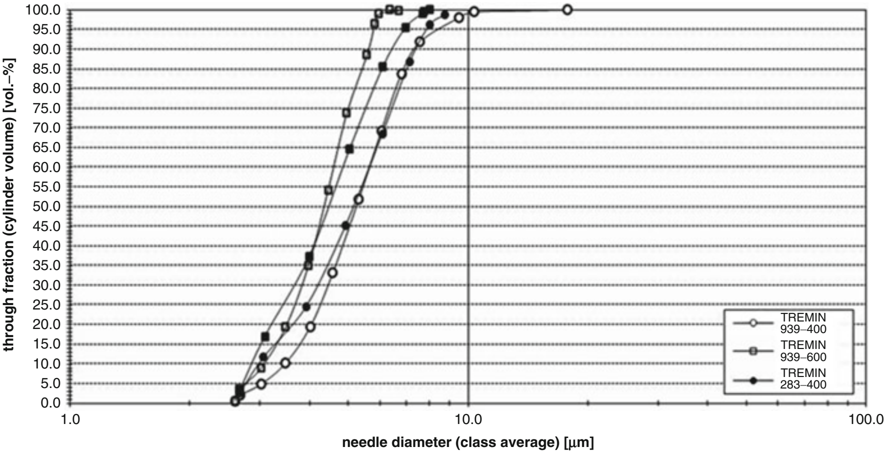


**Fig. 4** Volume trough fraction versus diameter of wollastonite fibers

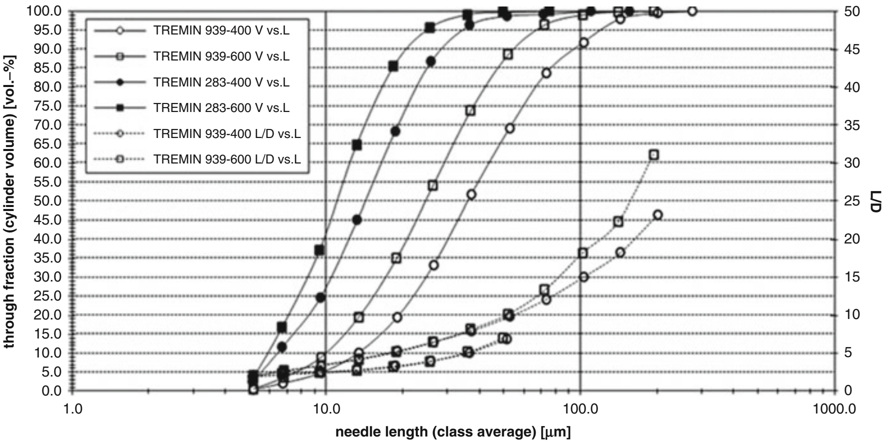


**Fig. 5** Minus mesh fraction versus length as well as aspect ratio versus length of wollastonite fibers

(400 type = 4 μm, 600 type = 5.5 μm) is described correctly although in mechanical behavior the difference between 283 (LAR) and 939 (HAR) is much larger than the differences between the subtypes −400 and −600.

Modern automated microscopic techniques allow to describe the particle itself as well as distributions regarding different dimensions (length, diameter) and forms on a significant statistical basis.

Figure 5 gives an impression on the different fiber length distributions on the products in comparison.

## Surface Treatment of Silicates

During the processing/grinding of siliceous products, molecular bonds are broken (Zilles and Nolte-Ernsting 2005). The unsaturated terminal silicon and oxygen atoms react with water molecules to form hydroxyl groups. Whereas other water molecules can be absorbed, these water molecules cannot be fully removed by compounding, even under vacuum conditions at high temperature over a long treatment time. As a result potential weak points can be formed at the interfaces of the polymer as well as the interfacial tension increases – filler system and matrix will not contribute their desired properties to a perfectly coherent compound.

By surface treatment of mineral fillers with silanes or silane-based compounds, those interfering effects at the interfaces between the polymer and the filler system can be minimized. Silanes can be bifunctional molecules that consist of stable organo-functional and hydrolysable reactive terminal groups. The hydrolysable group combines with the inorganic filler surface, according to the reaction scheme shown below.

$$R' - Si\,(OR)_3 \quad + \quad 3\,H_2O \rightarrow R' \quad - \quad Si(OH)_3 \quad + \quad 3\,R - OH$$

$$R' - Si\,(OR)_3 + H \cdot O - (Si - O)_x \rightarrow R' - Si\,(OR)_2 \cdot O \cdot (Si \cdot O)_x$$

It is important to choose the organo-functional groups (R′) to harmonize with the polymer matrix system the filler is compounded with.

An important advantage of this method of incorporating surface-treated fillers directly into a polymer system is that the condensation by-products escape during coating of the filler and do not remain in the polymer system, as they do in the case of in situ post-silane treatment during compounding. It is also easier to incorporate coated fillers into a polymer than non-coated ones. To achieve an optimum chemical bond between the polymer and the functional filler, a silane specially adapted to the polymer system must be applied to the surface of the filler.

The different tough fracture behaviors of silane-treated wollastonite in polypropylene homopolymer compared with non-surface-treated wollastonite are shown in Figs. 6 and 7. While the uncoated wollastonite fibers do form an interface as

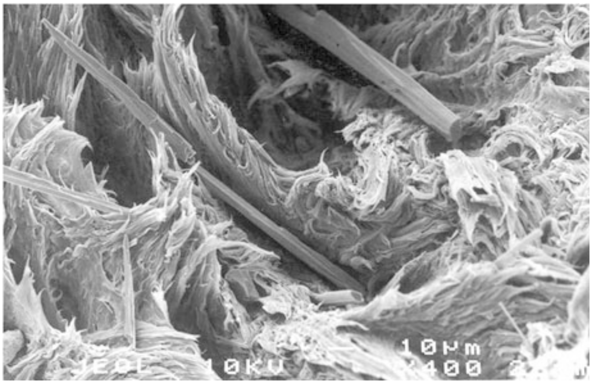


**Fig. 6** Scanning electron micrograph: micronized acicular wollastonite without surface treatment in polypropylene after a tough fracture

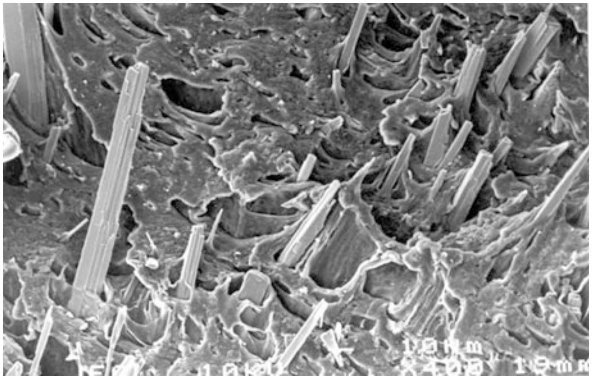


**Fig. 7** Scanning electron micrograph: micronized acicular wollastonite with surface treatment in polypropylene after a tough fracture

predetermined breaking point with the polymer, a much better compatibility can be identified between the surface-treated wollastonite fibers and the polypropylene.

Last, but not least, special surface treatments on wollastonite are able to reduce dust problems during handling of the micronized mineral.

## Wollastonite in Polypropylene

High-aspect-ratio (HAR) wollastonite mineral short-fiber compounds have been known now for over 10 years. New grinding technologies as well as surface treatment allow to tailor L/D ratio and fiber length distribution, as well as interfacial behavior to meet the increasing requirements for mechanical reinforcement, scratch resistance, dispersing ability, low shrinkage, high thermal stability, and dust-reduced handling.

Especially in cost-efficient PP systems, wollastonite can confer the compound's new properties necessary to replace other high-price polymeric systems, e.g., in automotive industry. Properties asked for by automotive applications are low thermal expansion (CLTE), zero-gap bumpers, painting ability, high flow, mold in color, high stiffness, reduced shrinkage, and improved resistance to UV and petrol.

Besides the fibrous structure of the mineral and its size distribution, the surface treatment plays a major role when looking at dispersing ability, scratch resistance, and mechanical properties.

In polypropylene systems, the very good reinforcing properties of surface-modified, HAR wollastonite flour have been successfully used for years. Due to the Mohs hardness of these products (4.5) compared to talc (1–1.5), compounds with excellent scratch resistance are accessible. In addition, these compounds are characterized by very good impact strength combined with high rigidity. The low thermal expansion coefficient of wollastonite is partially conveyed to the polymer as well as the reinforcement, resulting in a high heat deflection temperature. Because of the uniform lengthwise orientation of wollastonite HAR fibers, the molded part shrinks far less – an important requirement for "zero-gap design," e.g., in the manufacture of trims.

Typical wollastonite load is between 10% and 30% by weight in polypropylene compounds.

Table 2 shows the effect of different wollastonite types and talc on the mechanical values of filled polypropylene copolymer at 20 wt% filler load (Zilles and Nolte-Ernsting 2005).

The data reveal the superior mechanical properties of HAR wollastonite in comparison to LAR wollastonite and talc.

The tensile strength as well as even more drastically the HDT (heat distortion temperature) is increased by using 20% HAR wollastonite compared to the polymer without reinforcement, maintaining to a good extent the impact properties. The reduction of molding shrinkage of HAR wollastonite is superior to LAR wollastonite, talc, and the polymer itself. The anisotropic behavior in molding shrinkage can be explained by the anisotropy of the single grain itself and the orientation of the

**Table 2** Effect of wollastonites and talc on the technical data of reinforced polypropylene copolymer at 20 wt-% filler load

| | $s_M$ [MPa] | $e_M$ [%] | $s_B$ [MPa] | $e_B$ [%] | Et [GPa] | aiU + 23 [kJ/m$^2$] | aiA + 23 [kJ/m$^2$] | HDT B [°C] | II[a] [%] | T[a] [%] |
|---|---|---|---|---|---|---|---|---|---|---|
| PP copolymer without filler | 16.7 ± 0.2 | 7.2 ± 0.1 | 15.5 ± 1.2 | >500 | 0.79 ± 0.01 | NB | 55.2 ± 2.3 | 69.0 ± 1.2 | 2.03 | 2.1 |
| TREMIN 939–400 (HAR) | 19.7 ± 0.3 | 3.5 ± 0.1 | [b] | [b] | 2.13 ± 0.05 | 55.9 ± 8.2 | 20.5 ± 0.9 | 109 ± 1.8 | 0.99 | 1.31 |
| TREMIN 939–600 (HAR) | 20.4 ± 0.2 | 3.3 ± 0.1 | [b] | [b] | 2.24 ± 0.03 | 55.2 ± 2.4 | 20.4 ± 2.7 | 110 ± 2.0 | 1.18 | 1.55 |
| TREMIN 283–400 (LAR) | 16.5 ± 0.2 | 4.6 ± 0.1 | 13.5 ± 0.8 | 426 ± 177 | 1.18 ± 0.03 | NB | 32.8 ± 1.0 | 84 ± 1.0 | 1.79 | 1.84 |
| TREMIN 283–600 (LAR) | 16.4 ± 0.1 | 4.1 ± 0.1 | 12.3 ± 0.2 | 136 ± 96 | 1.20 ± 0.02 | NB | 48.8 ± 1.1 | 84 ± 1.5 | 1.79 | 1.86 |
| Talc | 18 ± 0.1 | 4.5 ± 0.1 | 9.9 ± 0.6 | 47.4 ± 6.6 | 1.40 ± 0.02 | NB | 22.4 ± 1.3 | 98 ± 1.4 | 1.53 | 1.66 |

*NB* no break

[a] Molding shrinkage

[b] Flowing/yield without break

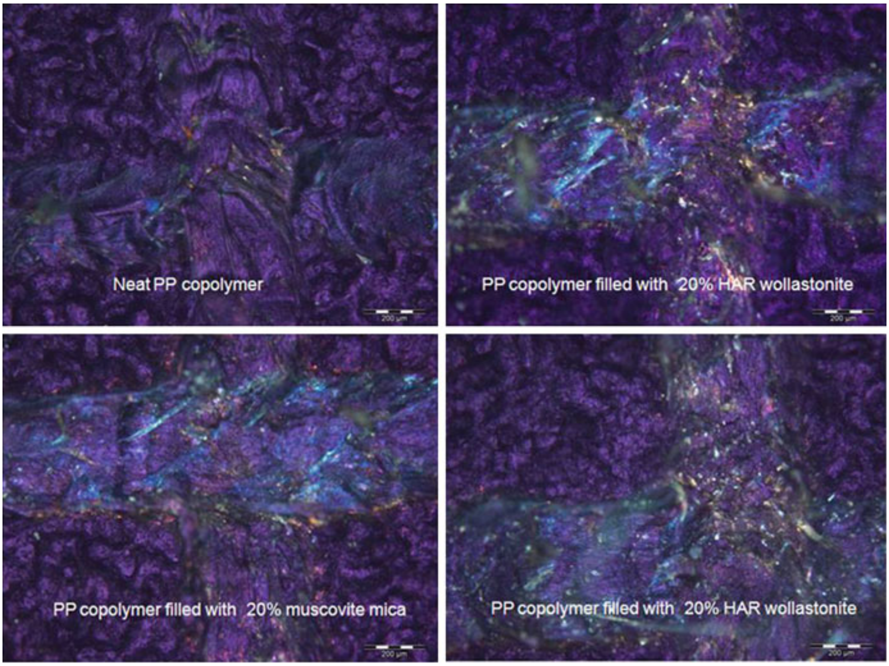


**Fig. 8** Microphotographs using polarized light of scratch intersections (GE standard test procedure) on the compound surfaces in comparison

mineral fiber during molding. It should be mentioned that the anisotropic behavior of pure fibers (like wollastonite and glass fibers) can be an obstacle when it comes to warping in complex injection-molded 3-D structures.

Chu et al. (2000) reported the scratch resistance of PP copolymer filled with HAR wollastonite in comparison to talc and the influence of PP-g MAH (maleic anhydride-grafted polypropylene compatibilizers) and a lubricant on those properties. They found that without a compatibilizer, scratch visibility was similar in talc and HAR wollastonite-filled PP copolymer, but addition of PP-g MAH and addition of PP-g MAH with lubricant decreased the scratch visibility of the HAR wollastonite-filled compound significantly down to the level of the unfilled PP copolymer. Talc-filled PP copolymer showed no effect to that addition.

Similar results were obtained by HPF (HPF – The Mineral Engineers 2009) which compared HAR and LAR wollastonite- and mica-filled PP copolymer. Figure 8 shows microphotographs using polarized light of scratch intersections (GE standard test procedure) on the compound surfaces in comparison revealing that the mineral lays open in the scratched surface.

Also data in PP homopolymer can be found in the literature in comparison to talc (Nolte-Ernsting 2004). Table 3 shows data of wollastonite and talc in polypropylene homopolymer.

**Table 3** Mechanical data of wollastonite and talc in polypropylene homopolymer

| Property | Unit | PP + talc | PP + HAR wollastonite |
|---|---|---|---|
| Filler rate | Wt-% | 20 | 20 |
| Izod-notched impact resistance | $kJ/m^2$ | 4 | 5 |
| Tensile modulus | MPa | 3,200 | 3,500 |
| Heat deflection temperature | °C | 70 | 85 |
| Scratch resistance | | Poor | Good |

Another source examined the influence of different surface treatments on HAR wollastonite in polypropylene (Švab et al. 2005) on the mechanical data at filler loads in the range of 2up to 16 vol.-%. Additionally the interfacial tension and adhesion enthalpy between the surface-treated wollastonites and the PP matrix have been calculated. The different surface treatments were a proprietary surface treatment named ZST-W1, an aminosilane treatment (AST-W2), and an alkyl silane treatment (FST-W3). Yield stresses were higher with ZST and AST surface treatment in comparison to the alkyl silane treatment (FST). This was attributed to a better interfacial adhesion between reinforcing filler and polymer matrix. In the same way, tensile strength at break behaved as well as vice versa elongation at break and notched impact strength.

Another reference examined extensively the dependence of mechanical data of the filler loading of polypropylene with submicronized wollastonite in the range of 5 up to 60% in dry blending of a wollastonite masterbatch with polypropylene during injection molding. All data showed the expected increase of tensile modulus, stress at yield, flexural modulus, and HDT with increasing wollastonite loading as well as decreasing notched and unnotched Charpy impact resistance and melt flow rate (Auinger and Stadlbauerl 2010).

Rheological and impact properties of PP composites with wollastonite depending on the particle size and surface treatment of the mineral were investigated by Shen and Ji (1993). It was found that the MFR (melt flow rate) decreased with decreasing particle size and that the surface treatment has a dramatic effect on the flow properties of the composite.

Stamm (1996) tested the properties of wollastonite in TPO (thermoplastic polyolefin) in comparison to talc and calcite.

Main advantages of wollastonite were found in better scratch resistance, lower shrinkage, lower CLTE (coefficient of linear expansion), higher stiffness, and lower density. Disadvantages were found in gloss, welding lines, and warpage.

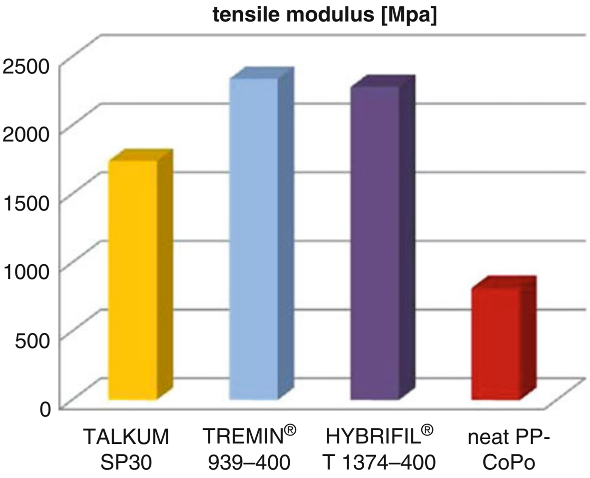
To avoid the inherent problem of warpage with wollastonite due to its acicular structure, HPF found and published an interesting approach to mix wollastonite with other minerals (named HYBRIFIL®) reducing the anisotropic shrinkage in injection mold parts by a factor of 4 in comparison to pure HAR wollastonite resulting in isotropic behavior like the neat polypropylene but reducing the absolute shrinkage by a factor of two in comparison to the neat polymer when filled with 20% of the mineral mixture. The level of stiffness was maintained and impact resistance improved. Table 4 shows the results of the study (HPF – The Mineral Engineers 2012).

**Table 4** Mechanical properties of talc, wollastonite, and a mineral mixture in polypropylene copolymer

| Filler at 20% in PP-CoPo | Tensile test |  |  | Impact resistance Charpy |  | Heat deflection | Shrinkage |  | D shrinkage |
|---|---|---|---|---|---|---|---|---|---|
|  | Yield stress [MPa] | Elongation at yield [%] | Tensile modulus [MPa] | Impact [kJ/m$^2$] | Notched impact [kJ/m$^2$] | HDT B [°C] | Parallel [%] | Perpendicular [%] |  |
| TALKUM SP30 | 18.6 | 4.2 | 1,740 | NB | 26.09 | 115.88 | 0.64 | 0.67 | 0.03 |
| TREMIN® 939-400 | 19.6 | 3.2 | 2,340 | 45.64 | 13.02 | 121.3 | 0.64 | 0.82 | 0.18 |
| HYBRIFIL® T 1374-400 | 19.7 | 3.1 | 2,280 | 60.61 | 17.18 | 123.52 | 0.58 | 0.62 | 0.04 |
| Neat PP-CoPo | 17.3 | 7.6 | 816 | NB | 62.06 | 73.95 | 1.35 | 1.39 | 0.04 |

*NB* no break

**Fig. 9** Tensile modulus of the mineral mixture in comparison to talc and wollastonite



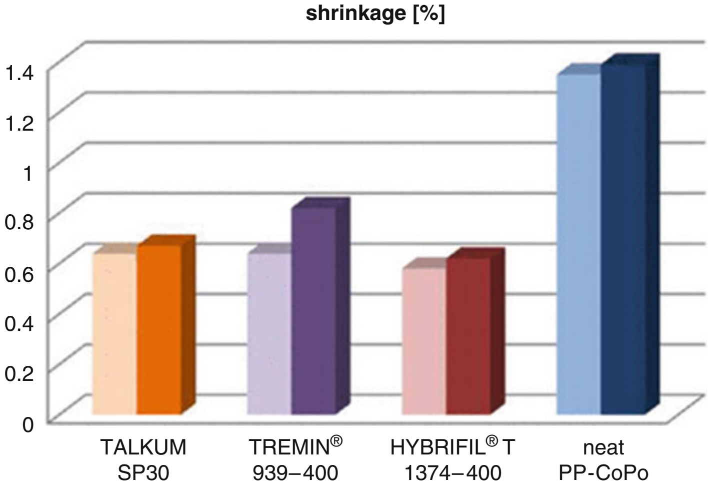


**Fig. 10** Shrinkage (parallel and perpendicular to injection molding direction) and anisotropy of the mineral mixture in comparison to talc and wollastonite

Figures 9 and 10 describe the reduced anisotropy of the mineral mixture at maintained modulus of the mineral mixture in comparison to talc and wollastonite.

## Wollastonite in Polyamide

LAR, aminosilane-coated wollastonite flours have been successfully used for many years as functional fillers for polyamides. With HAR wollastonite, the rigidity of the compound is even higher than with LAR wollastonites. The content of these fillers in

**Table 5** Comparison of mechanical data of LAR and HAR wollastonite-filled polyamide 6 with neat polymer

| | Tensile experiment | | Impact test Izod | Heat deflection temperature | Shrinkage | | |
|---|---|---|---|---|---|---|---|
| High-performance filler | Tensile strength [MPa] | Tensile modulus [MPa] | Impact strength [kJ/m$^2$] | HDT A [°C] | Parall. [%] | Perp. [%] | Delta [%] |
| **LAR wollastonite** | 85 | 4,000 | 65 | 84 | 1.34 | 1.35 | 0.02 |
| **HAR wollastonite** | 93 | 5,290 | 56 | 114 | 0.90 | 1.10 | 0.20 |
| **Neat polyamide** | 86 | 3,210 | 107 | 72 | 1.58 | 1.64 | 0.06 |

the compounds is between 20 and 40 wt%. Polyamides reinforced in this way offer a range of different possibilities for the design of low warpage, rigid moldings. They are used in, e.g., wheel covers, air filter housings, and electrical appliance parts.

Wollastonite-reinforced compounds are characterized by:

- Excellent rigidity
- Enhanced resistance to heat deflection
- Excellent dimensional stability with LAR wollastonites
- High-impact strength
- Outstanding paint adhesion

Data of LAR and HAR wollastonite in polyamide 6 were presented by Zilles (2010). Table 5 shows a comparison of LAR and HAR wollastonite-filled polyamide 6 with the neat polymer.

It is obvious that LAR wollastonite shows reduced and perfect isotropic shrinkage while not being as reinforcing as HAR wollastonite.

Similar work has been done by company R.T. Vanderbilt (R.T. Vanderbilt Company, Inc.). They conclude that in nylon HAR wollastonite and aminosilane-coated HAR wollastonite provided equivalent or improved performance at 30% loadings compared to ultrafine LAR wollastonite at 40% loadings. Of particular value was the improvement in nylon 6 of both stiffness and impact strength, which are usually inversely related.

In the same literature, HAR wollastonite in polypropylene offered similar benefits, providing better impact strength and substantially greater stiffness at a lower loading. Impact strength is further improved by the alkylsilane wetting agent on HAR wollastonite.

Polyamide 6-wollastonite compounds were also subjected to humidity storage, and deterioration of mechanical properties was found. These findings led to proposed modified surface treatments for the mineral (Järvelä 1986).

On a lab scale, also 50% cellulose fiber/50% wollastonite fiber pellets have been developed and were used to produce a 20% cellulose/20% wollastonite/60% nylon 6 hybrid composite. Although the mechanical properties could not compete with glass fiber-reinforced polyamide composites, hybrid composites of cellulose/mineral fiber (wollastonite or glass) make good sense in terms of density evaluations. Further developments in lightweight compounds will show if such concepts make sense and if they are accepted by the market (Jacobson and Caulfield 2003).

## Wollastonite in PUR R-RIM Systems

PUR RIM (polyurethane for reaction injection molding) is a microcellular (integral) hard foam for thin-walled moldings exposed to compressive and flexural stress. The PUR R-RIM-reinforced variants are used when a higher elastic memory is required. With this technique, materials can be produced with a variable reinforcement material content. Although in the early days milled glass fibers were used, they have nearly completely been replaced by wollastonite due to the same mechanical performance plus a better surface finish when using the mineral. Usually the long-wave roughness using milled glass fiber is reduced by a factor of three when replacing them by wollastonite, short-wave roughness even by a factor of 5.

Whenever the amount of parts – being produced in automotive or related applications – is small in comparison to the cost of the steel mold needed for injection molding (e.g., polypropylene), PUR R-RIM is the material preferred over PP, the latter having lower material cost, but the steel mold needed is several times more expensive than the mold made of aluminum for PUR R-RIM parts. Parts like trims, fenders, radiator grills, rear valances, car wings, back doors, door sills, and spoilers are produced from this material as well as bonnets and housings for agricultural tractors, auto hoists, and similar machines.

HAR wollastonite in PUR R-RIM provides high tensile strength, high scratch resistance, and a very good ability for high-gloss varnishing.

HPF published data on HAR surface-modified wollastonite in a PUR R-RIM system (HPF – The Mineral Engineers 2010). Table 6 summarizes data important for that application.

## Wollastonite in Epoxy Systems

Epoxy resins play an important role as raw material for electrical and electronic engineering due to the good adhesive strength and the heat and chemical resistance, as well as the excellent electrical properties. In electrical applications, epoxy resin molding materials are used for coating systems and as lamination resins for connections as well as for the production of circuit boards. Epoxy resins are used in electrical engineering for the construction of transducer, insulator devices, and

**Table 6** Mechanical data of surface-modified HAR wollastonite in a PUR R-RIM system at 17% and 22% filler load

| Surface-treated wollastonite in PUR RIM % | 17 | 22 |
|---|---|---|
| Fiber orientation | Longitudinal | Longitudinal |
| Sample specimen mm | 300 × 200 × 3 | |
| Density g/cm$^3$ (DIN 53420) | ≥1.23 | ≥1.25 |
| Hardness shore D (DIN 53505) | ≥68 | ≥70 |
| Flexural modulus MPa (ASTM-D 790) | ≥1,500 | ≥1,900 |
| Tensile strength MPa (DIN 53504) | ≥35 | ≥35 |
| Elongation at break % (DIN 53504) | ≥170 | ≥170 |
| Dynstat RT kJ/m$^2$ | No break | No break |
| Dynstat −25 °C | ≥10 | ≥10 |

dry-type power transformers. The required mechanical, thermal, and electrical characteristics of the epoxy resin are affected significantly by the functional filler chosen which can be based on silica, fused silica, wollastonite, or mica. For high demands in outdoor applications (long-term humidity/water resistance), fillers with surface treatment typically are used.

In comparison to other fillers in mid-voltage insulation applications, wollastonite is used due to its reinforcing properties when wall thickness in technical parts shall be reduced or resistance toward cracking – i.e., better flexural modulus – should be improved. The coefficient of linear thermal expansion is comparably low ($7 \times 10^{-6}$ 1/K) – right in between quartz ($14 \times 10^{-6}$ 1/K) and fused silica ($0.5 \times 10^{-6}$ 1/K).

Drawback is the relatively high surface area of the LAR as well as HAR wollastonite due to their acicular structure in comparison with other minerals used in those applications since those are nodular, leading to a lower viscosity at the same filler volume load or being able to realize higher filler loadings. That is the reason why wollastonite typically is used in mixtures with other fillers.

Patent US 5872163 (Grebenstein and Hollstein 1999) describes an epoxy resin with a mixture of calcite and 40–60% by weight of wollastonite to improve thermal shock resistance of ignition coils in comparison to other fillers in EP systems. The wollastonite in that mixture is described as needle shaped although the grade used in the recipe examples is de facto a LAR wollastonite.

Another patent describes a minimum 50% of wollastonite in a filler mixture in epoxy resin for the same purpose (Beisele 1999).

Viscosities and DMTA data of nanosilica, HAR wollastonite (obviously by accident mistaken as a nanofiller), and POSS (polyhedral oligomeric silsesquioxanes) were described. Tg of the mixtures depended significantly on the mixing conditions (Spero and Merchant 2006).

Ongoing investigations (HPF – The Mineral Engineers 2013) show that wollastonite used as an additive to enhance mechanical strength is a feasible option in mid-voltage insulation products. Wollastonite and silica flour (the standard filler for that application) were used and compared by means of mechanical and electrical properties. Tables 7 and 8 show the results.

The data reveal that an addition of 20% (by weight) of silane-treated wollastonite to 80% silane-treated quartz flour improves mechanical behavior (higher modulus, higher elongation at break, higher tensile strength at break, and better impact resistance) in comparison to pure quartz flours. Using only LAR wollastonite leads to lower filler rates and (when trying to achieve higher filler rates) viscosities that are not processible. Also electrical data after accelerated water storage was unacceptably high for pure LAR wollastonite. The 80/20 mixture of quartz and wollastonite improved mechanical properties without sacrificing electrical insulation properties.

For tribological applications, HAR and LAR wollastonites have been tested in comparison to short carbon fibers (SCF) in an epoxy composite (Xian and Walter 2006). Mechanical properties were measured as well as wear resistance tests were performed. Flexural modulus increased with concentration of the fillers with HAR wollastonite showing the highest increase. Flexural strength was slightly deteriorated by HAR wollastonite and SCF, whereas an increase was detected using LAR wollastonite at a load of 10%. A similar trend was found for elongation at break and unnotched Charpy impact resistance. Specific wear rate under sliding conditions showed best results with LAR wollastonite. The coefficient of friction was reduced

**Table 7** Mechanical data of quartz and LAR wollastonite-filled EP compounds for mid-voltage insulation

| Filler type | Wt-% filler in composite | Vol-% filler in composite | E-modulus [MPa] | Tensile stress at break [MPa] | Elongation at break [%] | Impact resistance (Charpy) [kJ/m$^2$] |
|---|---|---|---|---|---|---|
| **Quartz flour silane treated (16 µm = d50)** | 63.40 | 43.84 | 11,370 | 133 | 1.30 | 11.74 |
| **Quartz flour (16 µm = d50)** | 62.67 | 43.07 | 11,050 | 125 | 1.24 | 11.33 |
| **LAR wollastonite silane treated (12 µm = d50)** | 61.00 | 39.59 | 12,420 | 137 | 1.27 | 14.36 |
| **80% quartz flour silane treated (16 µm = d50)/20% LAR wollastonite silane treated (12 µm = d50)** | 64.50 | 44.65 | 11,920 | 145 | 1.39 | 12.45 |

**Table 8** Electrical data of quartz and LAR wollastonite-filled EP compounds for mid-voltage insulation

| | Virgin compound | | Compound after 100 days of accelerated water storage | |
|---|---|---|---|---|
| Filler type | Loss factor tan Δ | Permittivity $\varepsilon_r$ | Loss factor tan Δ | Permittivity $\varepsilon_r$ |
| **Quartz flour silane treated (16 μm = d50)** | 0.024 | 4.08 | 0.051 | 4.57 |
| **Quartz flour (16 μm = d50)** | 0.022 | 4.04 | 0.434 | 11.66 |
| **LAR wollastonite silane treated (12 μm = d50)** | 0.013 | 4.65 | 0.528 | 21.32 |
| **80% quartz flour silane treated (16 μm = d50)/20% LAR wollastonite silane treated (12 μm = d50)** | 0.017 | 4.13 | 0.120 | 5.97 |

by all fillers in comparison to the neat epoxy, but SCF could reduce it better than wollastonite. This was attributed to a transfer of different structured films from the composite to the steel counterpart, depending strongly on the kind of filler used. Finally it was concluded that the effect of improving the mechanical properties of the composite by LAR wollastonite is due to the low stress concentration together with a crack pinning effect of the particles.

## Wollastonite in Phenolic Resins

Brake pads and linings must be able to withstand the application of emergency braking at 200 kmph as well as mountain descents during which they reach a temperature in excess of 500 °C. The pad/lining brakes the vehicle with the disk or drum by means of friction. Only through careful coordination of the individual components' considerable wear and poor braking can be prevented. In recent years, the development of brake pads/brake linings has led to the use of environmentally friendly raw materials as a substitute for asbestos, which is critical to health.

### Fundamentally, Friction Pads/Linings Fulfill Three Tasks

#### Safety

Great importance is attributed to the good running-in properties of friction linings and constancy of the friction coefficient throughout the entire braking process, with hot or cold brakes, in the wet and cold, and with salt, grit, and dirt, or when decelerating from a high speed. The components used must be corrosion resistant, must have high strength, and must not be combustible.

### Convenience

Further requirements of modern friction linings are a sensitive reaction of the brake even with low-force application, a uniform braking progression, a very low-noise emission, and a reduced environmental load due to abrasion and odor emission.

### Economy

Neither the friction pad nor the brake disk should be subject to rapid wear. In addition low weight and a good cost/benefit ratio are required.

Already in 1984 the Borg-Warner company applied for a patent (Albertson and Nibert 1984) on a “pad-type friction material for brake and clutch linings containing an inorganic fibrous material, a binder, zinc oxide and molybdenum sulfide.” The wollastonite was used as a fibrous material replacing the asbestos used in those applications till that date. “In the past the fibrous material has invariably been chrysotile asbestos. Asbestos fiber imparts strength to the friction material and, at the same time, has a beneficial effect on friction properties. Moreover, in the past, it has been relatively cheap.

However, asbestos deposits throughout the world are rapidly being depleted, with the result that its cost is increasing. Moreover, the continued use of asbestos has recently come under a cloud because of the realization that it presents a serious cancer hazard for those who work with it. There has been an increasing concern about such hazard with the result that the expense of health precautions now required for the safe handling of asbestos has become a significant burden. Accordingly, it has become desirable to eliminate asbestos from frictional material formulations and to find a replacement.” The preferred fibrous material replacement was wollastonite or a mixture of wollastonite and glass fibers.

The mode of operation of the HAR wollastonite in comparison to the raw material magnesium carbonate and mineral fiber used as a rule in brake linings was investigated by HPF (HPF – The Mineral Engineers 2008) for passenger car and truck brake pads as published in detail.

The investigations were performed on a standard brake pad recipe. In the four series of tests (Table 7), the basic raw materials magnesium carbonate and the mineral fibers were successively replaced by the HAR wollastonite.

The influence of HAR wollastonite in friction linings was assessed in accordance with the following parameters: bulk volume after 4 min-mixing time, green strength, shear strength, friction values in accordance with the AK master test program (brake-program simulation test), and wear of pad/disk (Table 9).

After mixing for 4 min in a Papenmeier mixer, the materials were compressed at 300 daN/cm$^2$ and cured at finally 155 °C with a curing program lasting for 390 s in total.

**Table 9** Test series

| Raw material | Recipe 1 | Recipe 2 | Recipe 3 | Recipe 4 |
|---|---|---|---|---|
| Organic fibers | 2 | 2 | 2 | 2 |
| Phenolic resin | 6.5 | 6.5 | 6.5 | 6.5 |
| Graphite/coke | 18 | 18 | 18 | 18 |
| **Mineral fiber**[a] | **10** | **5** | **0** | **0** |
| **Magnesium carbonate**[b] | **5** | **5** | **5** | **0** |
| **HAR wollastonite** | **0** | **5** | **10** | **15** |
| Fillers 5 | 18.5 | 18.5 | 18.5 | 18.5 |
| Abrasive substances | 6 | 6 | 6 | 6 |
| Inorganic lubricants | 9 | 9 | 9 | 9 |
| Metals | 25 | 25 | 25 | 25 |
| **Total** | **100** | **100** | **100** | **100** |

[a] Mineral fiber with a fiber length from 125 ± 25 μm

[b] Magnesium carbonate with a grain size of 6% > 40 μm

## Results

### Physical Results of the Mixing Processes

A good green strength (pre-compression strength) results in better handling of the compressed bodies of the friction lining. These can be conveyed dependably with the values determined from the prepress to the hot press.

A higher green strength was achieved in the mixtures with an increasing proportion of HAR wollastonite. The values of the mixtures filled with HAR wollastonite were clearly higher than those filled with mineral fibers. This was attributed to the needle structure of the wollastonite. The HAR wollastonite needles obviously formed a braid with a higher degree of stability.

Figure 11 shows that there is no significant difference in bulk volume between the various recipes.

### Physical Results of the Pads

The compressed disk brake pads were formed completely after compression and grinding, without any flaws. The entire surface of the pads was thereupon sheared off in the testing machine by means of a shearing cutter. The shear strength values obtained and, with inclusion of the pad surface, the specific shear strengths result from this.

Figure 12 shows that the shear strengths of the mixtures with HAR wollastonite were greater than those of the pads containing mineral fibers. However, a decrease in shear strengths with an increasing proportion of HAR wollastonite can be detected in this case. The strength advantage of HAR wollastonite in comparison to mineral fibers is particularly clear when recipes 1 and 3 with the same proportions of magnesium carbonate are compared directly.

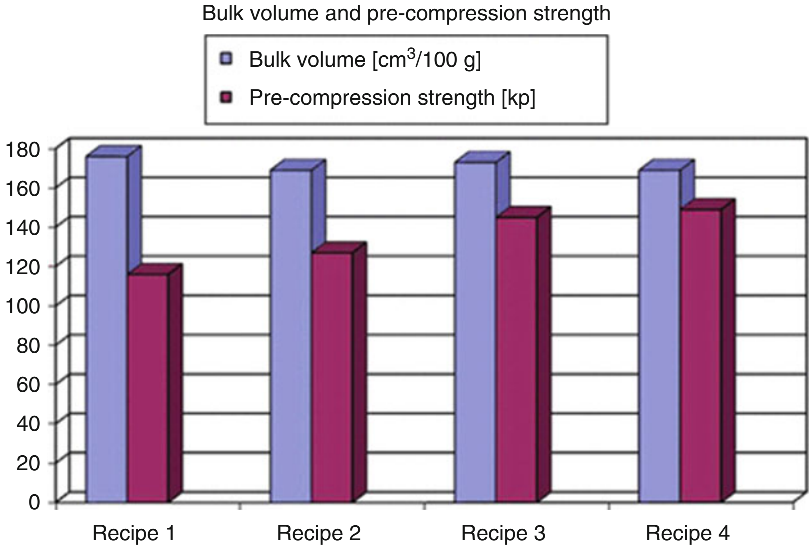


**Fig. 11** Bulk volume and pre-compression strength of the various recipes

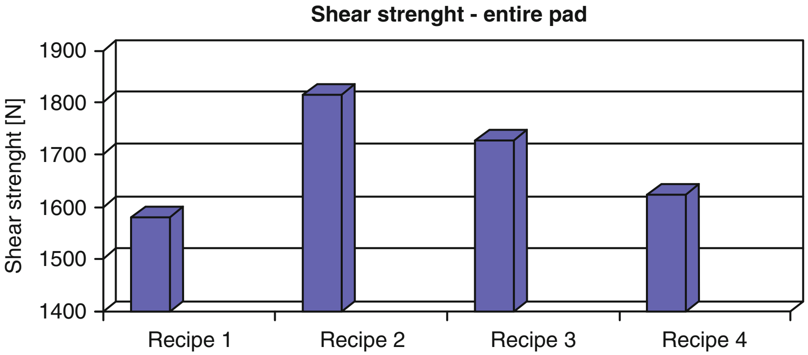


**Fig. 12** Shear strength of the recipes investigated

## Passenger Car Friction Results

The test was performed in accordance with the internationally standardized AK master test program SAE J 2522.

All friction values achieved were at the level of friction linings that are in general use in automobiles that are currently utilized. If the individual test sequences are considered in more detail, it is conspicuous that the friction values of the pads with higher proportions of HAR wollastonite have a slightly lower friction value at the beginning of the test. This assertion is put into perspective again after the fading series at temperatures of 500–600 °C. See Fig. 13.

## Pad Wear

The pad wear was at a similar level for all recipes. However, the pad wear for the recipe with a 15% (recipe 4) proportion of HAR wollastonite tends to be somewhat higher than the other pads.

The results obtained are shown in Fig. 14.

## Disk Wear

In Fig. 15 it shows that all recipes have similar disk wear and are well in range for use in passenger car brake pads.

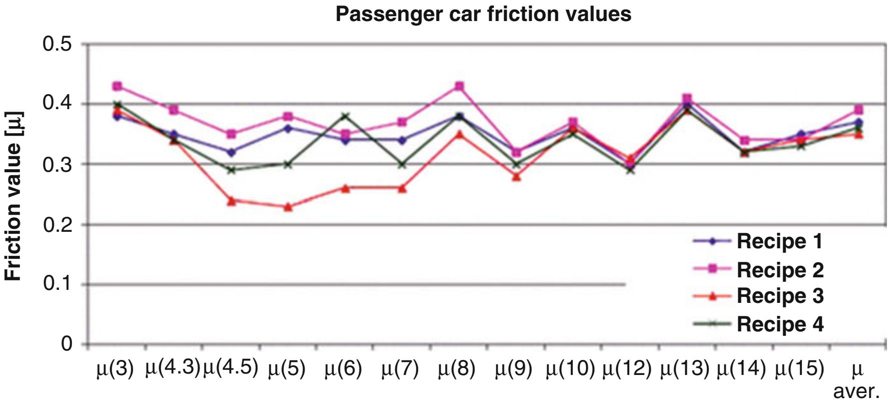


**Fig. 13** Passenger car friction values of the recipes investigated

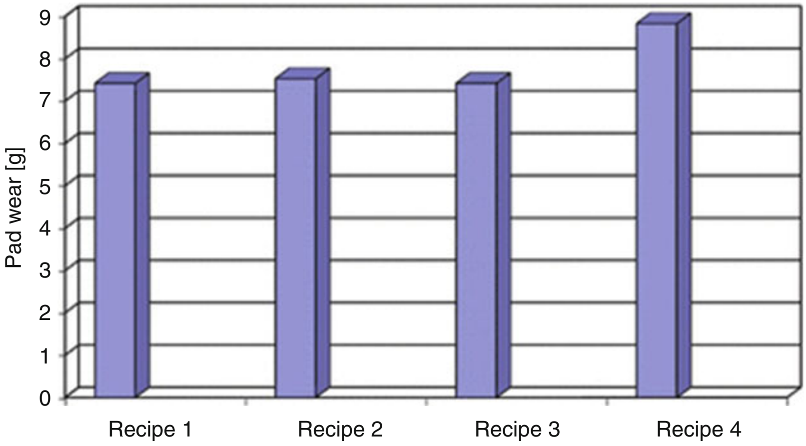
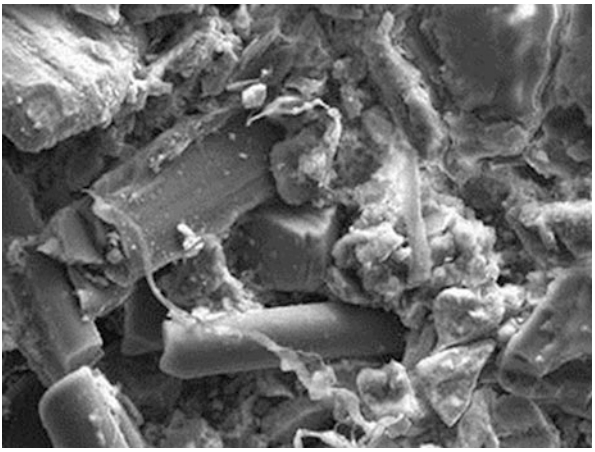


**Fig. 14** Pad wear in g of the recipes investigated

**Fig. 15** Disk wear in g of the recipes investigated

**Fig. 16** SEM image of a brake pad not subjected to a load; scale: 1:1,000



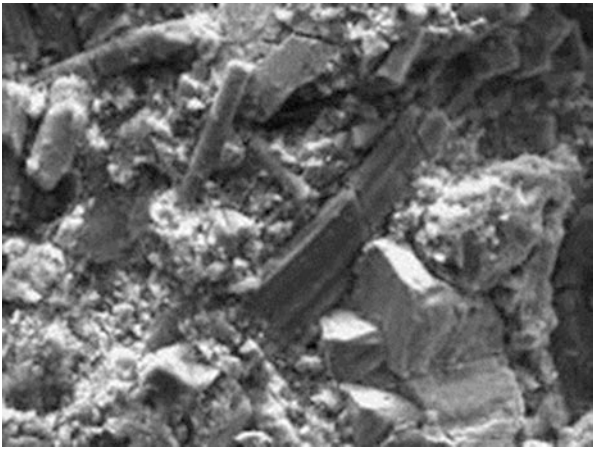
## Incorporation of HAR Wollastonite in Comparison to Mineral Fiber

Scanning electron microscope images (SEM images) of the brake pads subjected and not subjected to a load show the incorporation of the fibers into the brake pad recipes. The mineral fibers and the HAR wollastonite needles show the same incorporation behavior.

These SEM images from recipe 2 are shown in Figs. 16 and 17.

The incorporation of HAR wollastonite fiber into the phenolic resin can be improved even further through the use of silane-treated HAR wollastonite. The surface-modified HAR wollastonite types have higher friction values at the beginning of the test. A smaller spread of the friction value progression is achieved by the surface treatment. The friction values of silane-treated HAR wollastonite are shown in Fig. 18.

**Fig. 17** SEM image of a brake pad subjected to a load; scale 1:1,000



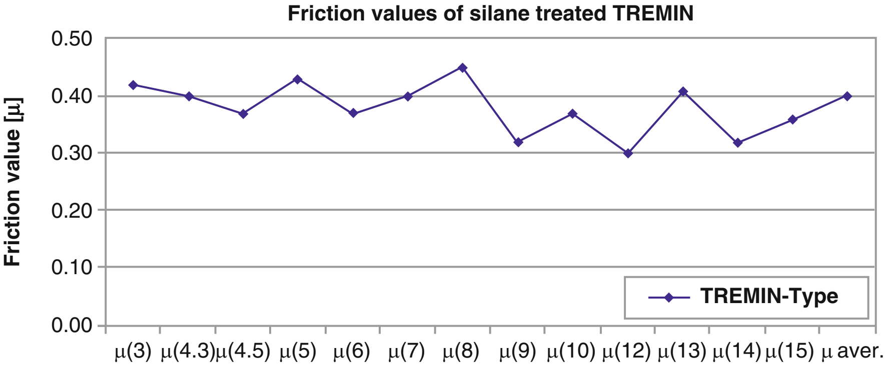


**Fig. 18** Friction values of a silane-treated HAR wollastonite

## Wollastonite in Fluoroelastomers

Fluoroelastomers are high-specialized materials for the most demanding applications in engine and mechanical engineering as well as in plant construction for chemistry. Only with fluoroelastomer seal rings, high-temperature applications and very sophisticated chemical resistances are possible.

LAR, silane-coated wollastonite flours are successfully used for many years as functional fillers in fluoroelastomers in order to adjust the hardness. Apart from the good reinforcement in fluoroelastomers, LAR wollastonite (due to its bright and neutral color) provides also the advantage of colored bright mixtures.

These optimized fluoroelastomers are ideally suited for the applications mentioned above under special conditions, e.g., high mechanical load and high temperatures.

**Table 10** Recipe and mechanical data of carbon black in comparison to LAR wollastonite in fluoroelastomer after curing and after aging

| Recipe | | A | B |
|---|---|---|---|
| Fluoroelastomer FLUOREL FC 2176 | | 100 | 100 |
| Carbon black MT900 | [phr] | 30 | |
| LAR wollastonite TREMIN 283–600 EST | [phr] | | 45 |
| Original properties after vulcanization (8 min, 176 °C) and post-cure (16 h, 230 °C) | | | |
| Tensile strength | [N/mm$^2$] | 14.5 | 14.2 |
| Elongation | [%] | 234 | 200 |
| 100% modulus | [N/mm$^2$] | 5.1 | 7.1 |
| Hardness | [Shore A] | 71 | 70 |
| Tear | [N/mm] | 23.7 | 22 |
| Original properties after heat aging, vulcanization (8 min, 176 °C), and post-cure (16 h, 230 °C) | | | |
| Tensile strength | [N/mm$^2$] | 10.3 | 9.7 |
| Elongation | [%] | 278 | 238 |
| 100% modulus | [N/mm$^2$] | 3.5 | 5 |
| Hardness | [Shore A] | 67 | 70 |
| Weight loss | [%] | −3.6 | −4.5 |
| Compression set (2,53 mm O-rings, 70 h, 200 °C) | | | |
| After vulcanization | [%] | 47 | 47 |
| Post-cured | [%] | 18 | 19 |

The following table demonstrates the good mechanical properties of fluoroelastomers with LAR wollastonite (coated with epoxysilane) in comparison to the usage of the common filler carbon black in the same fluoroelastomer (HPF – The Mineral Engineers 2011; Table 10).

Fluoroelastomers filled with LAR wollastonite can be characterized by the following properties:

- Outstanding dimensional stability
- Well-dyeable characteristics
- Large tear resistance
- Large tensile strength

A very elaborate work shows the behavior of different mineral filler types in fluoroelastomers (and EPDM) (Robinson and Sheridan 2002). Wollastonites have been compared to hard clay, calcite, carbon black, and two talc morphologies. Surface-treated wollastonite (treated with epoxysilane) showed the highest modulus, tensile strength, and lowest elongation. After immersion into different fuel types and methanol, the compounds filled with platy talc, carbon black, and surface-treated wollastonite showed best retention of those properties. The HAR wollastonite used showed pronounced anisotropic behavior in terms of modulus.

Hot tear strength was also remarkably increased by wollastonite leading to better mold release properties of the compound.

A patent (Anderson and Santosa 1985) describes the use of wollastonite in a wet friction material used for clutches and brakes which changes the ratio between dynamic and static coefficient of friction. Unexpectedly the use of significant amounts of wollastonite made the static and dynamic coefficient of friction more equal, leading to a smoother and quieter engagement of the brake system.

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# Feldspar and Syenites

# 12

Joerg Ulrich Zilles

## Contents

## Abstract

Feldspars are a group of tectosilicate minerals being the most important ones for rock formation of the Earth's crust having a share of 51% on it.

Syenite is a group of plutonic (or intrusive) rocks being rich on feldspars – nepheline syenite is the most important member of that group. In ceramics and glass, it is used like feldspar as a source of alumina and as a flux.

In polymer-bond systems, the feldspars and nepheline syenite are common as fillers in paints and lacquers as well as in pigment pastes. Refractive indices are in the region of 1.50–1.55 with little to no birefringence, so they match refractive indices of several resins very well to form highly transparent films with high abrasion and scratch resistance.

The use in thermoplastics is – due to their high Mohs hardness – limited to few applications like antiblocking in polyolefin films and lately also as a filler for

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dental composites. Apart from their use in ceramics and glass making, the most common use in polymer or resin bond systems is in paints and coatings where they provide excellent chalking and weathering resistance in exterior paints, high UV transparency in radiation-curable films (parquet coatings), and scratch resistance as well as high transparency for visible light in resins matching their refractive index due to their low birefringence.

In thermoplastics feldspars are used for antiblocking. Polyolefin films (mostly blown or cast polyethylene (LLDPE) and polypropylene (PP) – but also PVC and to some extent PET) tend to adhere to each other due to strong van der Waals interaction or electrostatic charges when being in close contact. To avoid the adherence of layers due to a close contact, particulate matter is introduced into the film in a highly diluted concentration. By that measure the contact area of film layers is minimized and adherence suppressed. Due to their optical properties, feldspars are preferably used in this respect.

Another application is light and thermal management in agricultural films. Greenhouses made from polyolefin films (LDPE) offer cost-effective solutions for intensified agriculture. Transmission and reflection of the solar spectrum are important key parameters for the growth of plants and the heat management in the greenhouse. The biologically active UV/VIS radiation for plant growth should pass the film as completely as possible, but heat should be reflected during the day to avoid overheating during the day but should be kept inside during cold nights to avoid cooling during the night. Feldspars are used to make those LDPE films suitable for thermal management. Advantages are early and high-quality crops, protection against cold/frost, and higher yields.

Apart from their use in veneers, highly pure feldspars become more and more interesting to dental applications like dental fillings, inlays, or artificial teeth in polymer compounds. Besides that these applications do not represent mass markets, they use similar principles in optical appearance and transparency and color like the applications mentioned before.

**Keywords**

Feldspar • Nepheline syenite • Film • Antiblocking • Greenhouse • Greenhouse thermal management • Dental compounds

## Definitions

Feldspars are a group of tectosilicate rock-forming minerals.

The syenites are a group of intrusive rocks rich in feldspar minerals, and, unlike granites, they have little or no quartz. The most important syenite is nepheline syenite.

PSD – particle-size distribution

## Introduction

Feldspars are a group of minerals being the most important ones for rock formation of the Earth's crust having a share of 51% on it. They are tectosilicates (3D network structure), occurring in mineral varieties containing different alkali and alkaline earth elements. The most common members are sodium, potassium, and calcium feldspars.

Syenite is a group of plutonic (or intrusive) rocks being rich on feldspars. In comparison to granites, they contain less/no quartz. Commercially – apart from their use as dimensional stone – nepheline syenite is the most important member of that group used in ceramics, glass, and polymers. In ceramics and glass, it is used like feldspar as a source of alumina and as a flux.

In polymer-bond systems, the feldspars and nepheline syenites are common as fillers in paints and lacquers as well as in pigment pastes. Refractive indices are in the region of 1.50–1.55 with little to no birefringence, so they match refractive indices of several resins very well to form highly transparent films with high abrasion and scratch resistance.

Mohs hardness of feldspars and nepheline syenite is in the region of 6–6.5, so they are fairly abrasive, and the use in thermoplastics is limited to few applications like antiblocking in polyolefin films and lately also as a filler for dental composites.

The major difference between the feldspars and feldspathoids like nepheline syenite is the extent of free crystalline silica. Since the genesis of feldspathoids (foids) took place in the deficit of silica, they stoichiometrically contain less silica and no free crystalline silica (quartz).

## Feldspar Mineralogy

The feldspar group is tectosilicates of the aluminosilicate type containing alkali and alkaline earth elements (some also ammonia cations as pseudo-alkali cation) in various proportions. The pure single-alkali/alkaline earth cation forms are microcline and orthoclase ($KAlSi_3O_8$, both with the same chemical formula but different elementary cell (crystal structure) microcline triclinic pinacoidal and orthoclase monoclinic prismatic), albite ($NaAlSi_2O_8$), and anorthite ($CaAl_2Si_2O_8$).

The theoretical end-member composition of the feldspar groups is shown in Table 1.

Due to the fact that the species are miscible (according to the phase diagram), commercial feldspars are mixtures of the pure mineralogical species, and the composition depends on the genetic conditions of the deposit they are sourced from. Beneficiation can be as easy as mining and crushing up to complex processes like flotation or electrostatic separation.

**Table 1** Theoretical end-member composition of the feldspar groups and nepheline (Carr 1994)

| Feldspar | $K_2O$ | $Na_2O$ | CaO | $Al_2O_3$ | $SiO_2$ |
|---|---|---|---|---|---|
| **Microcline** | 16.9 | – | – | 18.4 | 64.7 |
| **Orthoclase** | 16.9 | – | – | 18.4 | 64.7 |
| **Albite** | – | 11.8 | – | 19.4 | 68.8 |
| **Anorthite** | – | – | 20.1 | 36.6 | 43.3 |
| **Nepheline** | – | 21.8 | – | 25.9 | 42.3 |

**Table 2** Typical data of the pure mineral species (Modified from Robinson (2003))

| Mineral | Stoichiometric formula | Density [kg/L] | Mohs hardness | Refractive indices | Birefringence |
|---|---|---|---|---|---|
| **Albite** | $NaAlSi_2O_8$ | 2.62 | 7 | 1.52–1.54 | 0.010 |
| **Anorthite** | $CaAl_2Si_2O_8$ | 2.73 | 6 | 1.57–1.59 | 0.011 |
| **Microcline** | $KAlSi_3O_8$ | 2.56 | 6 | 1.51–1.53 | 0.007 |
| **Nepheline** | $(Na,K)AlSiO_4$ | 2.59 | 6 | 1.53–1.55 | 0.004 |
| **Orthoclase** | $KAlSi_3O_8$ | 2.56 | 6 | 1.52 | 0.005 |

Nepheline is also a mineral of the tectosilicates group with the stoichiometric formula $(Na,K)AlSiO_4$. Nepheline syenite is a rock formed from nepheline and feldspars. Other than typical feldspars, it is formed with silica deficit and so no free crystalline silica occurs in the rock. Typically, the beneficiation consists of crushing and density and magnetic separation.

A few typical data of the pure mineral species are listed in Table 2.

Natural feldspars and nepheline syenites are highly variable in color. The purest ones typically are white and highly transparent and their streak color is white. Most common impurities deteriorating the color are iron oxides tinting them grayish to brownish.

## Availability

Due to the fact that feldspars and feldspathoids form approx. 60% of the Earth's crust, they are readily available on each and every continent in abundance. Major quantities are sourced for glass and ceramic production. Special grades of feldspars are used for ceramic veneers in dentistry.

World production of feldspars and nepheline syenites accounts for 20 million tons per year (2011); biggest producers are Turkey, Italy, and China (USGS 2012).

Nepheline syenite is not that common – so suitable qualities for glass, ceramics, and filler applications are produced in Canada (580Ttpa), Norway (350Ttpa), and China (50Ttpa) (USGS 2010) apart from syenites used as aggregates for road construction and similar uses.

## Properties

Feldspars and nepheline syenite are weathering and chemical resistant against weak acids. Particle shape typically is angular/nodular due to the fracture habit (uneven – flat surfaces, fractured in an uneven pattern) which results in low surface area and as a consequence low oil absorption of the milled materials. Particle sizes from rocks down to few hundreds of nanometers commercially are available. pH typically is in the range of 6–9 for feldspars and at 9–10 for nepheline syenites.

The following Figs. 1, 2, 3, and 4 show typical particle shapes of milled feldspar and nepheline syenite products. Surfaces and structures of the grains in a feldspar flour depend on the chemical/mineralogical composition of the mineral and are a function of the genesis of the deposit.

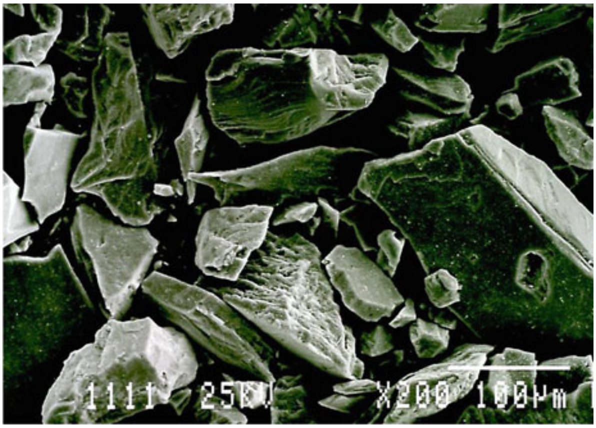


**Fig. 1** SEM of feldspar flour: 44% orthoclase, 45% albite, 4% anorthite, and 7% quartz

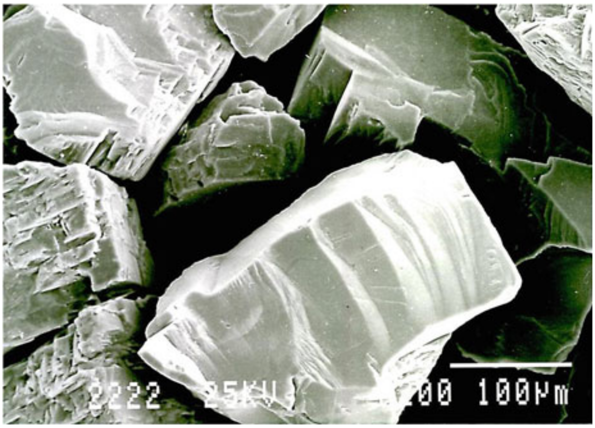


**Fig. 2** SEM of feldspar flour: 85% albite, 3% orthoclase, 4% anorthite, and 8% quartz

**Fig. 3** SEM of feldspar flour: 87% orthoclase, 7% albite, 4% kaolinite, and 2% quartz

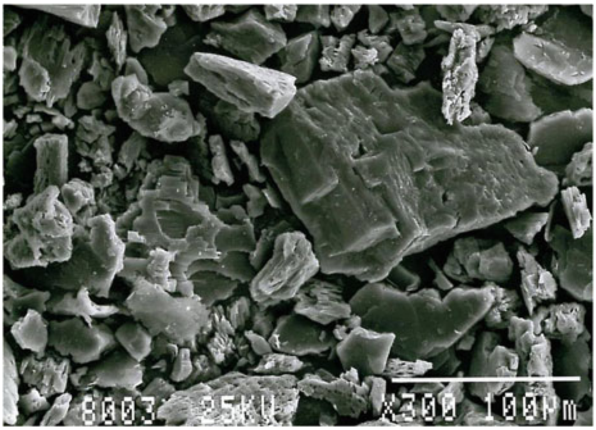
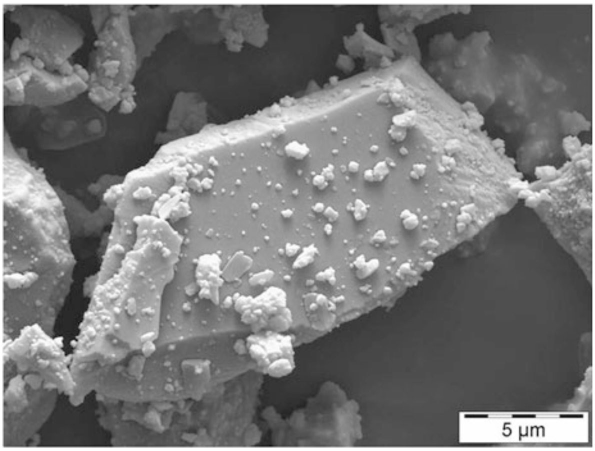


**Fig. 4** SEM of nepheline syenite flour: 25% nepheline, 73% feldspars, and 2% analcime and natrolite



## Applications

Although the use of feldspar in PVC and other thermoplasts is reported in the literature, its use in thermoplastics is limited due to its comparably high Mohs hardness of 6–7. Especially high filler loadings of coarser PSD feldspars and nepheline syenite are prohibitive due to their abrasive behavior.

## Paints and Coatings

Apart from their use in ceramics and glass making, the most common use in polymer or resin bond systems is in paints and coatings where they provide excellent chalking and weathering resistance in exterior paints, high UV transparency in radiation-curable films (parquet coatings), and scratch resistance as well as high transparency for visible light in resins matching their refractive index due to their low birefringence. The low resin demand due to low oil absorption also is a reason for the use in emulsion paints and powder coatings. Due to their matching refractive indices, their tinting strength in resins is low being the perfect "diluting agent" for pigments in pigment pastes.

## Antiblocking

Polyolefin films (mostly blown or cast polyethylene (LLDPE) and polypropylene (PP) – but also PVC and to some extent PET) tend to adhere to each other due to strong van der Waals interaction and/or electrostatic charges when being in close contact. The closer the distance between two layers, the stronger the adherence which occurs, typically when the material is wound up after film production. Once in close contact, it is nearly impossible to move the layers relatively to each other due to the resulting high coefficient of friction. The higher the temperature, pressure, and contact/processing time, the higher the tendency to stick to each other – to block.

To avoid the adherence of layers due to a close contact, particulate matter is introduced into the film in a highly diluted concentration. By this measure the contact area of film layers is minimized and adhesion suppressed. Typically, this is done by using concentrations up to 50 wt% of particulate matter in masterbatches which are added during film processing. Final concentration of the antiblocking agent in the film material typically is in the range of 0.1% up to 1.0% depending on the application. Minerals used for this application should have little to no impact on the mechanical properties of the film; must not deteriorate transparency, haze, color, and gloss of the film; and must be compatible with the film processing process. Several minerals are used for this purpose: talc, calcined kaolin, cristobalite, precipitated silica, diatomaceous earth, mica, calcium carbonates, calcium sulfate (anhydrite), magnesium carbonate, and magnesium sulfate.

Particle sizes chosen are in the range of a fraction of the film thickness with special care taken to eliminate any oversize in order to avoid blocking of nozzles or partial film rupture during processing. Additionally, minerals with matching refractive index do not deteriorate the optical properties (transparency, haze) of the films. Special care must be taken since some potential antiblock minerals (like talc) act as nucleating agents, changing completely mechanical and optical properties of the film even in small quantities. Also the absence of impurities (like iron oxides) promoting the oxidization of the polymer has to be taken into account. Finally, the hardness in combination with particle size of the mineral governs the wear at least on the extruders used to produce the masterbatch.

A comparison of different, common mineral products for antiblocking has been published by HPF (HPF The Minerals Engineers 2013). Table 3 shows the properties of mineral flours used in comparison.

Films have been produced by blow film extrusion using a 3% polyethylene mineral masterbatch (MFI 2.0 g/10 min) – feldspar additionally in a 60%

**Table 3** Physical properties of mineral flours used for antiblocking in polyethylene

| Mineral | Anhydrite | Anhydrite | Cristobalite | Feldspar | Nepheline syenite |
|---|---|---|---|---|---|
| **d 50** [μm] | 6 | 3 | 5 | 3 | 7.6 |
| **Hardness** (Mohs) | 3.5 | 3.5 | 6.5 | 6 | 6 |
| **Density** [g/cm$^3$] | 3.0 | 3.0 | 2.35 | 2.6 | 2.6 |
| **Refractive index** | 1.57 | 1.57 | 1.48 | 1.52 | 1.53 |
| **Brightness (Y/D65)** | $Y = 85$ | $Y = 89$ | $Y = 97$ | $Y > 90$ | $Y > 90$ |

**Table 4** Coefficients of frictions of polyethylene films with different antiblocking additives

| Film | Inside-inside | Outside-outside | Inside-stainless steel | Outside-stainless steel |
|---|---|---|---|---|
| Neat PE film | 0.48 | 0.42 | 0.45 | 0.40 |
| Anhydrite d50 = 6 μm | 0.46 | 0.45 | 0.32 | 0.34 |
| Anhydrite d50 = 3 μm | 0.43 | 0.37 | 0.22 | 0.24 |
| Nepheline syenite | 0.45 | 0.39 | 0.29 | 0.30 |
| Cristobalite | 0.46 | 0.43 | 0.27 | 0.31 |
| Feldspar | 0.38 | 0.38 | 0.28 | 0.30 |
| Feldspar from 60% masterbatch | 0.41 | 0.37 | 0.30 | 0.32 |

**Table 5** Optical properties of polyethylene films with different antiblocking additives

| Film | Gloss 60° | Haze | Transparency |
|---|---|---|---|
| Neat PE film | 69 | 12.7 | 92.1 |
| Anhydrite d50 = 6 μm | 71 | 16.2 | 91.7 |
| Anhydrite d50 = 3 μm | 72 | 16.6 | 92.2 |
| Nepheline syenite | 71 | 15.9 | 92.1 |
| Cristobalite | 73 | 14.8 | 92.8 |
| Feldspar | 71 | 13.3 | 91.8 |
| Feldspar from 60% masterbatch | 67 | 13.5 | 91.9 |

masterbatch. Final concentration of the mineral in the final film was 3,000 ppm; film thickness was 50 μm and MFI (190 °C/2.16 kg) of 0.75 g/10 min.

By dynamic friction coefficient measurement according to DIN EN ISO 8295/ ASTM D1894, differences in antiblocking behavior were recorded. The lower the friction coefficient, the less blocking occurs, i.e., the better the antiblocking performance. Table 4 summarizes the data.

Optical properties were determined by means of haze/transparency measurement according to ASTM D1003 and gloss according to DIN 67530/ASTM D2457. Table 5 shows the results (Table 6 shows UV/VIS transmission data for different PE films with/withoud additives).

**Table 6** Transmissions for different wavelengths of the UV/VIS spectrum of light for greenhouse films

| | UV/VIS transmission at wavelength | | | | |
|---|---|---|---|---|---|
| Film | 250 nm | 400 nm | 600 nm | 700 nm | 800 nm |
| Neat PE film | 68.0 | 79.1 | 84.2 | 85.5 | 86.6 |
| PE film with 10% nepheline syenite | 42.4 | 51.6 | 56.2 | 57.4 | 58.5 |
| PE film with 10% feldspar | 40.7 | 52.6 | 58.9 | 60.6 | 62.3 |

- Anhydrite showed excellent antiblocking, but optical properties (esp. haze) are comparably poor.
- Cristobalite and nepheline syenite showed comparable, good results.
- Feldspar showed best antiblocking and optical properties.

## Light and Thermal Management in Agricultural Films

Greenhouses made from polyolefin films (LDPE) offer cost-effective solutions for intensified agriculture. Transmission and reflection of the solar spectrum are important key parameters for the growth of plants and the heat management in the greenhouse. The biologically active UV/VIS radiation for plant growth (400–700 nm) should pass the film as completely as possible (good transparency, little haze), but outside heat (IR (irradiation), MID IR 7–14 μm) should be reflected during the day to avoid overheating but should be retained inside during cold nights to avoid cooling during the night. Weathering resistance is another key parameter of these films. Minerals are used to make LDPE films suitable for thermal management. Advantages are early and high-quality crops, protection against cold/frost, and higher yields.

Schwartz (2006) published a comprehensive comparison of different MID IR absorbers in polyethylene films for heat management in greenhouses. LDPE (density, 0.92 g/cc) MFI of 2 g/10 min was used and compounded with different additives based on silicates in concentrations of 5% and 10% by weight. 100 μm films were produced in an extrusion blow process. The minerals were cristobalite (CR), talc (TL), organically modified clay (OC), nepheline syenite (NS), calcined kaolin (CC), and synthetic aluminosilicate (SA).

All films showed good optical transparency because refractive indices of the minerals were in the range of 1.48–1.58 close to PE (1.50–1.51). Nevertheless, light scattering was dependent on PSD. Small particles tend to show less light dispersion (28–33%) and larger particles higher light dispersion (44%).

The thermal loss was depending on film thickness; the higher the film thickness at a given load of a given mineral, the better the heat retention/the smaller the heat loss.

Degradation due to weathering is an important factor where nepheline syenite has an advantage over other potential fillers. During QUV weathering tests, time to total degradation and amount of carbonyl groups have been measured. In organically modified clay, calcined kaolin, and talc, the speed of concentration increase of carbonyl groups was the fastest, and the exposure time to degradation was the shortest. This was attributed to the amount of iron oxide impurities being the highest in those minerals. Cristobalite and nepheline syenite showed the slowest degradation having the lowest iron oxide concentration. An exception to the rule was the synthetic aluminosilicate which showed the lowest amount of iron oxides but a high degradation rate. This was attributed to the extremely high surface area of the synthetic aluminosilicates.

Also, the effect of deactivation of light stabilizers has been studied. The higher the surface area of the mineral, the more they were absorbed which lead to insufficient performance.

The study concludes that talc and calcined kaolin are a good choice for thermal management in sunny countries due to the fact that they strongly scatter light and avoid shadow zones in greenhouses, promoting uniform photosynthesis. In less sunny countries, higher transparency is necessary to achieve maximum transmittance of indirect light. Here, nepheline syenite would be the best choice. Organically modified clay could not be recommended due to high degradation and low thermal management capabilities.

Another study performed by Van Aken (Aken) gives an overview over optical properties and thermal management potential of several minerals and experimental inorganic compounds: ATH (alumina trihydrate), barite, calcite, cristobalite, metal oxide compound, nepheline syenite, talc, calcined kaolin, and wollastonite. Those minerals were compounded at a concentration of 5% by weight in polyethylene.

Comparing the MID IR/heat retention (during the night), the ranking in efficiency was metal oxide compound > calcined kaolin > cristobalite = nepheline syenite > ATH > wollastonite > calcite > barite > talc. Transparency of all films was in the region of 89% (calcined kaolin) to 92% (metal oxide compound). Haze was lowest on nepheline syenite and highest on wollastonite.

Another study was published by HPF (HPF The Minerals Engineers 2013); here, feldspar and nepheline syenite were compared directly in a polyethylene with an MFI of (190 °C/2.16 kg) 0.75 g/10 min by using a 60% masterbatch of a polyethylene with an MFI of 2.0 g/10 min. Films with 10% mineral were extrude-blown to form films with 50 µm thickness.

Figure 5 shows the UV/VIS spectra of the samples.

Feldspar showed a slightly higher transmission in the biologically active range of UV/VIS radiation for plant growth (400–700 nm).

IR spectra were recorded for the films and displayed in Fig. 6.

Both minerals for thermal management show characteristic spectra in the region of 700–1,400 $\mathrm{cm}^{-1}$ (IR/heat radiation). Both are capable of retaining the warmth in the greenhouse preventing too much cooling in comparison to a neat PE during the night.

Optical properties of greenhouse films have been assessed by transparency and haze measurement according to ASTM D1003 and gloss according to DIN 67530/ASTM D2457. Table 7 shows the data.

In comparison with nepheline syenite, feldspar showed better optical performance by means of higher transparency, less haze, and more gloss of the films.

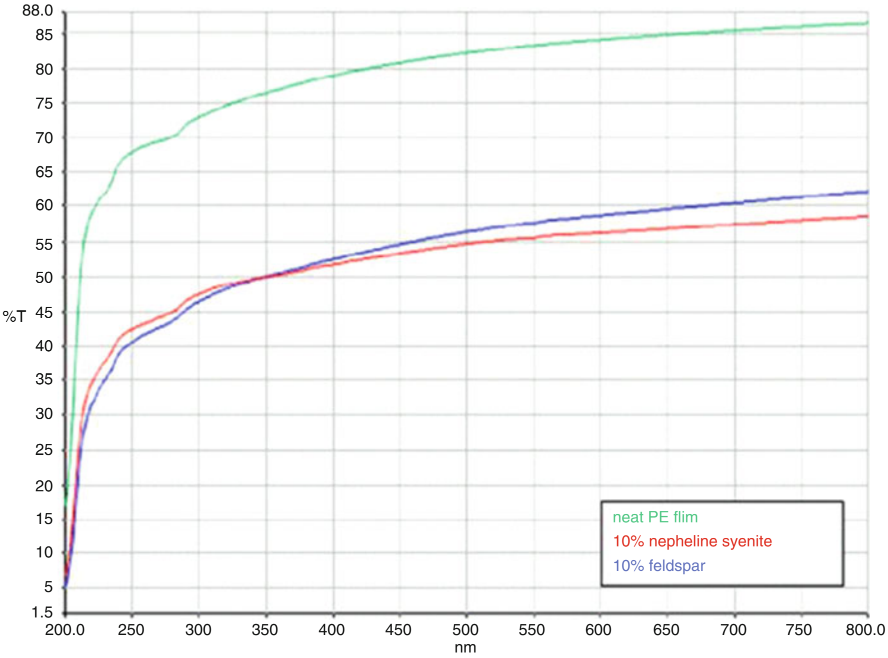


**Fig. 5** UV/VIS spectra of polyethylene films for thermal management in greenhouses

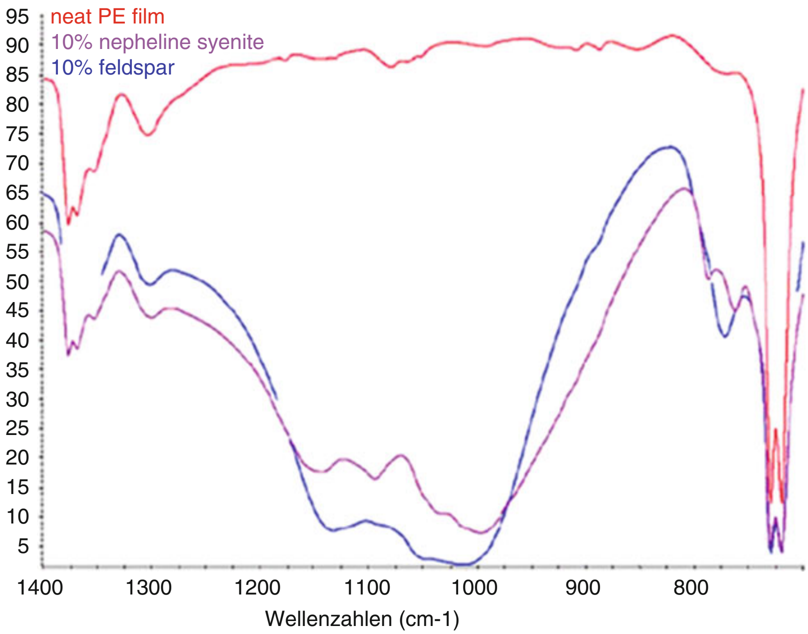


**Fig. 6** IR spectra of polyethylene films for thermal management in greenhouses

**Table 7** Optical properties of greenhouse films

| Film | Gloss 60° | Haze | Transparency |
|---|---|---|---|
| Neat PE | 69 | 12.7 | 92.1 |
| PE film with 10 % nepheline syenite | 26 | 51.2 | 90.7 |
| PE film with 10 % feldspar | 27 | 45.3 | 91.0 |

## Dental Compounds

Apart from their use in veneers, highly pure feldspars become more and more interesting to dental applications like dental fillings, inlays, or artificial teeth in polymer compounds. Although these applications do not represent mass markets, they use similar principles in optical appearance and transparency and color as the applications mentioned before.

Resin-based composites are more esthetic and are more widely used compared to traditional materials such as amalgam. Another advantage is that composites can be produced in a wide range of lifelike shades and are almost invisible on restored teeth. Furthermore, dental composites reinforce the natural teeth as they bond well to the tooth surface.

Dental composites based on a methacrylic resin matrix, such as one based on bisphenol A-glycidyl methacrylate (Bis-GMA), are widely used daily by dentists. Generally, they are mixtures of resin matrix and inorganic particles like quartz, glass, porcelain, etc. Predominantly, they are hardened by exposure of visible light.

The filling level of composites varies from 70% up to 85%. That indicates that the characteristics of the resulting composites are mainly influenced by the type of the filling material. Relevant properties of the filling material are the refraction index of the filler, particle-size distribution, and filler shape. Commonly, the filler itself is radiopaque, but there exist variations with non-radiopaque fillers or mixtures as well. Nevertheless, a surface treatment of the filler in order to increase the bonding between filler and matrix is essential. The filling level or loading of the resin influences the properties of the composites dramatically. The main effects are reduced shrinkage and increased physical properties. On the other hand, practical considerations like good handling as well as good polishing properties, together with appealing optical properties, are required by dentists and dental technicians.

Göbel and Kruber (Roland Göbel 2012) published properties of a new generation of feldspathic fillers in light-curable dental composites. Table 8 shows the composites tested.

They concluded from Table 9 that compared to common dental fillers based on Sr glasses and Ba glasses, respectively, the specially prepared feldspar systems showed similar or better physical properties such as flexural strength and hardness. This results in longer durability of dental restorations. All feldspar systems showed good curing depth, and their linear shrinkage values were between 1.4% and 1.7%. High loadings were possible. Good processability at high filler levels was assured.

**Table 8** Composition of experimental composites tested

| | Filler content [wt%] | Medium particle size [μm] | Composite type |
|---|---|---|---|
| Reference 0.7 μm[a] | 68 | 0.7 | Bis-GMA, TEGDMA[b] |
| Reference 1.0 μm[c] | 72 | 1.0 | Bis-GMA, TEGDMA[b] |
| **MICROSPAR®1351-980MST** | 60 | 0.3 | Bis-GMA, TEGDMA |
| **MICROSPAR®1351-900MST** | 67 | 0.8 | Bis-GMA, TEGDMA |
| **MICROSPAR®1351-600MST** | 73 | 3.5 | Bis-GMA, TEGDMA |
| **MICROSPAR®** mixture[d] | 74 | - | Bis-GMA, TEGDMA |

[a] GM 39923UF0.7; 6.0% methacryl silane

[b] Composition differs slightly to the other tests

[c] GM27884UF1.0; 4.6% methacryl silane

[d] Mixture of MICROSPAR®1351-900MST/MICROSPAR®1351-600 MST; 40 wt%/60 wt%

**Table 9** Mechanical data of the experimental composites made from feldspar fillers

| | Flexural bond strength [MPa] | Shear bond strength [MPa] | Vickers hardness [HV5-20] | Roughness; Ra [μm] |
|---|---|---|---|---|
| Reference 0.7 μm[a] | 115.6 | 22.6 | 47.0 | - |
| Reference 1.0 μm[b] | 145.0 | 31.3 | 54.4 | - |
| **MICROSPAR®1351-980MST** | 144.0 | 19.7 | 48.5 | 0.05 |
| **MICROSPAR®1351-900MST** | 212.0 | 29.7 | 53.9 | 0.05 |
| **MICROSPAR®1351-600MST** | 205.0 | 28.2 | 51.3 | 0.05 |
| **MICROSPAR®** mixture[c] | 203.0 | 31.3 | 47.6 | 0.05 |

[a] GM 39923UF0.7; 6.0% methacryl silane

[b] GM 27884UF1.0; 4.6% methacryl silane

[c] Mixture of MICROSPAR®1351-900MST/MICROSPAR®1351-600 MST; 40 wt%/60 wt%

The systems were highly transparent so it was not necessary to do extensive shade adjustments. The composites showed easy and smooth polishing of restorations.

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# Magnetite

# 13

Christopher DeArmitt

## Contents

## Abstract

Magnetite, $Fe_3O_4$, is a naturally occurring, safe iron oxide with an unusual and useful combination of properties compared to the better-known functional fillers for plastics. It is used to make high-density compounds for sound damping, particularly in automobiles, and also to lend heft, that is, the impression of quality. It is able to block x-rays and other types of radiation, making it useful as a nonhazardous replacement for lead-based blocking materials. A very high volumetric specific heat capacity allows it to absorb and release large amounts of heat energy, which is useful for green buildings. It is microwave and induction heatable, suggesting potential in cooking applications. Thermal conductivity is useful for heat dissipation in electrical devices and electricity conductivity allows

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it to be used as a permanent antistatic additive. Natural magnetite is composed of hard, angular particles that can enhance slip resistance of polymer flooring. Last, but not least, it is strongly attracted to magnets, so it can be used to impart magnetic properties to plastics. Applications of this multifaceted and relatively unknown specialty filler continue to expand.

**Keywords**
Iron oxide • Magnetite • High density • Microwaveable • Specialty filler • Radiation shielding

## Definition

Magnetite is a hard, black, ferrimagnetic, lustrous iron oxide, $Fe_3O_4$, which occurs naturally but may also be synthesized, especially when nanoparticles are desired. It is used as a specialty filler because of its unique combination of electrical, thermal, and magnetic properties as well as for its exceptionally high density.

## Introduction

Magnetite is a remarkable material with unusual properties and diverse applications. Probably the best-known example is magnetite iron ore used for steel production, which consumes millions of tons per year. Another lesser-known use is in water purification, where very-high-purity magnetite is used as a feedstock to produce iron-based chemicals. It is also used as a catalyst in the production of ammonia. There are many other less well-known places where we encounter magnetite. For example, true gun bluing is a thin layer of magnetite which passivates the surface of iron to help prevent corrosion and to lend a decorative effect. Magnetite and other iron oxides are widely used as pigments which, being inorganic, are highly weather resistant. Due to the industrial importance of iron oxides, comprehensive reference literature exists (Schwertmann and Cornell 2000, Cornell and Schwertmann 2003).

The above applications use magnetite just as a form of iron oxide without taking advantage of its exceptional properties. Over the last two decades, magnetite has seen adoption in a number of new applications as a specialty filler in plastics, rubbers (Mangnus 2003), and coatings. Its properties are not like those of traditional fillers, a fact which opens new possibilities. Because those properties are not so well known, it is worth highlighting them in relation to existing and potential new applications.

## Property Overview

The key properties of magnetite are compared and contrasted to those of some common mineral fillers. A cursory look at some chemical and physical properties reveals this to be a rather special material. Next we will look at some of the properties in more detail and relate the attributes to extant or emergent applications (Table 1).

**Table 1** Properties of magnetite in contrast to common fillers such as calcium carbonate and talc

| Property | Typical mineral filler | Magnetite |
|---|---|---|
| **Color** | White | Black |
| **Density** | 2.5–3.0 g $cm^{-3}$ | 5.2 g $cm^{-3}$ |
| **Mohs hardness** | 2–3 | 5.5–6 |
| **Attraction to a magnet** | No | Yes |
| **Electrical conductivity** | Insulator | Semiconductor |
| **Chemical composition** | Carbonates and silicates | $Fe_3O_4$ (an oxide) |
| **Volumetric heat capacity** | 2.1 kJ $L^{-1}$ $K^{-1}$ | 3.8 kJ $L^{-1}$ $K^{-1}$ |
| **Microwave heatable** | No | Yes |
| **Radiation blocking** | No | Yes |

## Chemistry

Magnetite is often written as $Fe_3O_4$ but is more correctly expressed as $Fe^{II}Fe_2{}^{III}O_4$ showing that it contains iron in the $2^+$ and $3^+$ oxidation states making it the only "stable" iron oxide containing $Fe^{2+}$. It is chemically inert but is dissolved slowly by acids (Tremaine and LeBlanc 1980) or bases at high temperatures (Ziemniak et al. 1995). The dissolution rate depends on the surface area, pH, complexing ligands, presence of oxygen, and dissolved salts such as $Fe^{2+}$, UV light, and temperature.

When heated above 300 °C, synthetic nano-magnetite experiences conversion to maghemite ($\gamma$-$Fe_2O_3$) and then to hematite ($\alpha$-$Fe_2O_3$) (Sidhu et al. 1981). Over 500 °C, it converts directly to hematite. However, natural magnetite is found to be much more stable. In fact, it is metastable under atmospheric conditions, which is how massive natural deposits have survived. Mechanical energy can also convert magnetite to hematite. Synthetic one-micron magnetite was ball milled and thereby completely converted to $\alpha$-$Fe_2O_3$ after 70 h (Sorescu 1998). This supports the above findings that finer particles are less stable. It might be expected that the high surface area of finer particles facilitates oxidation to hematite.

Interestingly, it has been found that encapsulation of magnetite within thermoplastics can alter the surface oxidation state, but in some cases, the polymer helps preserve the $Fe^{2+}$:$Fe^{3+}$ ratio and the half-metal nature of the surface (Parkinson et al. 2012; Fig. 1).

### Surface Chemistry

Magnetite is amphoteric, i.e., it can behave as an acid or a base. The reactive sites at the surface are hydroxyl groups (−OH) and the density of groups has been measured as 5 per square nanometer (Parkinson et al. 2012). Freshly ground natural magnetite has a pH of 6.5 (Milonjić et al. 1983). Organosilanes, titanates, sulfonates, and carboxylic acid groups (Korolev et al. 2002) have all been reported as surface treatments that bind effectively.

### Safety

Pure magnetite is considered safe for food contact applications. In fact, it has been shown to exist within every living organism from bacteria to plants and humans.

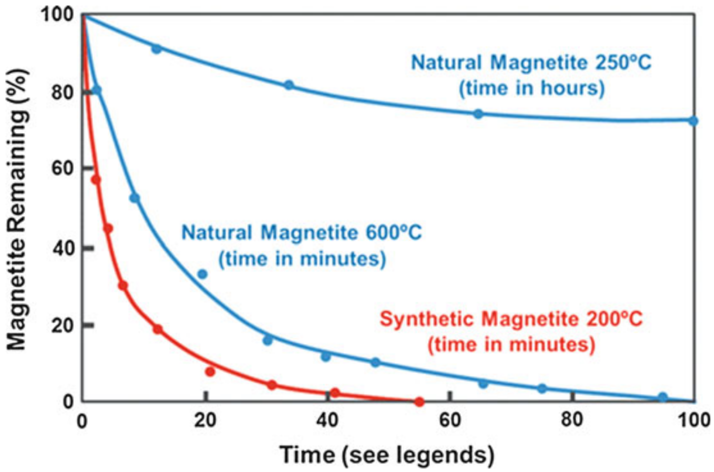

**Fig. 1** Stability of natural and nano-magnetite

Such biogenic magnetite is crucial to the guidance systems of bats, birds, and bacteria. All naturally occurring unmodified minerals are automatically TSCA listed and REACH exempt.

## Density

There are two main applications for dense fillers. The most obvious is to increase the density of plastics, where the added heft gives the perception of a quality product and is also sought for negative buoyancy, in counterweights and ballast. The other major benefit is in sound- or vibration-damping materials where added density leads to substantially better performance. Often a dense filler is used at high loadings in a soft polymer which is “lossy,” i.e., it is inelastic and flows when deformed thereby converting mechanical energy to heat. Such materials are characterized by a high loss factor, i.e., tan delta as measured by DMA, for example (Table 2).

Barium sulfate (barite) has been used as a high-density filler for decades. However, pure, natural magnetite is more effective due to its higher density (5.2 g cm$^{-3}$ compared to 4.5 g cm$^{-3}$ for $BaSO_4$) and has gained a market share especially where its other properties give additional advantages such as improved productivity when molding. A common misconception is that the density of composites increases linearly with filler loading, expressed as a percentage by weight. In fact, plotting the density versus the weight percent of the filler results in distinct curves. It turns out that all properties, including density, depend upon the volume percent of the filler and not the weight percentage. Thus, plotting the density versus the volume percent (or volume fraction) of the filler produces a straight line.

It can be seen that magnetite is more effective at increasing density than other particulate mineral products on the market with attainable densities of 3 g cm$^{-3}$ or

**Table 2** Magnetite is more effective than other fillers for density enhancement (example in PP)

| Mineral | Weight (%) | Volume (%) | Density (g cm$^{-3}$) | Density increase (%) |
|---|---|---|---|---|
| **$CaCO_3$** | **40** | 18.2 | 1.23 | 37 |
| **Talc** | **40** | 18.2 | 1.23 | 37 |
| **Magnetite** | **40** | 10.3 | 1.34 | **49** |
| **$CaCO_3$** | 68 | **41** | 1.64 | 82 |
| **Talc** | 68 | **41** | 1.64 | 82 |
| **Magnetite** | 80 | **41** | 2.66 | **196** |

more (Mangnus 2003) even in polyolefins. To reach even higher densities, metallic fillers are used. Tungsten is highly effective but is very costly and imparts electrical conductivity, which is not always acceptable.

## Magnetic Properties

It is often assumed that magnetite is "magnetic," i.e., it acts as a magnet and will attract ferrous metals or neighboring magnetite particles. However, this is not in fact the case. Magnetite is ferrimagnetic, meaning that it is attracted to a magnet but is not itself magnetic (Dionne 2009). Filler-grade magnetite is a free-flowing powder which makes shipping and handling straightforward. Magnetite also has a low remanence so that once removed from a magnet, it does not readily remain magnetized. Lodestone is a rare form of naturally occurring magnetite which is a weak magnet and was the basis for the first compasses. The Curie temperature of magnetite is ~585 °C or ~1,085 °F. Above that temperature, it is no longer attracted to a magnet. Once cooled down below the Curie temperature, it is once again susceptible to a magnetic field.

Magnetite is the most magnetic (i.e., strength of attraction to a magnet) of all the naturally occurring minerals (Harrison et al. 2002) with a saturation magnetization of 480 G at room temperature (Pullaiah et al. 1975). For nanoparticles, that value can be higher with a maximum value reported to be 10 nm diameter particles (Thapa et al. 2004). It can be blended into polymers and coatings to impart magnetic susceptibility (Kong et al. 2010a). An example is magnetic paint available from several manufacturers. Magnetite also finds application in automotive mats where it provides vibration- and sound-damping properties due to its high density combined with the ability to place the mats precisely using robots equipped with electromagnets. One of the best-known uses of magnetite is in ferrofluids which are colloidal dispersions that can be manipulated with a magnetic field. The first reported such fluids were made by NASA by milling natural magnetite in the presence of oleic acid as a dispersant (Papell 1965). Ferrofluids and magnetorheological fluids are now made using synthetic nano-particulate magnetite.

### Induction Heating

Induction heating of magnetite is very effective. An alternating magnetic field is applied and the losses incurred due to hysteresis manifest themselves as heat.

Because induction heating is tied to the magnetic properties of the material, it is only possible below the Curie point. So, in the case of magnetite, induction heating occurs up to ~580 °C and then the temperature levels out. Plastics, being neither magnetic nor electrically conductive, are not induction heatable. It has been shown that addition of magnetite particles as a functional filler imparts induction heatability to polymers and specifically to memory foams (Vialle 2009). As foams are thermally insulating, it is not a simple matter to heat them evenly. By adding magnetite, one can heat effectively throughout the shape memory foam triggering the shape change response. Adding magnetite filler to high-temperature plastic would enable induction-heatable plastic cookware.

## Electrical Properties

The vast majority of plastics and minerals are electrical insulators. Magnetite, in contrast, has significant electrical conductivity and is considered a half metal (Chang et al. 2007). It is a semiconductor and has a small bandgap of just ~0.1 eV due to electron exchange between $Fe^{2+}$ and $Fe^{3+}$. The resistivity for very-high-purity material can be as low as $1.73 \times 10^4$ μΩ cm or $1.0 \times 10^4$ μΩ cm for thin epitaxial films (Peng et al. 2002). The electrical conductivity of synthetic single crystals has been reported as 250 $\Omega^{-1}$ $cm^{-1}$ at room temperature with a broad maximum centered around 15 °C.

High-purity natural magnetite of differing particle size distributions was added as a filler to polypropylene as well as nylon 6 (Duifhuis and Janssen 2001). It was found that percolation began at 35 vol%, and by a loading of 44 vol%, the surface resistivity was just $1 \times 10^3$ Ω square and the volume resistivity approximately $1 \times 10^4$ Ω m for the coarser grades, whereas slightly higher values were attained for finer-particle sizes. The paper is especially helpful as it details the processing conditions needed to extrude magnetite up to 80 or even 85 wt% loading (Fig. 2).

As with other conductive particulates, one must reach a critical concentration of particles known as the percolation threshold in order to create a conductive pathway of touching particles. A subsequent paper looked at the same three commercial grades of natural magnetite in PP and nylon 6 (Weidenfeller et al. 2002). The percolation threshold was determined to be 33 vol%, in line with theoretical calculations. At 47 vol% magnetite, a resistivity of 10 kΩ m was reported.

## Thermal Properties

### Specific Heat Capacity

Specific heat capacity relates to the amount of energy required to heat and cool a substance. There is a common misconception that adding minerals to plastics helps reduce specific heat capacity. This misunderstanding is even supported by some textbooks (Xanthos 2010) and stems from the choice of units. Specific heat capacity is often expressed as kJ $kg^{-1}$ $K^{-1}$, and, on that basis, mineral fillers do have a

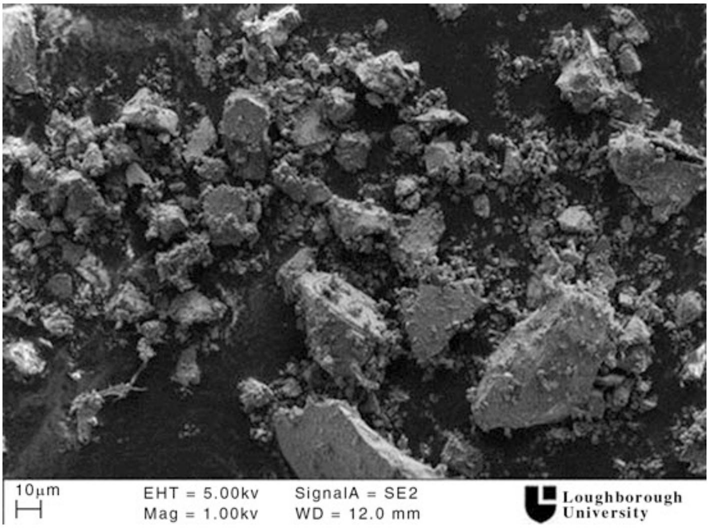

**Fig. 2** SEM image of MagniF 10 high-purity natural magnetite courtesy of LKAB minerals

**Table 3** Magnetite has higher volumetric heat capacity than other solids

| Material | Density ($g\ cm^{-3}$) | Mass-specific heat capacity ($kJ\ kg^{-1}\ K^{-1}$) | Volume-specific heat capacity ($kJ\ L^{-1}\ K^{-1}$) |
|---|---|---|---|
| **BN (hexagonal)** | 2.25 | 0.79 | 1.8 |
| **Quartz** | 2.65 | 0.8 | 2.1 |
| **Silver** | 10.5 | 0.19 | 2.0 |
| **Talc** | 2.7 | 0.82 | 2.3 |
| **Tungsten** | 19.4 | 0.09 | 1.7 |
| **Glass fiber** | 2.6 | 0.83 | 2.2 |
| **Magnetite** | 5.2 | 0.73 | **3.8** |

numerically smaller heat capacity than polymers. However, a more fitting choice of units is kJ $L^{-1}$ $K^{-1}$, i.e., the volumetric heat capacity, the reason being that the filler is added to displace a certain volume of plastic where the total volume of the final part is maintained at a constant value. When one looks at volumetric heat capacity (equal to mass-based specific heat capacity x density), it turns out that almost all solids have very similar values with an average around 2.2 kJ $L^{-1}$ $K^{-1}$. There are a few exceptions including diamond and magnetite, the latter having a value some 70% higher than other solids (Robertson 1988). An application of this property is in storage heaters where low-cost nighttime electricity is used to heat a heat sink with high thermal mass made of magnetite-filled ceramic bricks. The heat is then released in the daytime when electricity is significantly more costly. An additional advantage of magnetite in concrete is an increase in thermal shock resistance (Chan 2013) so the product does not crack even after multiple heat cycles (Table 3).

### Conductivity and Diffusivity

The thermal conductivity of magnetite is 5.1 W $m^{-1}$ $K^{-1}$ compared to just 1.7 W $m^{-1}$ $K^{-1}$ for $BaSO_4$ and 1.5 W $m^{-1}$ $K^{-1}$ for glass fiber (Clauser and Huenges 1995). Most thermoplastics lie in the range 0.2–0.4 W $m^{-1}$ $K^{-1}$. Magnetite has been proven effective at increasing these properties in plastics (Weidenfeller et al. 2002) and rubbers (Mangnus 2003) with reported thermal conductivities up to ~1 W $m^{-1}$ $K^{-1}$. Magnetite-filled injection-molded polypropylene showed far higher specific heat capacity and thermal diffusivity than barium-sulfate-filled material (Weidenfeller et al. 2004). Increasing the heat transfer rate in and out of a polymer translates to much faster productivity in molding processes such as injection molding (Weidenfeller et al. 2005), other forms of molding, and in extrusion.

Theory states that thermal conductivity of filled systems should also demonstrate a percolation threshold as is the case for electrical conductivity. However, this is often not observed in real filled materials including magnetite-filled polymers. The reason is that when the thermal conductivity of the filler is only one order of magnitude larger than the polymer, one finds that the system is lossy. That is, the heat is transferred out of the particles and into the matrix as quickly as it is transferred to the adjacent particles. The thermal conductivity therefore varies linearly with filler loading unless the thermal conductivity of the filler is exceptionally high compared to that of the matrix.

### Coefficient of Thermal Expansion (CTE)

The CTE of magnetite is $\sim 8.5 \times 10^{-6}$ $K^{-1}$ at room temperature (Huijbregts and Snel 1972), but below the Verwey transition of 120 K, it shows a remarkably low CTE (Hancock and Finlayson 1995) under $1 \times 10^{-6}$ $K^{-1}$, similar to Invar, a material known for an exceptionally low CTE.

## Microwave Properties

The microwave properties of minerals have been studied extensively because it is of interest in a variety of fields. One particularly detailed study by the US Department of the Interior surveyed over 160 chemicals, elements, and minerals to determine how rapidly they would heat under controlled microwave conditions (McGill et al. 1995). It was revealed that magnetite is exceptionally effective at adsorbing microwave energy and converting it to heat. For instance, temperatures of over 1,000 °C are reached in less than a minute when magnetite is heated in microwave oven with just 500 W power (comparable to domestic ovens). For the sake of comparison, one study reported (Yixin and Chunpeng 1996) the heating rate of magnetite to be 4.85 K $s^{-1}$, $CaCO_3$ to be 1.33, and quartz ($SiO_2$) to be just 0.32, and hematite ($Fe_2O_3$), another form of iron oxide, displayed a value of just 0.37 K $s^{-1}$. The heating rate is all the more remarkable when one considers that the volumetric specific heat capacity of magnetite is higher than that of most other solids by

50–70%. That means that magnetite has to be much more efficient at adsorbing energy in order to achieve the same temperature compared to other substances.

Temperatures as high as 1,500 °C have been attained by heating magnetite with microwaves (Takayama et al. 2007); although the experiment was performed in air, the presence of carbon acted to reduce the magnetite. This mixture of magnetite and carbon produced FeO at 2.45 GHz but high-quality pig iron at 30 GHz. The pig iron made in such a way contained 90% less impurities than that made using a blast furnace and with significantly lower carbon consumption (Nagata et al. 2001). Other workers heated carbon black with microwaves to reduce magnetite to iron which proceeded at just 770 °C under magnetic field heating (Ishizaki et al. 2012).

One might wonder why the microwave heating rate is so pronounced. This topic has been investigated in detail and it turns out that magnetite is unusual in that it is heated effectively by both the electrical and the magnetic components of microwave energy (Jiping et al. 2002). It has been established that electrical insulators tend to be microwave transparent and materials with high electrical conductivity reflect most of the energy. Semiconductors like magnetite adsorb the electrical energy effectively throughout the sample. Again, trace impurities can act as dopants, which affect electrical conductivity and, in turn, the heating rate in a microwave field.

Based on these observations, many applications suggest themselves. Magnetite has been used as a filler in thermoplastics (Kong et al. 2010a) and elastomers (Mangnus 2003; Kong et al. 2010b) to make them microwave heatable. An example is in footwear insoles which can be heated in 30–40 s in a domestic microwave. This provides a comfortable temperature which lasts for an extended period because of the unusually high specific heat capacity of the magnetite filler (Fig. 3).

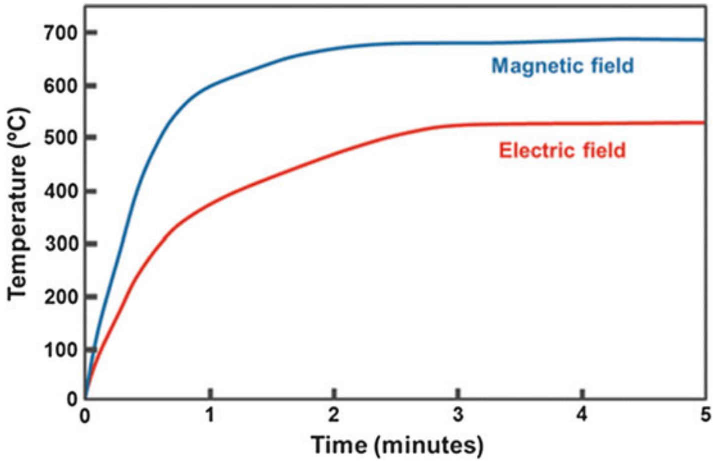

**Fig. 3** Heating of magnetite is effective using the magnetic and electrical field components

Most recently there has been a focus on magnetite-enhanced pothole repair whereby microwaves are used to heat the repair compound in situ to facilitate proper flow, wet out, and adhesion. Improved durability has been demonstrated.

## Radiation Blocking

A major use of magnetite is to make high-density concrete used in hospitals for radiation shielding of the radiology unit among others. Adding magnetite gives good-quality concrete and allows walls that are thinner by 40% without sacrifice in radiation-blocking performance (Creutz and Downes 1949). One recent example is the Puijo Hospital in Finland.

Similarly, magnetite can be used to shield against microwaves as mentioned above or to make plastics x-ray opaque (Hein et al. 2013). Radio-opaque fillers are used in dental and medical implants to make the plastics visible. Magnetite has also been found effective for gamma ray shielding.

## Sources of Magnetite

Magnetite occurs naturally and may also be produced synthetically (Schwertmann and Cornell 2000). Synthetic magnetite is usually favored when nanoparticles are required for scientific studies or for special applications such as immunodiagnostics or protein isolation. As mentioned, the smaller, synthetic type tends to be somewhat unstable where its high surface area makes it more prone to oxidation.

Natural magnetite occurs the world over. It can be separated from beach sand using a magnet and is also found in substantial deposits that can be mined. LKAB Minerals have spearheaded the drive to develop magnetite as a specialty filler for plastics. It has been shown that their natural magnetite from northern Sweden has exceptionally high purity (Müller et al. 2003) and even qualifies for food contact applications in plastic.

## Other Properties

Several examples of existing and potential applications of magnetite as a filler have already been given and there are certainly more waiting to be discovered. When considering the use of a novel filler, several practical questions arise, and this section will cover some of those.

### Mechanical Properties

Magnetite is a low aspect ratio filler and behaves similarly to other such particulates including calcium carbonate, dolomite, barium sulfate, or glass beads. So, modulus is increased by magnetite and tensile strength is somewhat lower, whereas impact and elongation are better maintained when smaller particles are used (Duifhuis and Weidenfeller 2002).

### Long-Term Polymer Stability

There is a widespread perception that iron is detrimental to the thermal stability of polymers. This stems from the use of talc in polyolefins where traces of iron compounds in the talc can catalyze degradation. In reality however, the idea that iron is generally deleterious is not founded in fact. Iron oxides, of which magnetite is one, are used as UV-stabilizing pigments to protect polyolefins (Halliwell 1992; Scott 1997). It turns out that magnetite is not deleterious to stability (Mangnus 2003) as illustrated by aging studies on highly filled natural rubber and EPDM.

### Abrasiveness

The relatively high Mohs hardness of magnetite might raise questions about possible wear on processing equipment. Magnetite actually has lower hardness than glass fiber which is a very common reinforcement. Natural magnetite was proven less abrasive than glass fibers or barium sulfate when all were injection molded at 30 vol% in polypropylene. Like glass fiber, the use of hardened steel in processing equipment is recommended, and control of injection-molding conditions can ensure the magnetite particles are kept away from the walls, thus preventing contact and preventing wear.

## Future Directions

Magnetite offers a property set unlike any other material and the opportunity to impart those properties to thermosetting and thermoplastic polymers, coatings, or elastomers. Since the introduction of filler-grade materials in the 1990s, many applications have arisen in a range of polymers including polypropylene, nylons, polyurethanes, and silicones. As people become aware of this comparatively new filler, applications emerge on a regular basis driven by the following properties:

- Magnetic properties
- High density
- Thermal conductivity
- High volumetric specific heat capacity
- Electrical conductivity
- Radiation shielding ability

Several new applications suggest themselves including magnetite as a tracer to make plastics detectable, as electromagnetic interference (EMI) shielding for cables (Aldissi 1993) with magnetite in the bedding compound or insulation, and for radiation shielding against microwaves or radar.

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# Part III

# Synthetic Particulate Fillers

# Carbon Black as a Polymer Filler

# 14

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## Contents

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**Abstract**

Carbon black is the generic name for a family of small-size, mostly amorphous, or paracrystalline carbon particles grown together to form aggregates of different sizes and shapes. Carbon black is formed in the gas phase by the thermal decomposition of hydrocarbons in the absence or presence of oxygen in substoichiometric quantities and is industrially manufactured in the form of hundreds of defined commercial grades that vary in their primary particle size, aggregate size and shape, porosity, surface area, and chemistry.

Carbon blacks are mainly used as reinforcing fillers in tires and other rubber products. The reinforcement effect is influenced by the interaction between the elastomer molecules, between the carbon black particles themselves, and between the carbon black particles and the elastomer matrix. For elastomer reinforcement, the primary particle size (specific BET surface area) and surface activity of the carbon black types are important as well as their carbon black structure. In addition, the degree of carbon black dispersion achieved and the carbon black loading used in the elastomer composite play a role. The type of carbon black can significantly influence the properties of the resulting rubber compounds. This explains the existence of many different standardized industrial carbon black grades being used in rubber compounds for the body and tread of tires.

Carbon blacks are expected to continue to dominate the rubber market for the foreseeable future, but they are coming under considerable pressure from precipitated silica in some important tire applications. This is because the silica offers lower rolling resistance properties and hence improved fuel economy and lower emissions. This trend is expected to continue to grow.

Specialty carbon black grades are used as black color pigments in plastics, paints, and inks, as ultraviolet (UV) stabilizers in polymers to avoid their degradation under the influence of visible and UV light, and as fillers to impart electrical conductivity to polymers for electrostatic dissipative and conductive applications.

**Keywords**

Carbon black • Furnace black • Dual-phase black • Reinforcement • Color pigment • UV stabilizer • Elastomer • Thermoplastics • Carbon black production

## Definitions

Carbon black is the generic name for a family of small-size, mostly amorphous, or paracrystalline carbon particles grown together to aggregates of different sizes and shapes and is a modification of carbon with high surface area-to-volume ratio. Carbon black is formed in the gas phase by the thermal decomposition of hydrocarbons from various sources and in that way is industrially manufactured in the form of hundreds of defined commercial grades that vary in their primary particle size, aggregate size and shape, porosity, as well as surface area and chemistry. The properties can be precisely controlled by varying the process type and process conditions. This distinguishes carbon black from other forms of soot being the term for mostly undesired, sometimes hazardous solid carbon by-products from the uncontrolled combustion of carbonaceous material. Carbon black is mainly used as a reinforcing filler in tires and other rubber products. Specialty grades are used as black color pigments in plastics, paints, and inks as well as fillers to impart electrical conductivity to polymers for electrostatic dissipative and conductive applications.

## Introduction

The use of carbon black as black pigment for paints and inks goes back to the early civilizations of mankind. With the invention of the book printing in the fifteenth century, which developed to be the most important way of communicating information until recently, the demand for strong black pigment has increased steadily. The traditional carbon black initially used for these coloring purposes was lampblack. In the first manufacturing processes of lampblack, wood was burnt smoldering under low air supply, and the smoke passed into a cone-like soot chamber where the carbon black settled on the walls of metal, linen, or wool. The charred wood was sold as charcoal. In the early 1900s, the lampblack producer Binney & Smith, later well known for their crayon products, began selling their carbon black chemicals to Goodrich Tire Company, initially as a coloring agent to change the white rubber tires into black. By this coincidence, it was found that the use of carbon black in rubber manufacturing significantly increased certain desirable qualities for rubber meant to be turned into tires. It was in 1904 in England when Sidney Charles Mote and a team of experimenters discovered the reinforcing effect that carbon black imparts to rubber, and some years later, this beneficial effect became common knowledge and general practice in tire tread compounding. In addition to the reinforcement, the resistance of carbon black to ultraviolet (UV) radiation and its function as ozone scavenger stabilizes the tire rubber toward UV light as well as oxidation and prevents the rubber tire from fissuring and cracking. Adding carbon black avoids electrostatic charging and also helps to conduct heat away from certain hot spots on the tire, specifically, in the tread and belt areas, which can get particularly hot at times while driving. This reduces thermal damage on the tire, which further extends its lifespan. The first larger industrial manufacturing plants for tire blacks were channel black processes using at a very low carbon black yield the natural gas which occurred in oil production as a by-product.

The introduction of synthetic rubbers, particularly of styrene–butadiene rubber (SBR), during World War II again stimulated large development activities for carbon black fillers as the strength of SBR as pure gum vulcanizate was too low to be used for tires. It was found that these synthetic rubbers with the newly developed oil furnace black fillers made tire treads of greater abrasion resistance than natural rubber with the traditional channel black boosting the demand for these grades.

**Table 1** Global markets for carbon black (CY 2013)

| Application/market | Quantity [ktons] | Main use |
|---|---|---|
| Total global carbon black consumption | 11,360 | |
| Rubber for tire applications | 8,320 | Reinforcing agent |
| Rubber for nontire applications | 2,240 | Reinforcing agent |
| Plastics | 350 | Pigment, UV stabilizer |
| Plastics, rubber | 105 | Conductive additive |
| Surface coatings | 190 | Pigment |
| Inks | 150 | Pigment |
| Others | 5 | |

The two fundamental properties of carbon black are closely linked to the two main polymer application areas: its reinforcing effect in natural and synthetic rubber and its color, which makes it the most widely used black pigment in plastics, paints, and inks. Moreover, within special applications, its thermal and electrical conductivity and its resistance to UV radiation and antioxidation effect play a role. In 2013, a total amount of about 11.4 Mio. tons of carbon black were consumed globally (Ita 2013). As shown in the market overview in Table 1, about 73% of this carbon black went into rubber compounds used for tires and about 20% into rubber compounds for nontire applications. Today, these rubber black grades are almost exclusively manufactured by variants of the modern furnace black process. The remaining 7% was consumed in specialty applications like color pigments, antioxidants, light stabilizers, and fillers for electrically and thermally conducting plastics or elastomer composites.

Depending on the application, carbon black has special property profiles that are specifically defined by the nature of the industrial production process and by varying the process parameters. This aspect distinguishes carbon black from soot which is the term used for mostly undesired carbon by-products from incomplete combustion of carbonaceous materials in heating systems, engines, and furnaces. The incomplete combustion also creates oily residues that may be found in the soot as well as polyaromatic hydrocarbons (PAH) absorbed at the soot surface and being potentially carcinogenic. The polluting and harmful effects have brought soot to the attention of public authorities such that the formation and emission of soot are increasingly restricted by legislation. Nevertheless, the increasing public environmental concerns and stricter regulations for pollution and energy and fuel consumption as well as for emission of climate-changing gases have also triggered the improvement of carbon black manufacturing technology. In this regard, more efficient manufacturing processes with an improved combustion and higher yield as well as the recovery of heat and chemical energy created as by-product of the carbon black production have become the objective of recent process development activities.

## Carbon Black Manufacturing

### Principles of the Carbon Black Formation

Carbon black is formed in the gas phase by the thermal decomposition of hydrocarbons. These can come from a variety of sources depending on availability and economics. Carbon black feedstock can be of carbochemical origin, such as coal tar oil, anthracene oil (creosote), soft pitch, coal tar, and mixtures thereof or can be of petrochemical origin such as decant oil, aromatic crude oil concentrates, steam cracker, or cat cracker oils. The principle process can be thought of the following steps: (i) feedstock heating and vaporization, (ii) thermal decomposition of the hydrocarbon into small carbon fragments and hydrogen, and (iii) growth of these fragments into the carbon black particles and aggregates with further hydrogen formation. While there are numerous process variants, they can be divided into two categories according to the absence or presence of oxygen in the thermal decomposition reaction and how the energy required for the heating of the feedstock and the endothermic decomposition of hydrocarbon is generated (Vohler et al. 1977; Dannenberg 1978; Lyon 1985; Kühner and Voll 1993; Wang et al. 2004):

(A) Thermal decomposition of hydrocarbons in the absence of oxygen
The thermal decomposition of hydrocarbon is carried out in closed systems, and two major processes belong to this category: the thermal black and the acetylene black process. The thermal black process is discontinuous and runs cyclically in two separate process steps. In the first step, the energy for the thermal decomposition of the feedstock is generated by the complete combustion of fuel like natural gas or oil without formation of any carbon black. In the second step, the feedstock is injected in the hot reactor and the thermal decomposition and carbon black formation occur. The acetylene black process is based on the exothermic decomposition of acetylene gas into acetylene black and hydrogen occurring above ca. 800 °C. The process reaction is initialized by burning acetylene gas with air. Once the reaction temperature is reached, the acetylene decomposition to carbon black and hydrogen is self-sustaining and runs continuously.

(B) Thermal–oxidative decomposition (incomplete combustion)
Here, the energy required for carbon black formation is provided by combustion of fuel or part of the feedstock by carefully controlling the air deficiency and the flow conditions in the reactor. Two principal processes can be distinguished, depending on the type of gas flow involved. The furnace black process produces carbon black in a turbulent flow environment of a closed reactor system with appropriately designed flow. The feedstock is injected in the hot off-gas providing the energy for the thermal decomposition of the feedstock from the combustion of fuel or feedstock in the combustion zone of the reactor. The gas black process (and historic channel black process) is operated with a diffusion flame generated by combusting oil or natural gas feedstock in a reactor system being open to the outer air atmosphere. Normally, the decomposition products are

burned as soon as they reach the outer zone of the diffusion flame containing sufficient oxygen. If a cooled object (typically water-cooled rollers) is put inside the flame where the oxygen diffusion rate is lower than the rate of the decomposition reaction and thus carbon particles are formed causing the flame to glow, the combustion is reduced, and carbon particles are deposited at the cooled surface.

The thermal–oxidative process is by far more important than the thermal decomposition process in the absence of oxygen and accounts for more than 98% of carbon black production worldwide. Also the traditional lampblack process carried out in a closed system falls in this category.

The carbon black formation seems, although not yet fully elucidated, to follow a basic formation mechanism consisting of different steps for the carbon black growth which essentially applies for all types of manufacturing processes (Bansal and Donnet 1993a; Taylor 1997; Bourrat 2000):

1. Vaporization of the feedstock (in the case of an oil feedstock) and fragmentation of the hydrocarbon molecules down to $C_1$ or $C_2$ units by the energy generated in the process.
2. Precipitation of nuclei or growth centers for the primary carbon particles from recombining fragments.
3. Growth of the nuclei to primary particles by deposition of carbon around the growth centers.
4. Possible adhesion of the primary particles and fusion to complex aggregates by deposition of pyrolytic carbon onto the aggregate surface (secondary particle growth).
5. Agglomeration of the aggregates (cyclic growth) may occur for some carbon black types.

This mechanism explains the carbon black morphology and determines the primary carbon black properties including primary particle size, porosity, aggregate shape, aggregate size, as well as surface morphology. From these primary properties, secondary properties such as carbon black structure (void volume), specific surface area, surface energy, volatile content, electrical and thermal conductivity, and compressibility can be derived. The carbon black morphology and surface chemistry are controlled by the manufacturing process and process conditions.

## The Furnace Black Process

The furnace black process is the most modern process for the manufacture of carbon black today. It is a continuous process in a closed reactor system and therefore is flexible, economical, and less polluting. High turbulent flow prevails due to high flow velocities. Due to its importance for large-scale industrial production of carbon black for polymer fillers, the furnace black process is described in more detail in the following section.

The gaseous or liquid fuel is completely converted with air in the combustion chamber of the reactor to combustion off-gas with temperatures ranging from 1,200 °C to 1,800 °C. The reactor and throat are made of refractory linings. In the mixing zone, the preheated feedstock is injected in the hot off-gas before entering in the reaction zone of the reactor where the atomization and vaporization of the feedstock are completed. Thermal decomposition (pyrolysis) of the feedstock and the carbon black growth occur in the reaction zone. Here, the competing reactions of nucleation and particle growth are controlled by process parameters such as reaction temperature, feedstock loading rate, and residence time so that the carbon black is produced with the desired morphological property profile. High reaction (flame) temperature, low feedstock injection rate, and short residence time (short quench) favor small particle sizes (high surface areas). High feedstock/air ratios reduce the concentration of feedstock vapor and lead to lower carbon black structures. Additives can also be introduced into the flame to help with morphology control. The reactor off-gas (smoke gas) formed during conversion of the feedstock to carbon black contains CO, hydrogen, and steam which, at the temperature level of the reaction zone, react with the carbon black. These occurring water–gas and Boudouard reactions reduce the yield of carbon black. To stop these side reactions, the process gas mixture after a certain residence time is quenched by water injection. The temperature of the reactor off-gas containing the carbon black is further cooled by heat exchangers at the reactor exit. Cooled down to a temperature below 400 °C, the carbon black is separated from the tail gas by bag filters. About 50–60% of the feedstock is converted into carbon black. The balance is converted into combustible tail gas that can be used as a fuel source in the plant due to its high content of carbon monoxide, hydrogen, and methane.

The carbon black discharged from the filters is conveyed pneumatically to other sections for further processing. Grit and magnetic separators are used to purify the carbon black from contaminants such as coke particles (“grit”), abraded particles from the refractory lining of the furnace, or rust particles. The furnace process produces fluffy, low-bulk density powders that are difficult to transport and handle. One of the key steps is the conversion of these into high-bulk density, but still free-flowing, powders. This is usually carried out by a wet pelletizing process with water and must be controlled so that the pellets are strong enough to survive transport and handling, but weak enough to break down easily in their final application. The carbon black pellets are dried and then packed. The waste gas is the final off-gas after all combustibles have been burned. A schematic process flow chart is given in Fig. 1.

## Dual-Phase Blacks

Products known as dual-phase blacks were developed and commercialized in the 1990s, notably by Cabot Carbon. This was largely in response to the threat from precipitated silicas in tire tread applications. These products are produced by

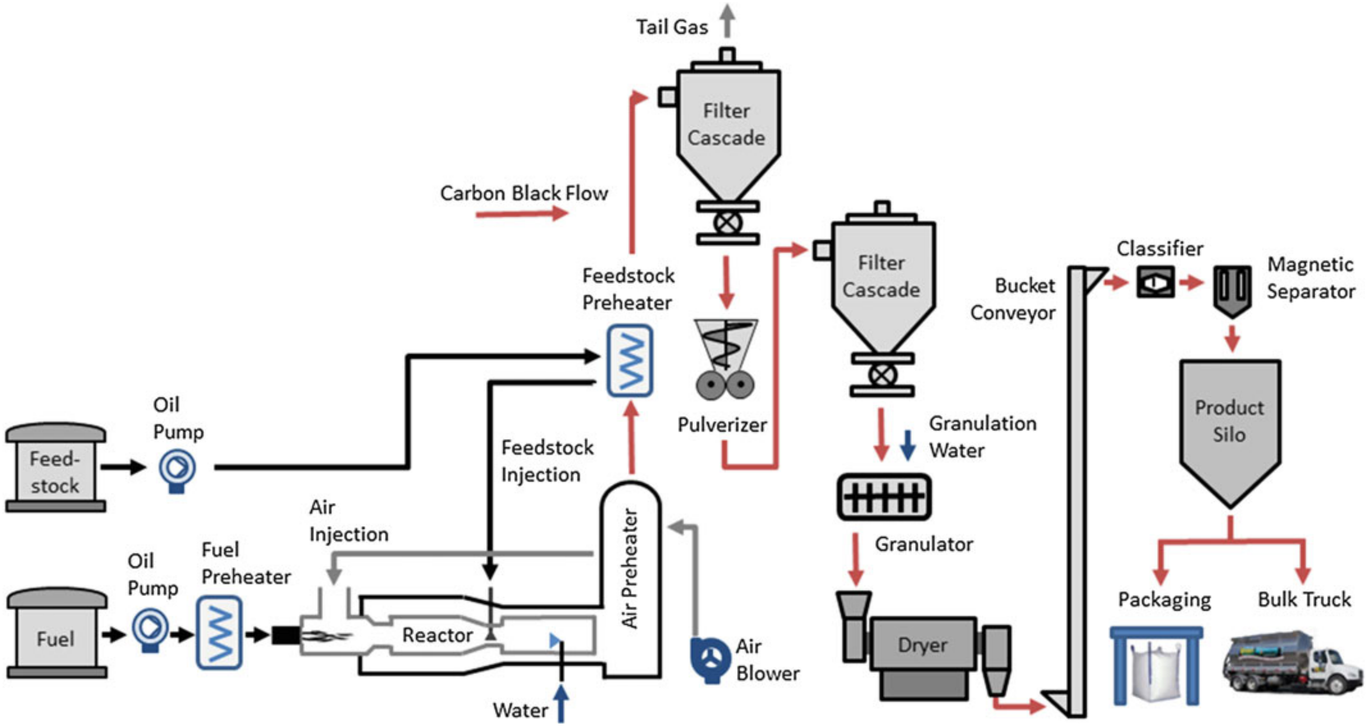


**Fig. 1** Schematic process diagram of the furnace black process (adapted from The Carbon Black Users Guide, The International Carbon Black Association, 2004, p. 5)

co-fuming hydrocarbon feedstock with a silica precursor which is typically an organosilicone compound such as octamethyl cyclotetrasiloxane. If the procedure is correctly carried out, then the aggregate particles are an intimate combination of silica and carbon black domains rather than a mixture of separate discrete silica and carbon black particles. Obviously, many variations of overall size and shape, of silica content, and of the distribution of silica within the aggregates are possible. It is also much easier to functionalize the surface in various ways, using the silica as the reactive point. These dual-phase products are claimed to give improved performance in some applications, especially tire treads.

### Surface-Modified Blacks

Posttreatment to modify the surface of carbon blacks is little practiced in the conventional filler applications, but has been used for a long time in some of the other areas (e.g., oxidation to increase porosity and introduce acidic functionality). A recent introduction has been carbon blacks that have had organic groups grafted to the surface by using diazotization. These can be used as such or as a means of attaching further functionality. The drive for improved tire tread performance has led to interest from at least one producer in use of treatments such as ozonization. This is for use with special functionalized elastomers, which typically contain carboxylic acid groups that can react with the surface groups introduced by ozonizing.

### Unconventional Sources

Sustainability issues are growing within the tire industry and also on the material suppliers to that industry. As one of the largest tonnage components, this very much affects carbon black. Nonoil feedstocks are being developed, as well as regeneration of carbon blacks by rubber pyrolysis. This is in its infancy, but will be of increasing importance.

## Carbon Black Properties

### Terminology of the Morphological Properties

Particle size and its distribution play a particularly important role in carbon blacks used in polymers and are quite a complicated subject with different types of size being referred to. The main classification is into three size types: primary particle, aggregate, and agglomerate. Primary particle size refers to the basic building block particles formed before collision leads to sticking and growth. These primaries rarely exist as such in polymer-grade blacks, but are an important concept and largely determine the specific surface area. Aggregates are the main effective particle in polymers. These result from partial fusion of primary particles and from further overgrowth and are strong enough to remain as discrete particles, instead of breaking

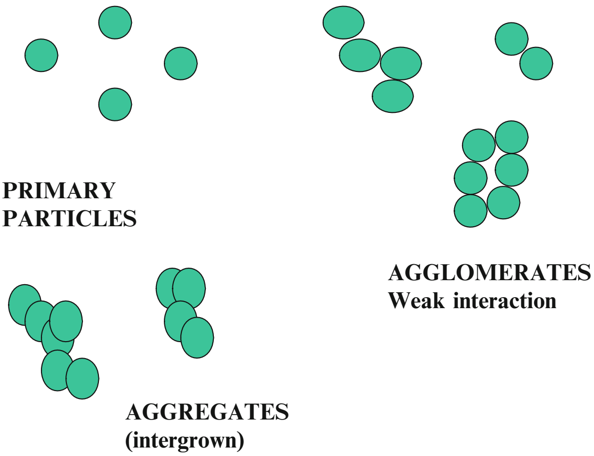


**Fig. 2** Primary particles, aggregates, and agglomerates

down to primaries even under the influence of high shear during dispersion. The largest level of size is due to agglomerates. These are collections of aggregates, but with no intergrowth and only physically held together, so that they are fairly easily separated. The main effect of these is on powder handling properties including bulk density, dustiness, and dispersion. The pyrolysis process naturally gives small, weak agglomerates with low bulk density and high dustiness, and various methods are used to increase agglomerate size and strength. These issues are illustrated in Fig. 2.

The complex arrangement of primary particles in the aggregates and agglomerates is called carbon black structure. Unfortunately, it is an ambiguous term as it implies chemical structure. To distinguish carbon black structure with the atomic arrangement of the carbon in the primary particles, the term microstructure was introduced for the latter.

## Carbon Black Microstructure

Carbon black materials can be distinguished from other carbons by their aggregates of mostly spherically shaped primary particles with diameters that may range from about 10 nm up to several hundred nanometers. There are many levels of morphology to be considered. The first is the atomic structure within these primary particles defining the so-called carbon black microstructure (Hess and Herd 1993). For most of the carbon black types, this can be described by the *paracrystalline model*, with continuous layers of hexagonally arranged carbon atoms forming the basic building blocks. Inside the primary particles, the carbon layers are concentrically arranged around one or more growth nuclei resulting in adjacent layers oriented parallel to each other. The order between these parallel stacked layers is described as turbostratic, i.e., the carbon layers are stacked parallel but rotated around the crystallographic c-axis. X-ray diffraction and high-resolution transmission electron microscopy (HRTEM) methods, like phase-contrast HRTEM, have been used to

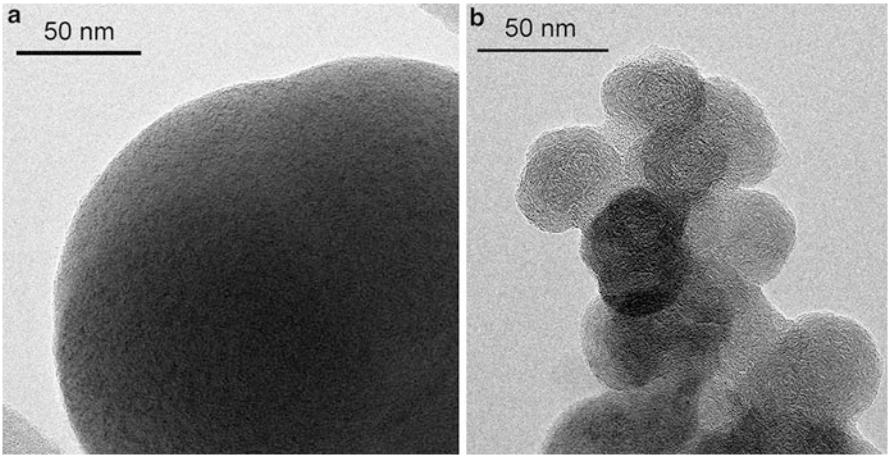


**Fig. 3** HRTEM images of primary particles of N990 (**a**) and N330 (**b**) carbon blacks

study this carbon black microstructure. Typical carbon blacks show an interlayer distance of 0.350–0.365 nm as compared with 0.3354 nm for graphite, indicating the turbostratic order of the carbon layers in carbon black (Medalia 1982). There are significant differences between carbon black types with regard to the sizes and quality of the stacked carbon layer domains (extent of the "aromatic" structural units) in the primary particles. Bourrat et al. classified different sizes of layers and their mode of stacking in four different categories based on the average stacking height ($L_c$) of the carbon layers and the size of the layer planes ($L_a$) (Bourrat 2000):

(i) Small isometric coherent domains with La ≈ Lc (isometric turbostratic piles)
(ii) Columnar turbostratic stacking with La < Lc (columnar turbostratic piles)
(iii) Wavy turbostratic stacking (large distorted layers)
(iv) Planar graphite layers (large straight layers)

In Fig. 3, HRTEM images illustrate two examples of the microstructure extremes observed for carbon black materials. The microstructure of N990 can be considered as amorphous, whereas the microstructure of N330 shows the frequent paracrystalline behavior with continuous carbon layers concentrically arranged around a growth center. Continuous carbon layers are also the reason for the stability of the aggregates as they overgrow arrangements of primary particles leading to strong covalent bonds between these primaries.

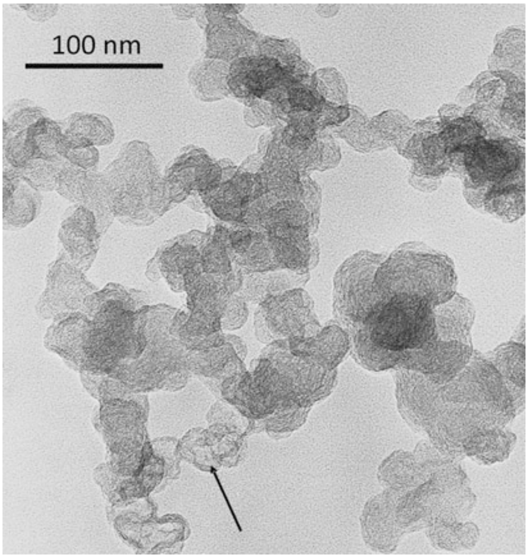
## Primary Particle Size and Porosity

The next consideration is the primary particle diameter (fineness) which is used to describe the primary particle dimension. Carbon black primary particle size is usually determined by electron microscopy. Specific surface area (SSA) is also widely used as a descriptor of particle size. The primary particle size can be approximately derived from the specific surface area assuming ideally spherical particle shapes and neglecting any particle porosity. A linear correlation between primary particle size and specific surface area is valid for carbon black grades with a specific surface area lower than about 150 $m^2g^{-1}$ as usually no porosity occurs in the primary particles of such materials.

Porosity is an important parameter for carbon blacks and needs careful definition. In the carbon black context, it refers to the presence of small holes, cavities, or channels in the particles themselves, as illustrated in Fig. 4. It does not refer to the space between the particles, despite this often being called void volume, which can give the impression that it refers to porosity. The first subdivision of porosity is into closed and open pores. Closed pores are entirely within the solid phase with no outlet to the exterior, while open pores do have some external outlet and may be at the surface or internal. Closed pores mainly affect the specific gravity of the particles and have little effect on other properties. They do not contribute to specific surface area. Open pores may or may not affect the specific gravity, depending on the method of determination. They do contribute to specific surface area, although this depends on the pore opening size and the size of the absorbing species being used for the measurement. Pores are conventionally divided into three types according to size: macropores with sizes >50 nm, mesopores with sizes between 2 and 50 nm, and micropores with sizes <2 nm.

Gas adsorption techniques such as the nitrogen adsorption method based on the theories of Langmuir and of Brunauer, Emmett, and Teller (BET) are applied to measure the total surface area (ASTM D6556). Nitrogen adsorption allows

**Fig. 4** HRTEM images of primary particles of extra-conductive ENSACO® 350G (BET SSA of 780 $m^2/g$) indicating pores in the primary particles (*arrow*)



measurement of the total specific surface area comprised of the geometrical surface area of the primary particles, open porosity, and surface morphology. Alternative techniques are the adsorption of iodine (ASTM D1510) or cetyltrimethylammonium bromide (CTAB) (ASTM D3765). The iodine number is expressed in milligrams of iodine per gram of carbon black and hence is not a true surface area value. However, the iodine number and nitrogen gas adsorption provide the same surface area as long as the iodine adsorption is not affected by porosity, surface chemistry, and impurities. Unlike nitrogen, the larger iodine molecules do not penetrate into small pores. In addition, oxide groups and hydrocarbon impurities at the carbon surface depress the iodine number. Due to the huge steric extension of the CTAB molecule, the CTAB method basically eliminates any contributions to the measured surface area from porosity but normally remains unaffected by the surface chemistry and therefore gives the best correlation with the primary particle size. For nonporous carbon black, the ratio of the specific BET surface area (BET SSA) or iodine absorption and the specific CTAB surface area (CTAB SSA) is roughly unity. An iodine/CTAB ratio of less than unity indicates surface impurities or surface oxides and greater than unity indicates the existence of open porosity (Kühner and Voll 1993). Real density measurements with different media can be used to distinguish internal closed porosity from open porosity.

## Aggregate Size and Shape and Carbon Black Structure

Aggregates play a critical role in most carbon black polymer applications, with their size and shape both being important. The term "structure" is frequently used to describe it. These days, the term structure occurs in two distinctly different ways when referring to carbon black. One relates to the size and shape of the aggregates and agglomerates and is often referred to as permanent structure, while the other refers to carbon black network built up between carbon black particles when they are in the polymer and is regarded as transient. Here, we only discuss the permanent structure, while the transient one is discussed later.

The carbon black aggregates arise because especially small primary particles formed during the early stages of carbon black production do not survive in isolated form but fuse together to form discrete, rigid colloidal entities of various sizes and shapes (Hess and Herd 1993; Taylor 1997). These are described as carbon black aggregates and are the smallest dispersible units composed of the extensively coalesced, nondiscrete primary particles which are separable from the aggregate only by rupture. Continuous carbon layers coat the coalesced primary particle units and in this manner connect them by strong covalent bonds to form rigid aggregates. The size and shape of the aggregates can vary from individual spheroidal particles to clusters of a few or a multitude of primary particles with a more or less irregular three-dimensional, chain-like, fibrous, or grape-like morphology. Usually, the tendency to form aggregates decreases with increasing primary particle size. Carbon black grades with large primary particles above 100 nm usually show low structure, and even isolated primary particles can occur (Figs. 5 and 7).

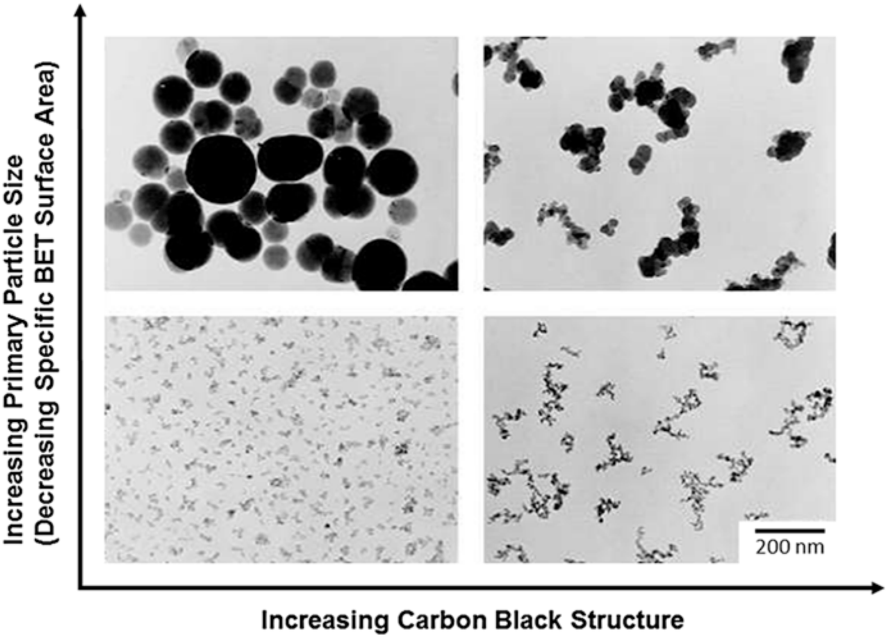
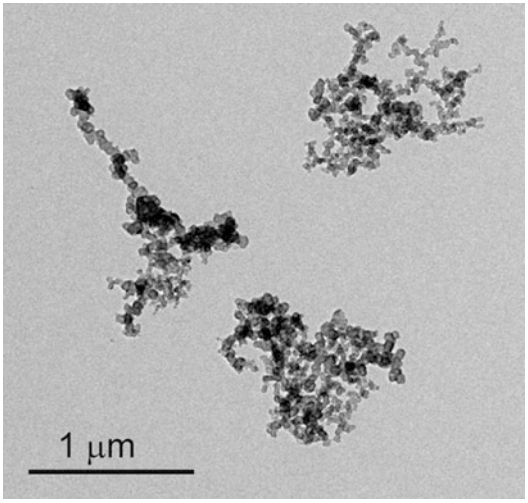


**Fig. 5** TEM images of carbon black grades indicating the relationship between carbon black structure and primary particle size (adapted from Lei et al. 2014)

**Fig. 6** TEM image of agglomerated carbon black aggregates of ENSACO® 250G indicating a high carbon black structure



Usually, the aggregates go on to form agglomerates which are physically held together. The TEM image of Fig. 6 indicates agglomerated carbon black aggregates of high-structure ENSACO® 250G. Hence, the principal problems to characterize aggregate size and shape are: (1) dispersion, (2) measurement in two dimensions,

(3) conversion to three dimensions, (4) choice of the parameters to measure and compute, and (5) application to a sufficient amount of aggregates for statistical reliability (Medalia 1982). Most of the studies have been based on TEM techniques resulting in two-dimensional images that have to be transferred to three-dimensional images by the appropriate stereological method. Nonmicroscopic methods to measure the aggregate size are based on aerosol and liquid measurements (Bart and Sun 1985). Hereby, the disk centrifuge photosedimentometry (DCP) is the most common method. DCP measures the distribution of an aggregate diameter, the equivalent Stokes diameter being the diameter of a sphere of equal specific gravity which settles in a centrifugal field at the same rate in the same fluid as the aggregate.

Like other morphological properties, the aggregate shape is distributive in nature and can be classified by four aggregate shape categories (Hess and Herd 1993): (1) spheroidal (discrete particles rather than aggregates), (2) ellipsoidal, (3) linear, and (4) branched. Carbon black products show different weight fractions of all four categories. Highly structured carbon black grades typically contain a high weight fraction of branched aggregates. With decreasing carbon black structure, the fraction of spheroidal, ellipsoidal, and linear aggregates increases. TEM pictures of a low- and high-structure carbon black are shown in Fig. 7a, b; a schematic illustration is given in Fig. 8.

The complexity of the arrangements of the carbon black particles, aggregates, and agglomerates results in a void volume, and this can be used as a convenient way to compare the structure of different carbon black materials. The void volume depends on the size and shape of the aggregate, the aggregate agglomeration, and the porosity on the primary particles. Therefore, the carbon black structure can be considered as the sum of a number of accessible voids by unit weight which is composed of: (i) the interaggregate space, (ii) the interstices within the aggregates, and (iii) the porosity of elementary particles. The higher is the structure level of the aggregate, the higher is the volume of the voids.

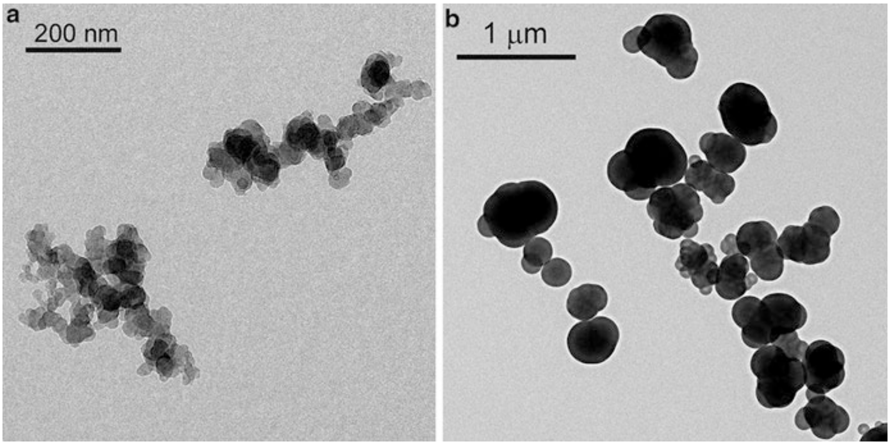


**Fig. 7** TEM images of aggregates of high structure N-472 with branched primary particle aggregates (**a**) and low structure N-990 with isolated spherical primary particles (**b**)

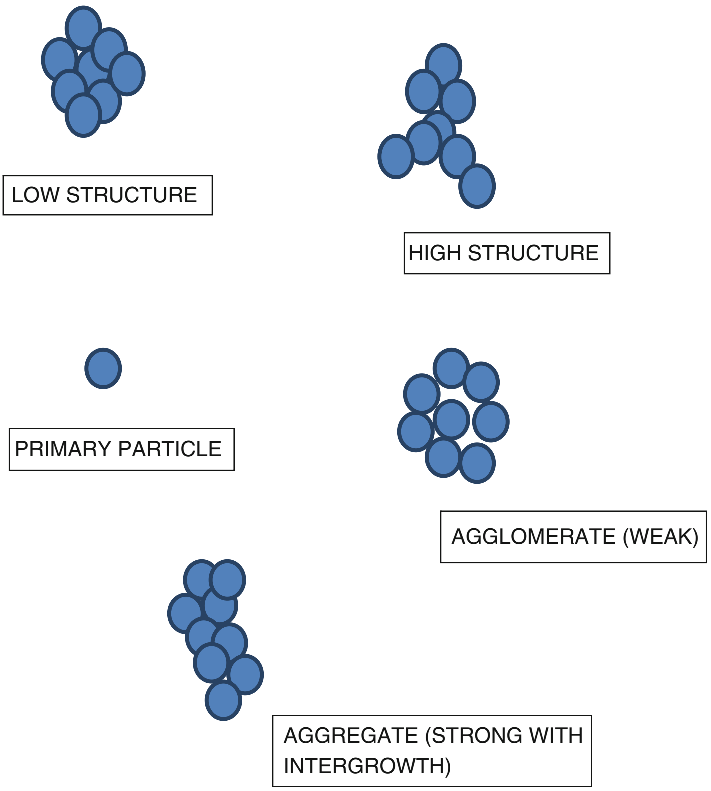


**Fig. 8** Schematic representation of low- and high-structure carbon black particles

Oil absorption is a simple method used to determine void volume and hence carbon black structure. In principle, many oils can be used, but the common ones are dibutyl phthalate (DBP) or a special paraffin oil (ASTM D2414). The DBP absorption (in mL $(100 \text{ g carbon})^{-1}$) is higher the more complex the structure of the carbon black aggregates is.

The carbon black structure is very sensitive to the state of compression of the carbon black. Important stages during carbon black production and processing that can cover a broad range of compression states are: (1) carbon black powder after the gas separation step in the manufacturing process, (2) densified carbon black flakes or pelletized carbon black, and (3) the polymer compound. The compressed oil absorption number (COAN) measured by ASTM D3493 at a given compression state is attributed to the difference in sensitiveness of the carbon black structure toward compression observed for different carbon black grades. A similar concept takes into account the mechanical resistance of carbon black to compression by measuring the decrease of void volume with increasing compaction pressure at a given weight (ASTM D6086).

## Surface Properties

The morphology of the surface is the final important property variable. Hereby, the surface activity describes the surface properties and is broadly defined as the tendency of the carbon black particles to interact with themselves and their surroundings. In polymers, more specifically elastomers where reinforcing effects are important, the surface activity dominates the polymer–filler interaction, filler–aggregate interaction, as well as the filler–ingredient interactions. In liquid systems like paints and inks, surface activity is more closely associated with the stability of the final coating dispersion and its rheology.

The surface activity in a chemical sense is linked to the surface group chemistry and surface microstructure. Surface heterogeneities given by graphitic planes at the surface, amorphous carbon, crystallite edges, and slit-shaped cavities all representing adsorption sites of different energies describe the surface microstructure. Also the nature and amount of surface functional groups attached to surface carbon control the interaction with the surrounding media. Oxygen functional groups at the surface being mainly carboxylic, quinonic, phenolic, or lactonic groups are subject to acidic reactions in organic solvents or aqueous media and affect the dispersion of carbon black during mixing. Such surface oxides can react as Lewis bases which may act as anchor atoms for Lewis acids. Higher molecular weight organic molecules may become adsorbed as impurities on the carbon surface during production. The qualitative and quantitative analysis of the surface groups is rather difficult especially if their amount at the surface is low. Chemical titration techniques, thermal desorption coupled with mass spectrometry, photoelectron spectroscopy, and time-of-flight secondary ion mass spectrometry are methods frequently applied for this purpose. The *volatile* content measured at 950 °C includes both the total amount of functional groups and the absorbed organics (Accorsi and Romero 1995). The *solvent extractable* content (ASTM D4527-99) measures the amount of the latter.

In a physical sense, the surface activity is linked to variations in surface energy that determine the absorptive capacity of the filler and its energy of absorption (Bansal and Donnet 1993b; Wang and Wolf 1993). The surface energy is the work being necessary to create a unit new surface of liquid or solid. This energy is caused by different types of cohesive forces, such as dispersive, dipole–dipole, induced dipole, and hydrogen bond forces. Inverse gas chromatography is today the most accurate way to measure the surface energy of carbon black.

The surface chemistry can, to some extent, be controlled by the process conditions, including additive additions. Some success has been achieved in increasing the extent and strength of polymer physical adsorption. This has been achieved by modifying the production process to increase the surface roughness and the amount of exposed crystallite edges. These blacks are known as nanostructure blacks. Many attempts have also been made to beneficially change the surface chemistry of carbon blacks by the use of modifiers. Historically, these have been largely unsuccessful, but have received recent impetus by the competition from silica in some tire formulations. Progress has now been reported, including polymer grafting of the surface. A related development is the dual-phase blacks where silica has been introduced into the structure thereby providing a surface receptive to modification.

### Solid Contaminants

Inorganic residues of refractory material, rust and metal particles from the process, and coke particles ("grit") formed during the carbon black synthesis are frequent sources of solid contaminants in carbon black. Even low levels of grit can have a significant deleterious effect on dynamic applications such as many filled rubber compounds. Metal impurities and anion impurities like halogenides, sulfates, nitrates, and phosphates are the most important impurities that occur in carbon black and could have an influence on the stability of the carbon black-filled polymer system.

### Electrical and Thermal Conductivity

Carbon black materials are semiconducting with intrinsic electrical resistivity values between $10^1$ and $10^{-2}$ Ω cm. For all carbon black types, the intrinsic electrical resistivity decreases with increasing applied pressure. A certain electrical resistivity level is usually achieved at lower volume density of the carbon black material the higher its structure is. Elevated resistivity values at high compression density observed for some of the carbon black materials could be explained by the microstructure or the high volatile content.

More details on this topic can be found in the ▶ Chap. 19, "Carbon Black for Electrically Conductive Polymer Applications".

### Typical Properties of Filler-Grade Carbon Blacks

Typical properties of furnace blacks used as polymer fillers are presented in Table 2.

## Carbon Black in Polymers

Carbon blacks find a number of uses in polymer composites with the main ones being reinforcement, pigmentation, electric conductivity, as well as light and heat stabilization. By far, the largest use is as a reinforcing filler in elastomers, especially

**Table 2** Typical properties of filler-grade carbon blacks

| | |
|---|---|
| Primary particle size [nm] | 20–65 |
| BET SSA [$m^2/g$] | 40–155 |
| DBP oil absorption [cc/100 g] | 50–150 |

for use in tires. This entry focuses especially on the reinforcement function of carbon black in elastomers. More details on use in elastomers can be found in the ▶ Chaps. 6, “Particulate Fillers in Elastomers”, ▶ 15, “Precipitated and Fumed Silicas and Related Products”. The main uses of carbon blacks in other polymer types (thermoplastics and thermosets) are for electrostatic dissipative and electrically conductive compound properties as well as for pigmentation and UV absorption. In thermoplastics and thermosets, the incorporation of carbon black, like other fillers, increases the rigidity and brittleness of the filled polymer which can be undesirable. Therefore, to reduce the deterioration of the mechanical polymer properties, the carbon black filler loading is minimized. Some more details on the UV absorption and pigmentation effect of carbon black can be found below and in other reviews (Funt et al. 1993; Taylor 1997); details about carbon black for conductive polymer applications can be found in the ▶ Chap. 19, “Carbon Black for Electrically Conductive Polymer Applications”.

## Reinforcement of Elastomers

### Carbon Black and Elastomer Interactions

The reinforcing properties of carbon black in elastomers have been extensively studied, with most of the groundwork carried out many decades ago. The work has been reviewed in several references (Boonstra 1979, 1982; Wolf and Wang 1993; Taylor 1997). Carbon black affects elastomer reinforcement by improving the mechanical strength as well as the wear and abrasion resistance. Carbon black makes rubber stiffer and less readily deformable under stress. Reinforcement of rubber is manifested by the increase in stiffness (tensile modulus and elongation), the improvement of the fracture properties (tensile strength, tear and abrasion resistance), and, with the exception of graphitized carbon black, the increased energy at rupture (the integrated area under the stress–strain curve). With an optimum loading of carbon black, the strength and rupture energy of an SBR gum vulcanizate may increase more than tenfold. Plastics which rely on strong secondary intermolecular forces for their strength are not reinforced by carbon black and other particulate fillers. The response to deformation of a rubber composite, i.e., the viscoelastic behavior, is influenced by: (1) the interaction between the rubber molecules, attraction, relative movement, and elastic recovery; (2) the interaction between the carbon black particles and the rubber molecules; and (3) the interaction between the carbon black particles.

### Interaction Between the Elastomer Molecules

The interaction between elastomer molecules is mainly determined by the chemical nature, the regularity and steric hindrance of the macromolecules, the mobility of their segments, as well as the presence of stable or transient cross-links and entanglements and loose ends in the vulcanizates. The relative segmental mobility of the polymer expressed by the glass transition temperature is only slightly influenced by a carbon black filler. The enormous tensile strength of a pure natural rubber is caused by the regular linear structure of the natural polyisoprene chain molecules, which on stretching above 400% elongation begin to crystallize where bundles of stretched-out chains run parallel. At break, up to one third of the elastomer can be in the form of crystallites which constitutes areas of extra-strong cohesion between the elastomer chains. It is important that chains arrange and rearrange themselves under tension to accommodate the stresses and thus distribute them uniformly and to be able to form these crystallites. The degree of cross-linking in a natural rubber vulcanizate is an important factor influencing the strength. Cross-linking is only needed in order to prevent plastic flow, thus permitting the molecules from becoming aligned by stretching and hence crystallizing. On the other hand, a highly cross-linked natural rubber is weak because the load required to stretch it is so high that the rubber is broken before the elongation becomes large enough to produce crystallization.

The crystallites carry out the same function as a reinforcing carbon black. Crystallizing rubbers such as natural rubber (polyisoprene), butyl rubber, and polychloroprene are self-reinforcing that cannot be significantly reinforced by carbon black in terms of tensile strength or high-elongation modulus, but beneficial effects of carbon black can be found on abrasion resistance at medium and high severity (e.g., tire treads during braking). The dramatic reinforcing effect of carbon black can be observed especially in the case of elastomers that do not crystallize under strain, e.g., the various butadiene copolymers like styrene–butadiene rubber (SBR) and nitrile–butadiene rubber (NBR) provided that the carbon black surface can be wetted by the elastomer.

### Interaction Between Carbon Black and Elastomer Matrix

The interaction between carbon black and an elastomer is evidenced by the phenomena of bound rubber and rubber shell formation as well as rubber occlusion. The incorporation of carbon black into a polymer creates an interface between a rigid solid phase and a soft solid phase. The interface area depends, for the mostly nonporous rubber-grade carbon blacks, on the volume fraction of the carbon black in the compound and specific surface area. The elastomer molecules can be absorbed onto the filler surface either chemically or physically. Bound rubber is the rubber portion in an uncured elastomer compound which, due to this absorption on the carbon black surface, becomes insoluble in ordinarily good rubber solvents and forms an insoluble gel with the carbon black filler termed as carbon gel. The soluble or extractable rubber is of lower molecular weight than the original rubber. The carbon gel contains all the carbon black particles or aggregates held together by strands of macromolecules attached to the carbon black surface and running from aggregate to aggregate forming an extremely loose network with the carbon black aggregates acting as multiple cross-links. A high percentage of bound rubber is indicative of high interaction activity and therefore is associated with a high degree of reinforcement by the filler. However, the cross-link density of the carbon gel is only a small fraction of that of a vulcanizate indicated by the high degree of swelling in, e.g., toluene or xylene observed for the rubber in this gel compared to the vulcanizate. The formation of bound rubber can be reduced by thermal treatment of the carbon black and completely disappear in the case of graphitized carbon black due to the deactivation of the surface.

Another result of the carbon black–elastomer interaction is the formation of a more or less immobilized layer or rubber shell surrounding the carbon black, in uncured compounds as well as vulcanizates, resulting from the restriction of the molecular motion of the rubber in the vicinity of the filler surface. This immobilization of rubber may also be related to increased entanglements due to filler–polymer attachments and can be confirmed experimentally.

Rubber occlusion explains the effect of the carbon black structure on the properties of the elastomer composite. When structured carbon black is dispersed in rubber, the elastomer portion filling the void volume of the carbon black aggregates and the elastomer portion located within the irregular contours of the aggregates are unable to fully participate in the macrodeformation. The partial immobilization of the occluded elastomer causes this elastomer fraction to behave like the filler rather than the elastomer matrix. Due to the occluded rubber phenomenon, the effective volume of the carbon black filler is increased considerably with regard to the stress–strain behavior of the composite. The ratio of occluded rubber volume and the solid volume of the aggregate depends on the crushed oil absorption number of the carbon black.

### Interaction Between the Carbon Black Filler Particles

Interactions between the carbon black filler particles are due to the existence of primary particle aggregates and the agglomeration of these aggregates by physical bonds. In contrast to isolated carbon black primaries that are practically completely incompressible and show a negligible deformation, high-structure carbon black exhibits a large amount of elastic recovery. The carbon black network which exists in a rubber vulcanizate containing about 50 parts per hundred (phr) of high-structure carbon black is broken at rather small deformation (about 5% in unidirectional elongation) and loses most of its elasticity. However, the network reforms after sufficient rest time and is assumed to play a part in the hysteresis losses of the vulcanizate under cyclic larger deformation: the fragments of the network continue to be broken and reformed. Under severe attrition conditions, the stronger, covalently bound particle aggregates themselves may break. The electrical conductivity of the elastomer composite follows the same pattern as the elastic modulus. At low amplitude, when the carbon black network is still intact, conductivity is high, but it diminishes rapidly at higher amplitudes in conjunction with the elastic modulus as the carbon black network is broken.

### The Effect of the Carbon Black Properties on the Elastomer Reinforcement

All the key particle properties, primary particle size (BET SSA), structure, and surface activity, are important for elastomer reinforcement plus the degree of dispersion achieved and the carbon black loading used in the elastomer composite.

### Carbon Black Loading

There is an optimum loading observed for reinforcement properties such as tensile strength and tear and abrasion resistance, whereas stiffness increases steadily and elongation decreases with increasing loading. The optimum loading varies for different carbon black grades and elastomers. Up to the maximum for each grade, the increase of the number of carbon black aggregates contributes to an increase in the length of the rupture path which enhances the strength. The optimum occurs because the increasing interface created between the carbon black and rubber while increasing the carbon black amount is counteracted and finally dominated by restrictions concerning the ability to wet effectively the carbon black aggregates with polymer. Therefore, further increases of the carbon black loading beyond the optimum simply create flaws initiating the onset of the tensile failure.

### Particle Size

The primary particle size is directly related to the surface area interacting with the polymer matrix. As most of the pores, cracks, and cavities on the surface of the primaries are not accessible to the polymers, they do not contribute to the reinforcement effect. Therefore, the CTAB surface area specifically measuring the external surface area of the carbon black is more significant for the interacting surface than the BET SSA. The external surface area increases with decreasing particle size. A convenient relationship used to estimate the surface area (SA) from the particle diameter (d) of a nonporous carbon black is $SA = 32{,}000/d$. Typical carbon blacks for the reinforcement of elastomers are nonporous and have primary particle sizes between 20 and 65 nm. Porous particles tend to absorb accelerator and therefore retard the vulcanization. In principle, decreasing particle size (increasing surface area) improves the reinforcement. Tensile strength and modulus (stiffness) and tear and abrasion resistance increase, while elongation and resilience decrease. The drawbacks of small-particle-size carbon blacks are the higher heat buildup in the tire and the compound processing: reduced scorch time leads to poor process stability; the Mooney viscosity and incorporation time in the rubber increase, while the loading capacity in the rubber and dispersibility decrease.

The effect of primary particle size is further illustrated in Table 3. It can be seen that the tensile strength doubles on reducing primary particle size from 180 to 20 nm, while the abrasion resistance increases over sixfold.

### Surface Activity

The surface activity of carbon black is the prerequisite for the carbon black–elastomer interaction. Whether chemical or physical nature of the interactions prevails depends on the elastomer type. In some cases, strong chemical bonding between the carbon black and elastomer even could be counterproductive. The influence of the surface activity on the reinforcement properties can only be clearly demonstrated by deactivating the carbon black surface by a thermal treatment above 1,500 °C in an inert atmosphere. Under these conditions, the surface groups are

**Table 3** The effect of carbon black primary particle size on tensile strength and laboratory abrasion resistance in a sulfur-cured SBR compound (adapted from Boonstra 1982)

| | Relative tensile | Relative abrasion |
|---|---|---|
| Primary particle size (nm) | Strength | Resistance |
| 20 | 1.00 | 1.00 |
| 28 | 0.89 | 0.74 |
| 39 | 0.72 | 0.47 |
| 49 | 0.64 | 0.41 |
| 70 | 0.58 | 0.35 |
| 180 | 0.50 | 0.16 |

**Table 4** The effect of carbon black surface activity on compound properties, as demonstrated by graphitization of ISAF carbon black (N220) (adapted from Boonstra 1982)

| Elastomer property | Unmodified ISAF black | Graphitized ISAF black |
|---|---|---|
| Surface area [$m^2g^{-1}$] | 108 | 88 |
| Oil absorption [mL $(100\ g)^{-1}$] | 133 | 154 |
| Mooney viscosity [100 °C] | 40 | 44 |
| Bound rubber [%] | 18 | 1 |
| Hardness IHRD | 68 | 65 |
| Tensile strength [MPa] | 27.4 | 22.5 |
| 300% modulus [MPa] | 10.3 | 2.9 |
| Elongation at break [%] | 630 | 750 |
| Abrasion loss [$cm^3$ per $10^6$revolutions] | 67 | 142 |
| Hysteresis | 0.204 | 0.297 |
| Dispersion [%] | 99 | 98.2 |

cleaved, and a recrystallization starting from the particle surface occurs, while the surface area and carbon black structure remain unchanged. Some effects of a deactivated surface on the reinforcement properties are illustrated in Table 4 for the case of an ISAF black (N220) before and after graphitization. Deactivating the surface by graphitization is seen to have significant negative effects on many properties, with the largest being on 300% modulus, abrasion loss, and hysteresis, whereas tensile strength only decreases by about 17%. One of the possible explanations given for the graphitized carbon black surface is the existence of a rather uniform absorption energy over the entire surface with only small ripples which are in the order of magnitude of the kinetic energy RT (ca. 2.5 kJ mol at room temperature). Absorbed molecules can move freely over the surface since the required activation energy is in the order of the kinetic energy of a free molecule. In contrast, the untreated surface of the carbon black comprises a number of adsorptive sites of varying energy content superimposed on a uniform surface of a relatively lower but absorptive capacity. This unique property of the carbon black surface could be responsible for its reinforcement of hydrocarbon rubber.

### Carbon Black Structure

The occlusion of elastomer molecules described above as carbon black–elastomer interaction is a consequence of the carbon black structure. The main effects associated with filler permanent structure are illustrated in Table 5. The carbon blacks used here are of similar specific surface area (and particle size), but differ significantly in oil absorption and hence structure. They both dispersed equally well in the elastomer. Some properties are little affected by the changes in structure, notably tensile strength and abrasion loss, but others show significant effects. With respect to processing, compound viscosity and the incorporation time in the rubber matrix increase, while extrusion shrinkage decreases and extrusion smoothness increases, and loading capacity and scorch time decrease with increasing COAN; these effects are consistent with the concept of occluded rubber mentioned earlier. High extension modulus increases, while elongation decreases with increasing structure, again consistent with occluded rubber.

The carbon black structure is responsible for the interactions between the carbon aggregates in the elastomer compound. These interactions can be evidenced in the cyclic deformation of carbon black-filled vulcanized rubber in compression or shear at various amplitudes or frequencies discovered by Payne. The Payne effect describes the elastic dynamic modulus which at very small amplitudes is high but then drops very rapidly as the amplitudes increase, to level off at the highest amplitudes. The effect is reversible provided enough time is allowed for recovery. The effect is more pronounced at higher carbon black loading; as concentrations decrease, it becomes less noticeable. The higher modulus at low strains is caused by the elastic deformation of the network formed by the carbon black aggregates. In the case of fumed silica where aggregates are well known to form, due to the hydrogen bonds between the particles, particle networks with higher strength, the Payne effect is even more pronounced. The dynamic properties of filled elastomers are described below in more detail.

**Table 5** The effect of carbon black structure on elastomer properties (adapted from Boonstra 1982)

| | Normal structure | High structure |
|---|---|---|
| Property | Carbon black | Carbon black |
| Filler-specific surface area ($m^2g^{-1}$) | 108 | 116 |
| Filler oil absorption ($cm^3$/100 g.) | 133 | 172 |
| Mooney viscosity (ML (1 + 4) 100 °C) | 73 | 83 |
| Extrusion shrinkage (%) | 40 | 30 |
| Dispersion rating (%) | 99 | 99 |
| Hardness IHRD | 68 | 73 |
| Tensile strength (MPa) | 27.4 | 26.5 |
| 300% modulus (MPa) | 10.3 | 14.7 |
| Elongation at break (%) | 630 | 450 |
| Abrasion loss ($cm^3$ per $10^6$ revolutions) | 67 | 62 |
| Hysteresis | 0.20 | 0.24 |

**Table 6** The direction and magnitude of the effects of the main filler properties on those of filled elastomers (adapted from Boonstra 1982)

| | Filler property | | | |
|---|---|---|---|---|
| Elastomer property | Particle size (Decreasing) | Structure (Increasing) | Dispersion (Increasing) | Interaction (Increasing) |
| Hardness | ++ | ++ | - | + |
| Tensile strength | ++ | LITTLE | + | + |
| 300% modulus | + | ++ | LITTLE | ++ |
| Elongation at break | - | – | ++ | - |
| Tear resistance | ++ | LITTLE | LITTLE | LITTLE |
| Hysteresis | ++ | + | - | – |
| Abrasion resistance | ++ | + | ++ | ++ |

Notes: + and ++ mean increase in that property and - and – mean a decrease. They do not mean that the change is beneficial or detrimental. This depends very much on the application. For instance, high hysteresis is good for sound damping, but bad where heat buildup has to be avoided

The effect of carbon black key particle properties on a number of important reinforcement properties of the elastomer composite is summarized in Table 6.

The main technical application where the reinforcement of elastomers is achieved with carbon black fillers is in tires. Table 7 lists the most common carbon black types used in tires, the ASTM designation, and key carbon black properties. Table 8 gives data for strength, abrasion, and wear for these carbon blacks in SBR composites.

## Dynamic Properties of Filled Elastomers

This subject deserves special treatment as it plays a vital role in many applications, especially in vehicle tires, which account for the majority of elastomer, and hence filled elastomer, applications. Only a brief description is given here. The reader is referred to ▶ Chap. 6, "Particulate Fillers in Elastomers" for more details.

Dynamic property testing involves repeated deformations with limited recovery times between them (e.g., compression and shear at various amplitudes and frequencies), and this can have a marked effect on performance. Energy losses during this repeated process are key issues and manifest themselves as heat and noise. In tire applications, this lost energy is of considerable significance for the fuel efficiency of a vehicle (through a property known as rolling resistance) and also for road grip. It will also manifest itself as heat buildup which is a frequent source of tire failure, especially for heavy vehicles.

It is with dynamic properties that transient structure becomes important. This is the network of loosely interacting filler particles which exists in the polymer matrix. These particles move together and apart as the matrix undergoes cyclic deformations, resulting in energy losses, the magnitude of which depend on how strongly the particles interact with each other.

## Reinforcement Mechanisms

Several mechanisms have been proposed to explain the reinforcement phenomena of carbon black in elastomers:

**Table 7** Main properties of typical carbon black grades for reinforcement of tires

| Name | Abbreviation | ASTM designation | Particle size range [nm] | BET SSA [$m^2g^{-1}$] | DBP/Crushed DBP [mL $(100\ g)^{-1}$] |
|---|---|---|---|---|---|
| Reinforcing carbon black | | | | | |
| Super abrasion furnace | SAF | N110 | 20–25 | 140 | 115/99 |
| Intermediate SAF | ISAF | N220 | 24–33 | 120 | 116/100 |
| ISAF-low modulus | ISAF-LM | N234 | 24–29 | 120 | 125/101 |
| High-abrasion furnace | HAF | N330 | 28–36 | 78 | 102/88 |
| Improved HAF, low structure | HAF-LS | N326 | 28–36 | 78 | 72/68 |
| Improved HAF, high structure | HAF-HS | N375 | 30–35 | 90 | 114/97 |
| Fast extruding furnace | FEF | N550 | 39–55 | 42 | 120/86 |
| General-purpose furnace, high structure | GPF-HS | N650 | 49–72 | 37 | 122/86 |
| General-purpose furnace | GPF | N660 | 50–60 | 35 | 90/75 |
| High-modulus furnace | HMF | N683 | 49–73 | 35 | 133/86 |
| Semireinforcing carbon black | | | | | |
| Semireinforcing furnace | SRF | N772 | 70–96 | 31 | 65/58 |
| SRF, nonstaining | SRF-NS | N774 | 70–96 | 28 | 70/59 |
| Fine thermal | FT | N880 | 180–200 | 14 | 35/– |
| Medium thermal | MT | N990 | 250–350 | 6 | 30/– |

- The improved abrasion resistance finds its origin in the high affinity of carbon black for hydrocarbon elastomers due to the significantly higher differential adsorption heat of natural rubber on carbon black at low concentration compared to the cohesive energy density of polyisoprene.
- The lag in the elongation response to an applied stress due to internal friction called hysteresis and observed in viscoelastic rubber systems is important because the stored mechanical energy is dissipated as heat. By replacing polymer with rigid, nondeformable carbon black particles, the elastomer compound is stiffened hydrodynamically. The compound becomes less elastic and the energy dissipation by heat is optimized. However, hysteresis is further increased by polymer occlusion in the carbon black structure, increasing the effective loading.
- During failure processes the failure path is directed toward the carbon black aggregates which act as stress concentrators in the polymer matrix. Carbon black aggregates therefore cause an increase in the total failure path through

**Table 8** Tensile and abrasion properties of SBR with carbon black at 50 phr

| Name | Abbreviation | ASTM designation | Tensile strength [MPa] | Relative laboratory abrasion | Relative road wear abrasion |
|---|---|---|---|---|---|
| Super abrasion furnace | SAF | N110 | 25.2 | 1.35 | 1.25 |
| Intermediate SAF | ISAF | N220 | 23.1 | 1.25 | 1.15 |
| ISAF-low modulus | ISAF-LM | N234 | 24 | 1.30 | 1.24 |
| High-abrasion furnace[a] | HAF | N330 | 22.5 | 1.00 | 1.00 |
| Improved HAF, low structure | HAF-LS | N326 | | | |
| Improved HAF, high structure | HAF-HS | N375 | 22 | 1.24 | 1.14 |
| Fast extruding furnace | FEF | N550 | 18.5 | 0.64 | 0.72 |
| General-purpose furnace, high structure | GPF-HS | N650 | | | |
| General-purpose furnace | GPF | N660 | 17 | 0.55 | 0.65 |
| High-modulus furnace | HMF | N683 | 16.1 | 0.56 | 0.66 |
| Semireinforcing furnace | SRF | N772 | 14.7 | 0.48 | 0.60 |
| SRF, nonstaining | SRF-NS | N774 | 15 | 0.48 | 0.60 |
| Fine thermal | FT | N880 | 12.6 | 0.22 | – |
| Medium thermal | MT | N990 | 9.8 | 0.18 | – |
| No filler | | | 3 | – | – |

[a] Standard

which break must grow before a catastrophic failure is possible, explaining the higher tensile strength by smaller-particle-size carbon black with more aggregates per unit weight.

- Many authors consider the phenomenon of mobile absorption in combination with the points of higher adsorption capacity as the basis for the unique reinforcement of rubber by carbon black. Rubber molecules are free to slip from one part and rebind to another active side at the carbon black surface. The mechanism is able to explain the stress softening (Mullins effect), i.e., the effect that after prestressing to a definite elongation and relaxing, a second extension needs lower stress up to the elongation of prestrain. The slippage could explain the negative temperature coefficient of the tension of a carbon black-filled vulcanizate and could contribute to their high hysteresis by dissipating the stored mechanical energy which otherwise would form and grow cracks. Typically, the effects of reinforcement (abrasion resistance and tensile strengths) and hysteresis are opposing, e.g., the use of a smaller-particle-size (higher surface area) carbon black causes an increase of the reinforcement but at the same time also an increase of the hysteresis which is an unwanted effect in tires. However, dynamic studies showed that large parts of hysteresis at practical deformation levels are due to the interactions between the carbon black aggregates, and by optimizing the carbon black aggregates and surface area, the aspects of reinforcement and hysteresis could be addressed independently.

## Carbon Black for Pigmentation

Carbon blacks are ideal black coloring pigments and are widely used as such. Only low addition levels are required. The pigmentary effects are a result of both light adsorption and scattering, and the balance of these is affected by both particle properties and the nature of the polymer matrix. Two distinct effects can be achieved: black (jet) coloration itself and modification of the color of other pigments (tinting). These two effects have a different dependence on the properties of the carbon black.

The blackness is a complex function of many effects with the main properties being primary particle size (specific surface area), aggregate size, and dispersion. Finer particles provide a higher amount of scattering centers per weight in a polymer volume for absorbing light, and they are more efficient at forward scattering of light and hence have a higher jetness. With smaller aggregate size, the backscattering decreases, while the forward scattering increases. Thus, lower-structure carbon blacks tend to be darker in color than higher-structure carbon blacks with the same particle size. A further property of importance is undertone or masstone. This results from the carbon black particles affecting the various wavelengths of light differently. This results in deviations from pure blackness and the color having blue to brown undertones. Also the “effective size” which the carbon black exhibits in the polymer dispersion affects the jetness. For a given carbon black, the smaller the size of the scattering centers is, the jetter and bluer a carbon black dispersion appears. The fact that large-particle-size carbon blacks have typically given bluer undertones than small-particle-size carbon blacks is related to their ease of dispersion so that the larger blacks may end up being better dispersed and thus the effective particle size is smaller.

The tinting effectiveness is measured by the tinting strength being the ability of a carbon black to modify the appearance of a white pigment. The tinting strength is largely a function of aggregate size and size distribution as, in general, decreasing particle and aggregate size increases tinting strength. The tint tone referring to the undertone imparted by carbon black usually is less blue due to the increasingly preferential absorption of the blue end of the spectrum as the particle size decreases.

## Carbon Black for UV Protection

Many polymers are unsuitable for outdoor use on their own because of rapid degradation through the action of visible light and especially UV light. In particular, in combination with ozone and other aggressive environmental chemicals, those components of the sunlight can cause an increased physical and chemical degradation rate. Carbon black absorbs both visible and UV radiation converting it to heat and thus makes an excellent stabilizer. In many cases, stabilities spanning decades can be obtained, making the polymers suitable for outdoor applications.

The main carbon black properties affecting UV stabilization are particle size, aggregate size, and surface chemistry. UV stabilization by carbon black in polymers depends on its ability to absorb and to backscatter light. While the absorption increases with smaller primary particles and aggregates, the backscattering decreases. This explains why UV stabilization tends to level off for primaries smaller than 20–25 nm with the accompanying small primary aggregates. Surface chemistry is also important, with oxygenated groups promoting the effectiveness. This is mainly through their action as radical scavengers, but they may also function as chromophores. As with pigmentation, only low addition levels are required and the effects plateau at about 3% loading. Typical end markets for carbon black used as a UV stabilizer are the wire and cable jacket markets, automotive plastic parts, plastic films for agricultural and industrial use, and plastic tubes and coatings in industrial applications.

## Dispersion

As we have seen, only low addition levels are necessary (typically 1–4% w/w) for pigmentation and UV adsorption. Good dispersion is, however, essential and is difficult to achieve with such low levels. For this and other reasons, carbon black–polymer concentrates, so-called masterbatches, containing much higher loadings are usually prepared first.

Dispersion of carbon black in the polymer matrix occurs by wetting the surface and breaking down the carbon black aggregates. High shear forces achieved by efficient mixing techniques are essential for good dispersion. High shear forces are often associated with higher viscosity systems which, however, may have poorer wetting tendency. The dominant carbon black properties for the viscosity of a carbon black-loaded polymer system are fineness, surface area, structure, and loading. Finer, higher-surface area, and higher-structure blacks yield higher viscosities than coarser, low-surface area, and lower-structure blacks.

Macrodispersion indicating the extent of dispersion down to a micron scale refers to clusters of nondispersed carbon black aggregates and is important for the letdown from a masterbatch. Detrimental aspects of poor macrodispersion on carbon black-containing products include reduced product service life, poor performance during service, poor appearance, and poor uniformity. Carbon black properties that relate to macrodispersion are fineness, surface area, and structure. Carbon blacks with smaller primary particle sizes and smaller aggregate sizes usually are more difficult to disperse due to the larger interfacial area that must be wetted and the reduced cross-section per aggregate over which shear forces can act to break up agglomerates. Also the hardness of pellets and grit contamination play a role for the dispersion quality. Microdispersion indicates dispersion on a size scale similar to the wavelength of visible light. Microdispersion is of primary importance to the development of color characteristics, UV protection, rubber reinforcement, and hysteresis. Structure and fineness as well as the compatibility of carbon black surface and the matrix are essential to good microdispersion.

## Future Directions

The carbon black industry will continue to be dominated by rubber applications, especially for the tire industry. As such, production will continue to move to the emerging economies. The products themselves are fairly mature, but still capable of fine-tuning. The main technical threat will continue to be that from precipitated silica where the producers are looking to increase their penetration beyond automotive treads. Environmental issues will also become important as tire makers strive to improve sustainability, energy and raw material efficiency of the manufacturing processes in the whole supply chain, and fuel economy of the tires by a further decrease of the rolling resistance. This is likely to dominate developments in various areas. Where carbon black is concerned, more efficient manufacturing processes with higher carbon black yields and the recovery of heat and chemical energy require the development of new innovative process technologies and the exploration of new feedstocks. Also the recovery or production from end of life tires could become a more important source of carbon black in the future.

## Cross-References

▶ Carbon Black for Electrically Conductive Polymer Applications
▶ Particulate Fillers in Elastomers
▶ Precipitated and Fumed Silicas and Related Products

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# Precipitated and Fumed Silicas and Related Products

# 15

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## Contents

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**Abstract**

Precipitated and fumed silicas are important, high-value, effect fillers mainly used in elastomers, sealants, adhesives, and surface coatings. They are amorphous materials, with primary particles in the nano-range and with high specific surface areas. The precipitated products are lower in cost and have the majority of the market in terms of volumes used. One of their most important applications is in fuel-efficient, energy, or green tires. The fumed silicas are an essential component of many silicone elastomer formulations. Both forms are excellent thixotropic agents for liquid systems such as surface coatings, sealants, and adhesives, with the fumed product being the most effective. Silica fume, a by-product from the manufacture of silicon and alloys, is a totally different product to fumed silica, although it is often confused with it and has very limited polymer applications today. Silica gels, which have much in common with precipitated silica, are used in a number of specialist polymer applications, including coatings and films. Surface treatments play a key role in many of the applications, with both functional and nonfunctional organo-silanes being widely used.

**Keywords**

Silica • Precipitated • Fumed • Gel • Production • Properties • Applications • Safety • Sustainability • Silanes • Rubber • Tires • Coating • Reinforcement • Microporous polymers • Rheology control • Thixotropy

## Definitions

The precipitated and fumed silicas used as fillers are very small particle, high specific surface area, forms of amorphous silica ($SiO_2$). As their names imply, the precipitated forms are made by precipitation processes from (aqueous) solution, while the fumed forms are made by gas phase (“combustion”) processes. Silica gels are produced in a similar way to precipitates and have some special applications. Fumed silica should not be confused with silica fume which is also known as micro-silica; this is a by-product of the manufacture of silicon and has very different properties and limited polymer applications. For some specialized applications, metal salts are included in the precipitation process making the related precipitated calcium and aluminum silicates which are also included here.

## Introduction

Precipitated silicas and silicates and fumed silicas can be produced as very small-sized particles and have a long and distinguished history as specialized effect fillers for polymer applications, especially for use in elastomers and surface coatings. The first commercial precipitated products were introduced in 1939 and the first commercial fumed silica in 1946. Along with carbon blacks, they can be considered as the earliest nanoparticle fillers. Silica fume is larger in size and finds limited polymer applications.

## Precipitated Silicas and Silicates

### General

The precipitated products are less costly to produce than the fumed ones and so find more widespread application. Their original development was spurred by the introduction of synthetic styrene-butadiene rubbers (SBR) during the Second World War. Unlike natural rubber, SBR is very weak when unfilled, or in the presence of coarse fillers, and requires very small filler particles if it is to achieve adequate strength. While carbon blacks fulfill this role well, there is a need for an equivalent white filler for many applications. This is where precipitated silicas come in; and they are often referred to as white carbon blacks.

Producing such fine particles in a form that allows for good washing (to remove coproducts) and ready redispersion is not easily achieved, and many variants were tried in the early days. The first commercial product was in fact a calcium silicate, as this was easier to make using the technology and knowledge available at that time. It was followed by aluminum silicate, and finally, more than a decade later, the first precipitated silicas themselves became available. The silicas now dominate, and there is almost no commercial use of precipitated calcium silicates, while aluminum silicate is now only found in niche applications.

Originally only one type of precipitated silica was recognized; today this has developed into two distinct classes: conventional (old technology) and easy or higher dispersing types. There has been a steady evolution of the higher dispersing types, and so a number of subdivisions such as easy dispersing (ED) and highly dispersing (HD) are met in the literature. The higher dispersing products were developed specifically for the demands of the tire industry.

### Production

Today, precipitated silicas are produced by reacting a sodium silicate solution with an acid, usually sulfuric acid, although many variants have been used in the past. The sodium silicate is usually produced by reacting sand with sodium carbonate (soda ash) to produce sodium silicate. A low sodium oxide content silicate solution is usually produced, as this minimizes the amount of acid which has to be added at the precipitation stage. The process is relatively expensive because of the energy involved in producing the two reagents and in dewatering and drying the fine particle product. For example, one manufacturer reports that 4–6 tons of water have to be evaporated for each ton of dry product. In some variants of the process, calcium or aluminum can be added to produce metal silicates.

The precipitation processes used industrially are designed to produce very small-particle, high-surface-area, and amorphous silicas and silicates. In common with most precipitation processes, the rate of reaction and form of the final product are influenced by many factors including temperature, reagent types and concentrations, rate and method of mixing, degree of agitation, presence of seeds (very small particles on which the new precipitate can form and grow), and impurities. By varying these factors, products with a wide range of particle size and specific surface area can be achieved. Careful control of process parameters is thus necessary, and the exact recipes used in commercial production are proprietary in nature. The underlying principles controlling the precipitation process have, however, been well described by Iler (1979a) and Patterson (1994).

In common with most fine particle production processes, washing to remove coproduct (e.g., sodium sulfate, when sulfuric acid is used as the precipitant) and then filtration and drying of the final product are important to both economics and to final form. Complete elimination of coproduct by washing is very difficult, and most commercial products contain some residual sulfate or chloride. Filtration and drying affect not only the economics but also the final product form, especially ease of redispersion. Removal of as much water as possible during filtration aids the economics (removal by heating during the drying stage is more expensive than removal by filtration) but can make redispersion more difficult. The best redispersability is achieved by processes such as spray drying (ultimately by using critical point drying, although this is not economically practical for filler applications). The higher cost of spray drying has limited its use in the past, but it has become of considerable interest more recently, because of the requirements of the tire industry and is used in the production of the easy and highly dispersing grades. This technology was pioneered by Rhodia (now part of Solvay).

While frequently used with surface modifiers in polymer applications, precipitated silicas have traditionally been produced uncoated, with any modifiers added during composite preparation (the “in situ” method). This has started to change recently, with most leading producers now offering some surface-treated grades, especially for tire applications, but the uncoated types continue to dominate the market.

The main producers of precipitated silica are given in Table 1.

**Table 1** Major precipitated silica producers

| Company |
|---|
| Evonik |
| Solvay |
| PPG |
| Huber |
| OSC/Tokuyama |

## Properties

Precipitated silicas are made up of small (10–30 nm) primary particles, aggregated into larger structures of complex shape. Because of their amorphous nature and high specific surface area, these products have a high absorbed water content (up to 7% w/w). In addition, the surface is highly hydroxylated, with the hydroxyls being equivalent to another 2–3% of water, although this is only released as such at much higher temperatures and does not contribute to the water content, as determined by conventional tests (e.g., drying at 105 °C).

This water plays an important role in polymer applications. It reduces the dustiness and appears to reduce particle/particle interaction, making dispersion easier. Both the absorbed water and surface hydroxyls are also important for reaction with the silane coupling agents frequently used in polymer compounds. On the other hand, the water often makes processing more difficult, as it has to be removed during compounding, if porosity is to be avoided during molding or extrusion. One little mentioned, but significant, advantage of all amorphous silicas is their relatively low specific gravity (about 2.0 for precipitated silica) compared with most other mineral fillers. Indeed, their specific gravity is not much higher than that of carbon blacks, and this is a distinct benefit in tire applications.

Because of their fine particle size and complex aggregate shapes, precipitated silicas in powder form have a low bulk density, usually about 0.2 kg per liter; as a result, they can also be very dusty. These problems are tackled by making densified and pelletized forms. While this sounds simple, it must be carefully carried out if the particles are to disperse readily in the final application. All the main producers offer such densified products, and they have been an important factor in the recent growth of the energy or green tire technology (see later).

For polymer applications, the very small size of the particles makes them most suited to elastomer use, where they can provide a similar reinforcing role to carbon blacks. Such applications require control over far more properties than is usual in the filler industry, and detailed measurements of size, surface characteristics, and aggregate structure are involved.

The main physical properties that are important are specific surface area and aggregate porosity. Specific surface area provides a guide to primary particle size. There are two measures of specific surface area in common use for fine fillers in the rubber industry: BET or nitrogen adsorption and cetyl trimethyl ammonium bromide (CTAB). The former uses a very small molecule (nitrogen) to access the surface, whereas the latter uses the much larger CTAB molecule. CTAB is regarded as being more representative of the surface available to the rubber molecules. As not all the surface detected by nitrogen is accessible to CTAB, the CTAB value is usually lower than the BET one.

Today, microporosity (a better term than the often used alternative of internal porosity, which wrongly implies closed pores) is also becoming an important parameter. This is usually determined by the difference in specific surface area when it is measured by the BET or nitrogen surface area method and the CTAB one. Microporosity is believed to be a good measure of ease of dispersion. Pore size distribution is also sometimes used as a guide to dispersability.

The primary particles of the precipitate are aggregated into secondary structures, and the porosity of these is of considerable significance for polymer applications. An old, but still useful, method for estimating the openness, or porosity, of the aggregates is the oil absorption test. In this test, a nonvolatile liquid which readily penetrates the pores is mixed with the precipitated silica until the mass loses its friable nature and can be molded into a putty. The oil absorption value is the amount of liquid just required to form this putty. Dioctyl phthalate (DOP) is often used as the liquid, and the results are usually expressed as milliliters of liquid per 100 g of powder. As mentioned above, precipitated silicas are subdivided into conventional, easy dispersing (ED), and highly dispersing (HD) grades. The more readily dispersing silicas are characterized by a more open structure, giving them a higher oil absorption. Thus, conventional precipitated silicas have dioctyl phthalate (DOP) oil absorption below 180 ml/100 g, ED silicas are in the range 180–200 ml/100 g, and HD silicas are above 220 ml/100 g.

The pH of the surface is also important, mainly because it may interfere with elastomer cure systems. Most precipitated silicas are slightly acidic, while the metal silicates are alkaline. Acidic surfaces have the most effect on elastomer cures, especially peroxide cures.

The hydroxylated nature of the surface of precipitated silicas also leads to poor wetting and dispersion in many polymers. Surface treatments are widely used to overcome this, the most common being organo-silanes (often referred to as coupling agents). These additives can be pre-reacted with the filler, or added during the composite manufacturing process, with the latter being by far more usual. The high specific surface area and high hydroxyl density means that very significant amounts of surface modifier (up to 10%) are needed to fully treat the surface. This level of treatment is expensive and proves to not be necessary or even useful in many applications. Tire treads are a notable exception and require high levels, approaching complete (monolayer) surface coverage.

The density of surface hydroxyls is of considerable significance and can be measured by titration with sodium hydroxide in strong salt solution. This gives what is known as the Sears number (Heinroth et al. 2008).

In addition, compacted forms are generally required by the tire companies for their ease of dosing. This must be achieved while still retaining good dispersability and adds further to the production complexity and costs.

## Safety

While crystalline silicas have some associated health issues, the synthetic amorphous forms are nontoxic products. The assessment studies focus on respiratory exposure, and all studies conclude that at the current exposure limit of solids in air, there is no risk associated to long-term exposure. In common with all dusty materials, they can cause skin and eye irritation. They are also approved for food applications and used as food additives.

Silica makers are syndicated in the ASASP association. Amorphous silicas have been registered in REACH in 2010 (http://www.reach-sas.org/index.htm).

## Sustainability

Precipitated silicas are made from sand, soda ash (sodium carbonate), and sulfuric or hydrochloric acid. Life cycle analyses show that the environmental impact of their manufacture and use in tires is lower than for any other component (source: Goodyear) and also that it is dwarfed by the savings during use (OECD 2014). Some producers are starting to use waste amorphous silicas (such as rice hull ash) instead of conventional crystalline silicas like quartz, as the raw material. This reduces energy consumption, both by eliminating mining and by lowering the temperature needed for solubilization. An interesting new sustainable sourcing opportunity is arising from plans to recover useable silica from geothermal power plant operations (see www.environmetals.co.nz).

## Polymer Applications

The world production of precipitated silica is about 2.0 million tons, with approximately 65% of this being used as a reinforcement in elastomers. The other main polymer use is in sealants and coatings. The main non-polymer markets are in dentifrice, nutrition, and hygiene applications. The total precipitated silica market for rubber applications is about 1.2 million tons, of which the conventional types have 850,000 tons and have been growing at 3.5% per year, while the improved dispersion types have about 350,000 tons and have been growing at 7% (source: Rhodia).

There is very little relevant information on polymer uses in the recent scientific literature, but a good review can be found in Leblanc (2010).

The small size and high specific surface area of precipitated silicas make them most suited to elastomer applications. They can give high levels of reinforcement, similar to carbon blacks, although with a different property profile. They also differ from the carbon blacks in requiring chemical treatment of the surface (usually with an organo-silane coupling agent) to produce effective filler polymer interface adhesion. The high specific surface area of the precipitated silicas means that significant levels of these expensive additives are required for maximum performance in some applications.

Making meaningful comparisons with other fillers in elastomers is difficult, as there are a wide range of products available for each filler type; a wide number of properties have to be considered, according to the application, and additives and cure conditions can be used to control property profiles. Despite this, useful indications can be made using model formulations. Table 2 summarizes the differences observed between a highly reinforcing carbon black (HAF), a conventional (old technology) reinforcing precipitated silica grade, an aluminum silicate, and a ground natural carbonate. This has been carried out at constant volume loading of additive, although formulation to a given hardness is usually employed in practical applications. Using the conventional elastomer terminology, the silica and silicate are seen to be less reinforcing than the carbon black (lower tensile strength and modulus) but much higher performing than the carbonate. There are benefits in other areas though, notably the much higher tear strength obtainable from the precipitated silica. This higher tear strength is one of the reasons why precipitated silica is frequently used in tires for tough applications (off-road tires).

The above results were obtained in the absence of coupling agent. This is not required for carbon blacks on which they have little effect, but they can improve the performance of precipitated silicas. Two silane types are in use for sulfur-cured elastomers, mercapto and polysulfidic. Table 3 shows the type of improvement that can be obtained from using a polysulfidic silane.

Abrasion resistance was unfortunately not included in the work summarized in Tables 2 and 3 but is a key requirement in tire treads and one where precipitated silica has traditionally been found lacking against carbon black (if it had been included in the work in Table 2, then the abrasion resistance would have been only about 75% of the HAF black value).

For many years, precipitated silicas were unable to compete directly with carbon blacks in elastomers. This is because they are more difficult to disperse, require significant levels of processing aids or coupling agent to achieve full potential, and are not as versatile in terms of the property palettes obtainable. The main uses were where high-strength non-black compounds were required (notably in many shoe sole applications) or where they could offer some special benefit, such as better tear and chunking resistance in off-road tires or grip in winter tires. The next section explains how this changed with the advent of what is generally called “energy or green tire technology.”

### Energy or Green Tire Technology

This is a complex topic and only discussed briefly here; more details can be found in ▶ Chap. 6, “Particulate Fillers in Elastomers.”

**Table 2** A comparison between a reinforcing carbon black, old technology precipitated silica, and an aluminum silicate in elastomer (all at 25 parts by volume in sulfur-cured SBR 1500) (Data derived from Westlinning and Fleischhauer (1965) and normalized to carbon black as unity)

| Filler | Tensile strength (normalized) | 300% modulus (normalized) | Elongation (normalized) | Rebound resilience (normalized) | Tear strength (normalized) | Hardness (normalized) |
|---|---|---|---|---|---|---|
| Carbon black (HAF type) | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| Precipitated silica | 0.84 | 0.58 | 1.28 | 0.89 | 1.42 | 1.12 |
| Precipitated aluminum silicate | 0.49 | 0.28 | 1.24 | 1.08 | 0.83 | 0.94 |
| Ground calcium carbonate | 0.13 | 0.18 | 1.10 | 1.25 | 0.41 | 0.84 |

**Table 3** Examples of the use of a silane coupling agent with a conventional precipitated silica in a sulfur-cured elastomer

| Silane level% on filler | Tensile strength MPa | 300% modulus MPa | Elongation % | Hardness |
|---|---|---|---|---|
| 0 | 16.3 | 1.9 | 880 | 50 |
| 2.9 | 17.9 | 3.2 | 810 | 54 |
| 5.7 | 20.3 | 4.1 | 800 | 56 |
| 8.6 | 18.5 | 5.4 | 680 | 61 |

A rotating tire continuously deforms and recovers; and these processes lead to significant energy losses (rolling resistance) manifested as heat generation and resulting in increased fuel consumption. The filler network plays a major role in determining the amount of energy loss which can be much reduced by changing the conventional carbon black for precipitated silica plus a silane coupling agent. This is known as green (or energy) tire technology. The precipitated silica itself is responsible for the improved rolling resistance and also gives better grip. Both of these desirable properties can be achieved by conventional grades alone; but these cannot match the tread wear (abrasion resistance) achievable with carbon blacks, and this is where the silane coupling agent and the improved dispersion precipitated silicas both become important.

The relatively poor abrasion resistance is associated with two factors. The first and most important is the relatively weak filler to elastomer bonding that silica achieves, compared to carbon blacks. The second is the relatively poor dispersability associated with the conventional precipitated silicas. It was only when ways of overcoming these two issues were found that the benefits of this new technology could start to be fully realized.

Improvements in interfacial bonding were realized through the development of specialized organo-silane chemicals, which can react with both the filler surface and, during vulcanization, with the elastomer and so strongly tie (couple) the two together. Such chemicals are known as coupling agents (see ▶ Chap. 2, "Surface Modifiers for Use with Particulate Fillers"), and the first successful coupling agent introduced for this purpose was a polysulfidic triethoxysilane known as TESPT. While other types have been developed since, this continues to be the dominant product today. In order to maximize the improvement in abrasion resistance and achieve something similar to the tread life associated with carbon blacks, it is necessary to approach complete coverage of the filler surface with the coupling agent. Because of the high specific surface area of the fillers, this translates into quite high addition levels (between 5% and 10% w/w on the filler), making the coupling agent a significant factor in raw material costs.

The results in Table 4 give a comparison of a carbon black and silica of similar specific surface area in a typical low rolling resistance tread formulation (solution SBR/BR blend) and provide a good illustration of the effects discussed in the previous section. It is seen that, even without coupling agent, the silica gives better grip and lower rolling resistance but markedly worse abrasion resistance. The use of the silane coupling agent brings the abrasion resistance close to that of the carbon

**Table 4** Comparative results for carbon black and silica fillers in a tire tread formulation (normalized to carbon black as unity)

| Property | With carbon black | Precipitated silica | Precipitated silica + coupling agent |
|---|---|---|---|
| Abrasion loss (DIN) | 1.00 | 1.54 | 0.97 |
| GRIP | 1.00 | 1.05 | 1.05 |
| Rolling resistance | 1.00 | 0.60 | 0.60 |

**Table 5** Effect of improving dispersion of precipitated silica on abrasion resistance

| Percentage of undispersed filler | Abrasion loss (relative to 6.6% undispersed filler = 1.00) lower = better abrasion resistance |
|---|---|
| 6.6 | 1.00 |
| 3.3 | 0.89 |
| 0.5 | 0.87 |

black, without any loss in grip or rolling resistance. (Note the laboratory abrasion test is only a guide to actual road wear, which varies according to the severity of the test conditions. It is generally accepted that silica plus silane, while about equal to carbon blacks under modest road-wear conditions, is still inferior at the highest severity.)

As shown above, improving dispersability further increases abrasion resistance (reduces tread wear) (Table 5).

## Microporous Polymer Products

Precipitated and fumed silicas and silica gels are used to make microporous polymer articles, notably for use as battery separators and polymer-based papers.

Separators for lead acid batteries are a significant but frequently overlooked application for precipitated silicas. The function of the separator is to prevent short circuiting by providing a barrier between the cathode and anode of the battery. At the same time, it must be permeable and allow ions to move freely between the electrodes and must also be robust and mechanically stable.

Separators for lead acid batteries can be made from various polymers, such as polyethylene (PE), polyvinylchloride (PVC), resins, or rubber, but polyethylene is the most common polymer used, due to its superior puncture resistance, flexibility, ability to be folded and sealed, oxidation resistance, and low acid displacement.

Ultrahigh molecular weight polyethylene (UHMW-PE) is preferred and is compounded with the precipitated silica, processing oil, and selected additives, such as lubricants, wetting agents, and carbon black. The compound is extruded as a sheet, and then the oil is solvent extracted to leave a microporous sheet where the pores are interconnected to generate a pathway.

The primary function of silica is to help generate the porosity. It also remains in the sheet making it hydrophilic and wettable by the sulfuric acid. The silica for battery separators needs to be tailor made for optimum performance.

A related application is in synthetic (polymer) papers. Synthetic paper is a print material made from plastic rather than wood pulp and mainly used in applications where the ability to perform in demanding environments is required. In its production, a precipitated silica is aggregated in a matrix with polyolefin to produce a smooth but highly porous printable surface. As with battery separators, the polymer is usually UHMW-PE, and a processing oil is used to aid compounding and extruding and is then solvent extracted.

### Rheology Control Additives

This important application is common to both precipitated and fumed silicas and is covered later (section "Rheology Control Agents (Applicable to Both Fumed and Precipitated Silicas)")

## Future Directions

It is highly probable that development of precipitated silicas to better meet the varied and complex needs of the tire industry will continue to be a key activity. In particular we can expect to see more use in replacement and truck tires than is the present case. We may also see better uptake of silane pre-coated products, again principally for the tire industry, but this is by no means certain.

## Fumed Silica

## General

Fumed silica is a specialized, high-price, niche product, and its main polymer use is as a reinforcing filler for silicone elastomers. Like the precipitated products, it is amorphous and with a very small particle size. But it is less aggregated and has a more inert surface. This surface has a lower hydroxyl content and much less adsorbed water. Also, unlike the precipitated silicas, it is frequently sold in pre-coated form. In some cases, a trace of another metal oxide (usually alumina) is also incorporated, and the product is then known as a mixed oxide, although the silica content is still usually well over 90%.

## Production

This is carried out by "burning" silicon tetrachloride in a hydrogen/oxygen flame. The actual reaction is really hydrolysis rather than oxidation.

$$\mathrm{SiCl_4} + 2\mathrm{H_2O} \rightarrow \mathrm{SiO_2} + 4\mathrm{HCl}$$

**Table 6** Major fumed silica producers

| Company |
|---|
| Cabot |
| Evonik |
| Wacker |
| OSC/Tokuyama |

There are two broad product types commercially available, hydrophilic and hydrophobic, with the latter being coated postproduction to reduce water absorption.

The starting raw material is sand, which is converted to silicon metal and then to silicon tetrachloride used for combustion. Silicon tetrachloride can be distilled to remove impurities. The combustion process has to be well controlled to produce the desired particle size and degree of aggregation (partial fusion of the particles to produce chain-like structures). The initial fumed product has to be collected and well washed to remove all but the last traces of the hydrogen chloride coproduct. It can be appreciated that the process is costly, and the economics very much depend on being able to recycle the hydrochloric acid (e.g., in making silicon tetrachloride on the same site). There is considerable synergy with the manufacture of silicones, and some companies produce both.

The main producers of fumed silica are given in Table 6.

## Properties

The product is an extremely fine powder, containing very small primary particles of silica, fused together into larger aggregates. Particle size and aggregate structure obtainable for both precipitated and fumed silicas are broadly similar. The specific gravity of the fumed product is slightly higher (2.1–2.2) but still low compared with other minerals. The main differences are in purity, water content, surface hydroxyl content, and surface pH. These differences are summarized in the Table 7.

The origin of the low pH of the fumed silica has been the subject of much debate. It is now believed that this is due to the strained silicon to oxygen bonds at the surface.

As mentioned above, there are both hydrophilic (uncoated) and hydrophobic fumed silicas (coated). The hydrophobic ones have various types of surface treatment applied. Where simple hydrophobization is required, then methyl groups are frequently used. These can be introduced by reaction with substances such as dimethyldichlorosilane or hexamethyldisilazane. Silicone fluids can also be used. Organo-silane coupling agents are used when elastomer reinforcement is required, with the principal ones being the vinyl and methacryloxy types.

There are a large number of these hydrophobic products with properties such as particle size and level and type of coating adjusted to suit particular applications (the Evonik web site lists 12 different products). The coated versions are considerably

**Table 7** Typical properties for precipitated and fumed silica

| Property | Typical for precipitated silica (uncoated) | Typical for fumed silica (uncoated) |
|---|---|---|
| Purity | ~98% (excludes water) main impurity sulfate | >99.5% |
| Surface pH | 6–7 | 3 |
| Free water% (lost at 105 °C) | 4–7% | <1.5% |
| Surface hydroxyls | 8–10 per nm$^2$ | 2–4 per nm$^2$ |
| Specific surface area m$^2$/g | 35–235 | 130–350 |

Source: Intertech-Pira

more expensive than the uncoated and probably have no more than about 25% of the market.

The general trends in polymer applications with particle size and surface treatment have been summarized by one of the producers (Cabot) as:

Increasing specific surface area leads to:

- More difficult wetting and dispersion
- Increased thixotropy
- Increased reinforcement
- Increased transparency

Increasing surface treatment level (standard non-coupling type) leads to:

- Increased hydrophobicity
- Reduced moisture pickup
- Reduced rubber plasticity
- Lower crepe hardening in silicone rubber
- Lower reinforcement

## Applications

The high price of fumed silicas rules them out of most volume polymer applications, and their main use is as a reinforcing filler for silicone rubber, including silicone sealants. Not unexpectedly, they perform well in this polymer, where they are much more effective than carbon blacks. They have the added advantage of matching the polymer refractive index and thus giving a transparent product.

Fumed silicas are difficult to disperse fully in the low-viscosity silicone elastomer gums and hence are mostly supplied premixed by the silicone rubber producer using special methods. Silicone elastomers are exceptionally weak unfilled, and published information on the effect of filler addition to unfilled gum silicone rubber is scarce

**Table 8** Illustration of the effect of adding fumed silica to a gum silicone rubber (peroxide cure)

| System | Tensile strength (MPa) | Elongation at break% |
|---|---|---|
| Gum rubber | 0.4 | 130 |
| With 35 phr. fumed silica | 7.0 | 300 |

for this reason. Table 8 gives a brief summary of the results to be expected, based on a variety of sources.

Michel (2007) provides information on the use of fumed silica in a variety of other elastomers. This includes hydrogenated nitrile rubber, ethylene acrylate rubber, and fluoroelastomers.

Fumed silicas are able to produce a strong thixotropic effect in many polymer systems, including epoxies and PVC plastisols. This is discussed in more detail later. The thixotropic effect can be achieved at quite low loadings, making their use cost-effective, despite their relatively high price. It is particularly valuable in sealants and coatings, and these have become significant application areas. Not surprisingly, given their high price, they have come under pressure from other types of filler for this, including precipitated silicas and calcium carbonates.

Given the success of precipitated silica in tire treads, it is reasonable to ask whether this is an opportunity for fumed silica. In the absence of any extralarge benefit in rolling resistance, this is felt to be unlikely, due to the higher cost. It is true that the fumed silica will probably require significantly less of the expensive silane, but rough calculations show that, even if no silane is required, the raw material costs with fumed silica will exceed those of precipitated silica/high silane addition level combinations.

## Safety

Fumed silicas are amorphous products like the precipitated ones, and the same comments regarding safety issues apply (see section "Safety").

## Sustainability

While the raw material (usually some form of crystalline silica) is extremely abundant, its extraction and conversion are an energy-intensive process. There is also currently little or no recovery or recycling of the material or its composites. Even so, the relatively low volumes involved do not make this of great concern at present.

## Future Directions

The production costs of fumed silicas are relatively high for polymer applications, and this means that they are likely to remain niche products and prone to competition from lower-priced products. This has already become apparent in the thixotropic markets, where alternatives such as precipitated calcium carbonate have already made a significant impact. There is also significant effort in upgrading the lower-cost precipitated silicas for use in silicone elastomers.

## Silica Fume

### General

Silica fume is a completely different product to fumed silica and should not be mistaken for it. Silica fume is a by-product of the reduction of quartz with carbon in electric arc furnaces used for the manufacture of silicon and silicon alloys. Originally this by-product was allowed to discharge to the atmosphere, but environmental issues have prevented this since the 1970s. It is now collected and marketed for a number of applications. While polymer use is very small today, silica fume has been included because of the confusion that sometimes occurs with fumed silica.

### Properties

Silica fume is an ultrafine powder consisting of spherical particles with an average particle diameter of 150 nm (0.15 μm). The specific surface area is about 20 $m_2/g$ by the BET nitrogen method. The primary component of silica fume is amorphous silicon dioxide ($SiO_2$) which can vary from 85% to 98%. The main impurities include carbon, silicon carbide, and oxides of alkaline (earth) metals.

### Applications

The particle size is of interest for several polymer applications, and in the early days of fumed silica recovery, there was interest in using it as a filler in polymers; but this has largely disappeared today. This is because it has found a higher added value application as a special additive (pozzolan) for concrete.

### Safety

Respirable crystalline silica (RCS) of silica fume is very low at $<0.1\%$, and the silicon carbide is in its safer nonfibrous form.

### Sustainability

Being a by-product, silica fume can be regarded as a sustainable material. The finding of higher added value applications that has occurred illustrates one of the recurring issues with developing by-products for polymer applications.

### Future Prospects

The concrete market is expected to continue to dominate and limit any use in polymers.

## Silica Gels

Silica gels are related products to precipitated silicas, and while many of their applications are outside of polymers (such as use as desiccants), they do find some applications as particulate polymer additives, principally in paints and coatings. Patterson (1994) describes the production and uses.

### Production

The principal production method for silica gels is similar to that for precipitates and starts with the production and acid neutralization of sodium silicate. The difference is that the primary particles are built up into a massive three-dimensional structure, instead of into small aggregates. This structure is highly porous and entraps all of the aqueous phase. The gel is then washed to remove by-product sodium salts, dried, and milled to produce small, highly porous particles. Two different drying processes are used, resulting in different classes of product. Conventional drying leads to significant shrinkage and loss of structure due to capillary forces and results in products known as xerogels. This structure collapse can be mitigated by various alternative drying methods, which reduce the capillary forces. One way is to replace the water by a liquid such as alcohol or acetone, which has a lower surface tension, and then to carry out critical point drying. Such products are known as aerogels.

### Properties

All silica gels are high-specific-surface-area, high-oil-absorption products, with their properties mainly determined by the following factors:

pH and method of gel formation
Washing procedures
Drying process
Any particle size reduction employed (e.g., milling)

## Applications

Milled xerogels are the most commonly met types in polymer applications. Their principal uses are as flatting and matting agents in coatings and as anti-blocks in polymer film and in battery separators. In many of these, they compete with precipitated silicas.

## Rheology Control Agents (Applicable to Both Fumed and Precipitated Silicas)

Although reinforcement of solid elastomers is the prime polymer application for both precipitated and fumed silicas, they also find extensive use as rheology control agents, especially thixotropes, in liquid polymer systems. These effects are achieved at much lower addition levels than required for elastomer reinforcement accounting for the reinforcement applications dominating in terms of tonnage used.

Thixotropy refers to a phenomenon in which a substance is relatively viscous at rest, but thins considerably on shearing, only to recover once the shear is removed. This is called time-dependent shear thinning and is a very useful effect in products such as sealants, adhesives, and surface coatings, including paints. Among the beneficial effects are reduced settling of other additives, sag control, and elimination of edge defects such as “picture framing” and “fat edges.” Properly formulated, shear thinning can occur easily, allowing application by methods such as brushing, and there can be sufficient time for air escape from a coating before the viscosity increases again.

There are various ways to induce thixotropic behavior into liquids and gels, but the use of fine particulate additives is one of the most common approaches, with high-surface-area silicas, especially fumed silica, being among the most effective additives. Barnes (1997) provided a good review of the general topic.

Thixotropic effects from particulate additives arise when the particles are able to form relatively weakly bonded chain networks throughout the liquid phase. The mechanisms involved in establishing this network can be quite complicated but have been well described by Iler (1979b). Essentially the effective particles (aggregates in the case of synthetic silicas) need to have patchy surfaces, with both hydrophilic and hydrophobic spots. In organic media, they can then chain through hydrogen bonding of the hydrophilic regions. This two phase nature is essential. If the surface was all hydrophilic, the particles would form clumps and not disperse in the medium. If they were all hydrophobic, then they would disperse fully and not chain. In aqueous, or polar systems, the reverse is true, with chaining being through the hydrophobic regions and wetting by the water being through the hydrophilic ones.

The way in which this patchy surface is generated is quite complex and varies from system to system. Features that play a role include the water content of the filler, the presence of surface active additives in the liquid system, and the presence of surface treatments on the filler. A further factor is the breakdown of coated aggregates during formulation, as this generates new, untreated surface.

## Cross-References

- ▶ Antiblock Additives
- ▶ Particulate Fillers in Elastomers
- ▶ Surface Modifiers for Use with Particulate Fillers

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# Part IV

# Organic Particulate Fillers

# Fillers from Organic Sources

# 16

Roger Rothon

## Contents

**Abstract**

While the growing interest in sustainable sourcing has led to a revival of interest in particulate fillers derived from biomaterial sources, this is nothing new. Wood flour was one of the first fillers used in plastics, and rice hull-derived silica was being promoted for use in place of some carbon blacks in the 1970s.

In addition to their sustainability credentials, many of these fillers offer other advantages, particularly weight saving, over minerals. On the other hand, they frequently have a number of limitations including higher cost, poorer thermal stability, color issues, and moisture sensitivity which have hindered their acceptance. Even so, renewed effort is going into their development, especially that of nano-sized particles.

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Wood flour is the standout commercial example today, with large volume use in wood polymer composites. Starch, cellulose, lignin, and even proteins are being explored as nanoparticles, especially for tire use. Although their use as a carbon black replacement failed to develop, rice hulls are still being developed for other applications and even as a raw material for precipitated silica filler manufacture.

**Keywords**
Bio-fillers • Wood flour • Cellulose • Starch • Lignin • Proteins • Rice hulls • Coupling agents

## Definition

Particulate bio-fillers in the present context refer to products which are derived from plant sources and have low-aspect ratio particles (under 10:1), when dispersed in a polymer. The actual products can be either organic (e.g., wood flour, starch) or inorganic (e.g., rice hull ash (RHA)) in nature. Higher-aspect ratio (fibrous) products, such as silk, rayon, refined cellulose, etc., are excluded.

## Introduction

While some of the earliest particulate fillers were based on plant materials such as wood, they were soon surpassed by inorganics such as calcium carbonate and talc. Recently there has been a revival of interest in organics, mainly due to the desire to have more sustainable and lighter products. Lightweighting is also becoming increasingly important in the automotive industry, and most plant-derived products have a clear advantage over mineral ones in this respect. While much of the current development is directed at the use of natural fibers such as wood, cellulose, hemp, silk, and rayon, there is starting to be some attention given to particulates. The main products of this type are wood flour, starch, and rice hull silica. Most of the current literature is in trade publications and patents, rather than peer-reviewed journals, and the current understanding, which is largely based on these, is discussed in this article.

## General

Currently, particulate mineral fillers, such as calcium carbonate and talc, dominate the filler market. This is because they are low cost, are fairly easy to extract and purify, have good thermal stability, and have little effect on color or water absorption of the final product. The main drawbacks of such products are lack of true sustainability and for some applications high specific gravity, with the lightest being amorphous silica (or oil-derived carbon blacks) at 1.8–2.0, while other common mineral fillers are in the range 2.5–3.0.

While plant-derived products have significant limitations, especially thermal stability, presence of deleterious impurities, color, and hydrophilicity, they are potentially more sustainable and also can often have specific gravities in the range 1.0–1.5. These two advantages are beginning to outweigh the limitations in some important applications, especially for automotives.

In order to offer good economics for volume applications, any filler has to be available in large quantities at any given location, which also needs to be near to the consumer. This limits the choice, with the main opportunities currently identified being wood flour, starch products, lignin, and rice hulls.

There are several different routes to particulate filler particles from plant sources. The first is through mechanical size reduction of plant materials such as wood. This is the simplest but generally results in complex mixtures, often with some significant limitations. Another method is the extraction and possibly size reduction of particulate species present in the plant. This is more complex but gives a simpler product with potentially superior properties. The final option is to extract a solution of a biopolymer and convert this into particulate form (e.g., by precipitation). Each of these approaches has received some degree of attention and is covered in the following sections.

## Products Obtained by Size Reduction of Plant Material

### Wood Flour

Wood flour is the largest volume organic filler in commercial use today. The wood fibers in it are of such short length that it can be regarded as a particulate. Wood flour was one of the first fillers to be used commercially in polymer applications, being an important component of Bakelite, a phenol-formaldehyde composite, first produced over 100 years ago, and it is still used in this type of material today.

Wood flour is generally regarded as being wood particles which are fine enough to pass through a 20 US standard mesh (about 850 μm). It is made from scrap wood sources and can thus be regarded as recycled as well as sustainable. The inherent properties of wood flour dictate that it cannot be regarded as a direct substitute for inorganic particulate fillers and must find applications of its own.

#### Production

Wood flour is a very variable material with a variety of wood sources and types being used to make it. The main steps in production are purification, size reduction, and classification. Size reduction can be accomplished in a variety of ways, including hammer mills, chippers, rollers, or attritors. The methods used will depend on the source material, especially its initial size. Classification can be achieved by standard methods such as screens or by using air classification. Some drying is also often necessary, although, for practical reasons, wood flour is usually shipped with some moisture.

The particles contain significant amounts of porosity. When fully compressed, the specific gravity is in the range 1.4–1.5, depending on the type of wood and moisture content, but this is not always achieved in polymer composites. The chemical composition of wood flour is complex. The main components are cellulose, hemicellulose, and lignin. There will also be some extractables such as oils together with an inorganic residue (ash). The exact ratio of these major components and the nature of the minor ones will vary with the wood type. Typical values are as follows:

| | |
|---|---|
| Cellulose | 37–45% w/w |
| Hemicellulose | 19–30% w/w |
| Lignin | 21–34% w/w |
| Extractables | 2–5% w/w |
| Ash | <0.7% w/w |

The cellulose is a highly crystalline, high-molecular-weight, linear polymer and is present in the form of microfibrils. It gives most of the strength to the wood. Hemicellulose is a branched polymer of much lower molecular weight but still makes some structural contribution. Lignin is a cross-linked amorphous polymer of variable structure and acts as a glue to hold the fibers in place.

## Applications

The applications for wood flour are dictated by a number of important properties. On the positive side, as well as being regarded as sustainable, it is relatively low in density and gives some reinforcement, although not as much as wood fibers.

Important limitations include:

- Color. It can only be used for dark-colored products and can show color fade on outdoor exposure.
- Thermal stability. This limits processing temperatures to about 200 °C, unless special precautions are taken.
- Moisture content. It will rapidly pick up moisture from the atmosphere when dry and so must be processed immediately after drying in applications where moisture would affect processing.
- Flammability. It is flammable which creates some hazards in transportation, storage, and processing; it can also decrease the fire rating of the host polymer.
- Weathering. Water absorption, swelling, and discoloration can be issues.
- Durability. Biological attack including mold and fungal effects can occur unless additives are used to prevent it.

These problems are least important in thermoset applications, explaining the early use of this material in such polymers. The processing temperatures here are low, and the moisture present can be tolerated in many instances. The limitations are far more important in thermoplastic applications.

Despite these issues, the main application today, and one that has seen rapid growth, is in what are known as wood polymer composites. These are combinations of wood flour in thermoplastic matrices, predominately polyethylene, but also using polypropylene and rigid PVC. About 80% of this market is in outdoor products, particularly decking. This market is most developed in North America. These applications frequently use reclaimed polymer as well, further increasing their green image. Estimates for the size of the market vary, but most agree that several hundred thousand tons of composite are used, with wood flour contents from 40 to 65% w/w.

When used in polyolefins, the wood flour gives useful increases in stiffness, partly due to the development of transcrystallinity, nucleated by the particle surfaces. There is usually a negative effect on unnotched impact, while the effect on notched impact can be either positive or negative depending on the source of the wood used. Processing is difficult due to high melt viscosity and low melt strength, and various additives are usually employed to allow economically acceptable extrusion rates. Coupling agents, such as maleated polyolefins, are also frequently employed to improve bonding between the polymer and the particles, and this can improve impact strength.

While the effect on composite properties varies significantly with the wood source, the trends are all similar and typical results are presented in Figs. 1 and 2. It should be noted that the relatively low specific gravity of wood compared with mineral fillers means that the volume loading is significantly higher than that of a mineral at equal weight level.

Figure 1 shows the effect on stiffness which is seen to increase significantly with filler loading. The effect on notched and unnotched impact resistance is presented in

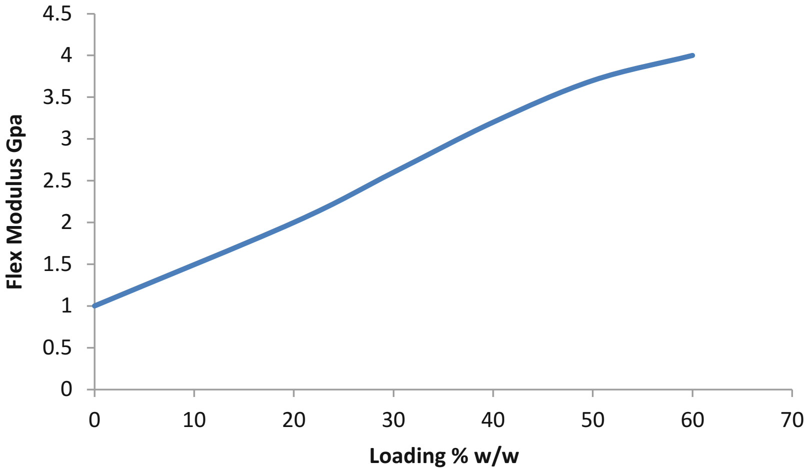

**Fig. 1** Effect of wood loading on the flexural modulus of a polypropylene homopolymer (adapted from C.M. Clemons 2010)

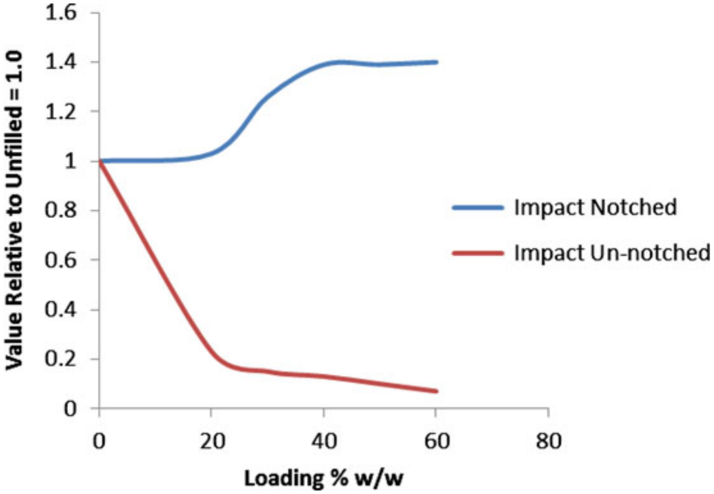

**Fig. 2** Effect of wood loading on the impact resistance of a polypropylene homopolymer (adapted from C.M. Clemons 2010)

Fig. 2. While there is a modest increase in notched resistance, there is a marked drop in unnotched. This is explained by the notched property being controlled by crack propagation, while the unnotched is controlled by crack initiation. Particulate inclusions can have very different effects on these two properties, and the wood particles are clearly acting as flaws in the composite and thus lowering unnotched impact strength, an effect that is frequently seen with particulates. Fortunately, the notched figure is more important than the unnotched one in most cases.

In theory, wood polymer composites are themselves recyclable, although there are significant problems to doing this on an industrial scale. Some are those related to collection and variability common to nearly all recycling operations. The others are due to deterioration of both the polymer and wood flour during processing and also use in an outdoor environment. These include molecular weight degradation of the polymer and oxidative, light, and weather degradation of the wood. These issues can be overcome sufficiently by careful processing and addition of stabilizers, to at least allow some level of incorporation into a new product.

## Products Obtained by Extraction of Particulate Material from Plant Matter

Plants are complex composite structures, which mainly consist of fibers, particulates, and amorphous regions. In some cases, such as wood discussed above, the plant composite itself can be turned into a useful particulate filler, but this is rare. The most useful parts of a plant for use in composites are the fibers and particulates, and these have to be extracted from the rest of the plant matter before they can be used. Starch, lignin, and cellulose are the most abundant organic materials being investigated for use as particulates, together with silica obtained from rice hulls and are discussed in this section. Fibers are outside the scope of this work.

## Starch

Starch is an inexpensive and renewable natural polysaccharide based on D-glucose. It actually consists of two different polymers: amylose (AM) and amylopectin (AP). Amylose is a linear polysaccharide and has a molecular weight of 0.2–2 million daltons. Amylopectin is a highly branched polymer of glucose with a massive molecular weight (100–400 million daltons).

In nature, starch is found in plants as semicrystalline beads with a size range of 2–100 μm in diameter, depending on the plant. These beads have a complex, onion-like structure, containing densely packed polysaccharides and a small amount of water. The inner structure of starch is believed to be formed from two regions – crystalline and amorphous lamellae – which together form the growth rings. The principal component of the crystalline region in native starch granules is thought to be amylopectin lamellae, packed together to form a double helix crystal structure.

One of the attractions of starch (but also a limitation) is the fact that it is totally biodegradable in a wide variety of environments, and degradation or incineration of starch products would recycle atmospheric $CO_2$ trapped by starch-producing plants and would not increase potential global warming.

There are various uses for starch-derived products in polymers. Thus it can be used as a particulate filler, or as a polymer, either alone or in blends. If the semicrystalline bead form is preserved in the polymer matrix, then a particulate filler is arrived at. For various reasons, starch beads have limited application as particulate fillers, and most work has focused on producing thermoplastic starch polymers or blends, rather than using it in particulate form. Starch can be made into a thermoplastic polymer by destroying the crystalline structure; this can be done by pressure, heat, mechanical work, and plasticizers such as water, glycerine, or other polyols. The principal use for such products is for making biodegradable film.

There are two approaches to using starch beads as a filler in polymers. The first makes use of the bead in its semicrystalline form, while the second extracts the crystalline material from the bead as a nano-sized filler. The second approach is covered in ► Chap. 23, “Nanofillers” and only the first is discussed here. More details on nano-starch can also be found in the review by Lin et al. (2011).

### Production

In order for the starch bead to be used as a particulate filler, it must be recovered from the plant in a suitable particle size and then prevented from melting and becoming a blend during processing of the composite. Extraction of the starch particles is accomplished by various crushing, grinding, size separation, and drying methods, which are varied to suit the plant feed used (e.g., maize, wheat, or potato). The native starch produced in this way is in the form of a fine powder, looking like flour.

Depending on the plant source, beads as fine as a few microns can be obtained. The specific gravity of starch beads is close to 1.5.

In addition, it is generally necessary to modify the polar surface of the starch particles in order to improve compatibility with the polymer, which is usually hydrophobic. Various methods of surface modification can be used for this. Fortunately, starch is readily functionalized through the abundant reactive groups on the surface, especially the hydroxyls. Most functionalized starches are made by taking the starch into solution followed by chemical reaction, precipitation of the derivative, separation by filtration, and drying to recover the product. For polymer filler applications, only the particle surface needs to be treated, and this can be done by dry methods, by which a variety of treatments can be applied, including silanes, silicones, and fatty acids. It is also possible to carry out modification during composite formation, for which various carboxylic anhydrides and organo-silanes can be used. The thesis by Linero (1979) gives details of various treatments for starch beads.

### Use in Polymers

Maintaining the particulate form during compounding is difficult, as processing temperatures need to be below the crystal melting point, which is itself influenced by moisture and plasticizers. Thermal decomposition of the starch also needs to be avoided. Under optimum conditions, the maximum practical temperature is about 230 °C.

Despite their apparent attractiveness, there is little sign of commercial interest in particulate starch beads as opposed to thermoplastic blends or nanocrystals. This is probably due to a number of issues, including water sensitivity, thermal instability, and cost of production. In support of this, there is also little literature on the use of starch beads as polymer fillers. Hashimi (1983) does describe their use in high-density polyethylene. Bastioli (2002) has reviewed starch-polymer composites but most of this concerns blends, rather than particulate reinforcements. The main commercial interest so far would seem to be from tire companies such as Goodyear Tire and Rubber (US Patent 5,672,639 to a starch reinforced rubber composition and tire). Working in conjunction with Novamont and BMW, Goodyear went on to develop tires using starch as a partial replacement for precipitated silica or carbon black fillers, and these have been commercialized. It seems that, while often referred to in the trade literature as a starch filler, it is more probable that a blend morphology is actually present.

## Cellulose

More recently, other polysaccharides in abundant supply have become of interest, notably cellulose. Micro- and more recently nanocrystalline cellulose has been rumored as being studied for tire applications, but few details are available. The most interest is in nanocrystalline cellulose, and this is covered in ▶ Chap. 23, "Nanofillers." One of the problems with plant-based cellulose technologies is the need to disrupt cell walls to access the cellulose and then to separate this from the rest of the plant matter. In what may prove to be a breakout development, the University of Austin, in Texas, USA (2013), has recently announced the development of a route that starts from a blue-green algae (a genetically engineered cyanobacteria). This offers the prospect of a much more efficient and environmentally sound process than those starting from cellulose-containing plants such as wood.

## Lignin

Lignin is the second most common organic material on earth (after cellulose), with about 20 billion tons being formed each year by photosynthesis. It makes plant cell walls fibrous and hard and has great credentials for making sustainable products. Chemically, lignin is a cross-linked phenolic polymer, the exact structure of which varies with plant source. Its specific gravity also varies with source but is in the range 1.3–1.5.

Lignin is responsible for the yellowing of low-grade paper and is thus removed from wood during higher-quality paper production, a process which generates about 60 million tons of lignin a year as a waste product. There are various chemical methods used for removal of the lignin; often these result in an aqueous solution of lignosulfonates. This lignin stream can be used on site as low-grade fuel.

Lignin or lignosulfonate powders of various sizes can also be produced from such waste streams and have a number of established uses. Recently they have begun to receive attention for the production of particulate fillers for polymers.

While still in its infancy, there have been some interesting developments. The carmaker Volkswagen, working with the TU Dresden and the Faserinstitut Bremen, has investigated the effect of lignin powder as filler in polypropylene (Mainka et al. 2015). They claim that the use of lignin as a thermoplastic filler offers “an enormous lightweight potential” for large volume auto-production and that “a (polypropylene) compound filled with up to 30% lignin powder offers a 20% weight reduction compared to traditional filled PP compounds and provides the same mechanical performance.” They further claim that costs would be reduced as much as 30% through replacement of fillers such as glass, talc, carbon black, aluminum oxides, and silicates. The use of maleated polypropylene coupling agent is claimed to enhance the adhesion between the lignin and polymer and improved some of the properties. Improvements in lignin extraction methods are also being commercialized (e.g., see http://renmatix.com).

The tire industry is under pressure to lightweight their products and to improve the sustainability of the raw materials used. A recent patent to Goodyear (US 8,664,305, 2014) describes the use of lignosulfonate as a filler for rubber, which is claimed to be able to replace precipitated silica in energy-efficient tire applications. A key aspect of the invention is the functionalization of the lignin surface to improve interaction with the polymer. The preferred functionalizing reagent is a silane coupling agent (e.g., (trimethoxysilyl)propyl methacrylate). An even more recent patent to the same group (US 9,102,801, 2015) describes a method for manufacture of lignin nanoparticles suitable for use as a polymer filler. These are very early days and it will be interesting to see how this develops.

## Proteins

Proteins are large biomolecules, or macromolecules, consisting of one or more long-chain amino acid residues and are a vital constituent of most living organisms. Large quantities of protein waste can be generated by the use of plants, such as rape, for biodiesel manufacture. Loughborough University researchers have investigated the use of such material for elastomer reinforcement as part of a project to improve the efficiency of the biodiesel process (www.iom3.org/fileproxy/303562). This work demonstrated that blending of gelatinized rape meal protein with carboxylated nitrile (XNBR) rubber latex resulted in a material ten times stiffer and four times stronger than the unreinforced rubber and similar to that achievable with a carbon black. Latex blending was used to ensure good dispersion in the rubber and resulted in particles of about 2 μm.

## Rice Hulls

Rice hulls or husks are the outer coating on rice grains and provide protection to the seeds during the growing period. They contain large amounts of amorphous silica and lignin and are not very digestible for humans. As a result, the hulls are usually removed when rice is harvested. They are then usually burnt as a source of energy and leave behind an ash known as RHA (rice hull ash), which is largely silica.

The RHA silica is seen as a very significant waste stream, estimated at over three million tons of silica annually worldwide. Moreover it can be regarded as sustainable, due to the plant origin. As such, it has been much studied as a raw material for many applications, including as a polymer filler. These efforts have been ongoing for at least 50 years and saw the launch of commercial filler products in the USA in the 1970s, but this initiative does not seem to have made much progress since. The early work directed at a carbon black substitute is described by Haxo and Mehta (1974); more recently, the use of rice hull ash in polymers has been reviewed by D.S. Chaudhary et al. (2004). R. Srilathakutty et al. (2002) have described the successful use in microcellular shoe soles, and E.P. Aysawarya et al. (2012) have described its potential for use in HDPE. As described in ▶ Chap. 22, "Sustainable and Recycled Particulate Fillers," there is also growing interest in using the ash as the raw material for producing precipitated silicas, with some of the tire majors seeing it as a useful way to produce precipitated silica for tire use.

### Production

The problems with producing a useful silica filler from the rice hulls exemplify the more general issue of turning waste into useful products. The silica present in the rice hulls is in a finely divided, hydrated, amorphous form and makes up 15–20% of the initial material. The remainder is mainly cellulose, lignin, and moisture. If combustion is used to turn the organic content into energy, then an ash results, which is mainly silica. Unfortunately, normal combustion conditions mean that this silica is dehydrated and fused into larger particles, with some crystallization occurring as well, and this product is thus unsuited to filler use. This difficulty can be overcome by more controlled and gentler burning which leaves behind an amorphous silica ash containing about 10% of carbon. Grinding of this ash yields a product with a particle size in the range 0.1–2 μm, a specific surface area of about 30 $m^2/g$, and oil absorption of 30–40 ml/100 g. Due to the carbon content, it is dark colored. The applications for this product are very much dictated by the particle size and specific surface area. It is too fine to be considered for most thermoplastic and thermoset filler applications and is more suitable for use in elastomers. Unfortunately, the size is too large for good reinforcement, and it fits into a very special niche, that of the thermal blacks. This was the market that the US products of the 1970s, such as opal blacks, were aimed at (Rubber World 1977). For various reasons, this attempt did not prosper. One of the key reasons for lack of development is that a simpler alternative, use as a cement additive, was developed.

## Cross-References

- ▶ Nanofillers
- ▶ Sustainable and Recycled Particulate Fillers

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# Part V

# Speciality Particulate Fillers

# Mineral Filler Fire Retardants

# 17

Fiona Hewitt and T. Richard Hull

## Contents

## Abstract

Mineral filler fire retardants are one of the most important classes of fire retardant, and one of the most important classes of polymer additives. In addition to

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reducing the flammability of the polymer to within acceptable limits, they can also provide structural integrity and reinforcement to the polymer composite. Mineral filler fire retardants operate through endothermic decomposition with the release of an inert gas or vapor. Four fire retardant effects have been quantified: heat capacity of the filler, decomposition endotherm, heat capacity of the gas or vapor, and heat capacity of the residue. In specific fire scenarios, other factors, such as shielding from radiant heat, may also play a critical role. Unfortunately, the screening techniques for assessment of fire retardant performance do not adequately capture real fire behavior. The common techniques, and their deficiencies, in relation to mineral filler fire retardants are reviewed.

**Keywords**
Fire • Flame • Retardant • Aluminum hydroxide • ATH • Alumina trihydrate

## Introduction

The flammability of synthetic polymers, coupled with the ease of incorporation of additives, has created a large market for mineral filler fire retardants. On exposure to external heat, such as the conditions of fires, the long chains composing a polymer's structure are thermally decomposed to shorter fragments. Eventually fragmentation occurs to such an extent that the small molecules produced volatilize and enter the gas phase. With continued heat application and the presence of an ignition source (flame, spark, etc.) or under autoignition conditions, these gas phase molecules undergo rapid reactions propagated by high-energy radicals resulting in flaming combustion.

## Fire Retardant Development

With the increased growth of the plastics industries, and the resultant widespread use of synthetic polymers derived from crude oil, the flammability of our work, domestic and travel environments, has also increased. During the 1960s and 1970s, as the availability of synthetic polymers began to rise, fires became more common, faster growing and more severe. Fire fighters reported changes, from fires with limited visibility, to those with almost no visibility due to dense smoke, primarily resulting from newly available low-cost polyurethane foam furniture. A timeline of the events that emphasized the need for fire retardant solutions is given in Table 1.

Fire retardants have found widespread use to limit the increased flammability of our surroundings and address the associated threats. They represent one of the most important plastic additives with approximately 2.2 million metric tonnes sold in Europe, Asia, and the United States in 2014. This number is predicted to rise to 3.1 million metric tonnes by 2019, valued at $7 billion (Roskill Information Services Ltd 2014; Freedonia Group 2016). Use of ATH as a flame retardant is forecast to grow by 7.1% per year between 2014 and 2019, largely due to increasing regulation in China

**Table 1** The events and resultant demands that can be addressed with fire retardant solutions

| Decade | Event | Demand |
|---|---|---|
| 1960s | Widespread availability of cheap polymer products – more serious fires | Reduced ignitability |
| 1970s | Smoke becomes a major obstacle to escape | Reduced smoke |
| 1980–1990s | Development of cone calorimeter (and emphasis on peak heat release rate, rather than ignitability) | Reduced peak heat release |
| | Increase in deaths from smoke inhalation | Reduced fire toxicity |
| 2000s | Halogen FRs found across the ecosystem | Halogen-free FRs |
| 2010s | Climate change and other environmental concerns become mainstream | Sustainable FRs |

and India. There has also been an increase in the use of magnesium hydroxide, with much of the market growth in China.

Early fire retardants were halogen-based compounds often known as *flame* retardants, due to their action in the gas phase. Halogens replace the high-energy free radicals responsible for flame propagation with less reactive species, such as Cl·and Br, thus quenching the flame. These flame retardants are easy to incorporate into a polymer and were selected based on compatibility with the host polymer and its decomposition temperature range. However, interference with flame reactions inhibited hydrocarbon oxidation and the conversion of CO to $CO_2$, which resulted in very smoky, highly toxic fire effluents, rich in products of incomplete combustion.

Halogen flame retardants have also been shown to leach out of polymers into the natural environment, where their presence is now ubiquitous, and some are proven endocrine disruptors (De Wit 2002; Shaw et al. 2010). These combined toxicity and environmental problems have driven the search for alternative "halogen-free" fire retardants, which include metal hydroxide (Hull et al. 2003; Rothon and Hornsby 1996) and carbonate fillers (Rigolo and Woodhams 1992), phosphorus compounds (Price et al. 2002), low melt glasses (Bourbigot et al. 1999), as well as a range of more esoteric materials, such as clay and silica nanoparticles (Hull et al. 2009; Schmaucks et al. 2009), carbon nanotubes (Bourbigot et al. 2010), expandable graphite (Li and Qu 2003), and metal chelates (Wang et al. 2007, 2008). Halogen-free fire retardants are generally much more polymer specific; while one fire retardant may work well in one polymer, it may not work at all in another.

## Mineral Filler Fire Retardants

Mineral fillers represent an important class of alternative, "halogen-free" fire retardants. While the Oxford English Dictionary defines "mineral" as "a solid, naturally occurring, usually inorganic substance with a definite chemical composition and characteristic physical structure and properties (such as crystalline form)," within the scope of this chapter, this definition has been extended to include synthetic inorganic substances with fire retardant applications, in line with usage within the industry. Mineral fillers are more difficult to incorporate into a polymer at the loadings necessary to achieve the required level of fire retardancy than halogenated flame retardants, so it is vital to understand their mode of action and the options available.

The materials of interest include: aluminum hydroxide, magnesium hydroxide, magnesium carbonate, and mixed magnesium/calcium carbonates and hydroxides, such as naturally occurring mixtures of huntite and hydromagnesite. Of course, several other inorganic materials with fire retardant applications fit the definition of "mineral fillers," such as nanoclays, zinc borates, and zirconium phosphates, although they are typically used at lower loadings.

All mineral fillers act in the condensed phase, diluting the combustible polymer, forming barriers to heat and mass transfer, and resulting in a subsequent reduction in the rate of mass loss and heat release. However, the focus of this chapter is those mineral fillers that also contribute to fire retardancy through endothermic decomposition in the condensed phase, releasing inert gas and leaving a solid residue. In order to be effective, the decomposition must occur in a narrow window above the polymer processing temperature, but at or below its decomposition temperature. The different types of mineral filler fire retardants are described, and their modes of action and applications discussed. The common test methods used to assess the performance of fire retardant polymer composites are also described, and their environmental sustainability and recycling potential, a topic of increasing concern and relevance, is evaluated.

## Types of Mineral Filler Fire Retardants

Table 2 shows the main physical properties and chemical formulae of the main mineral filler fire retardants, using data derived from thermogravimetric analysis and differential scanning calorimetry (see section "Thermal Analysis Techniques").

### Metal Hydroxides

Aluminum hydroxide (ATH, $Al(OH)_3$, often incorrectly called alumina trihydrate or aluminum trihydroxide) is the highest-tonnage fire retardant on the market as a combined result of its low cost and the need for high loadings (usually above 50%) to achieve satisfactory fire retardancy in a polymer composite (Beard 2007). Production methods for ATH involve the use of mineral bauxite, followed by a chemical process involving sodium hydroxide, which results in storage and disposal problems of an equal volume of a caustic red sludge by-product.

Magnesium hydroxide (MDH, $Mg(OH)_2$), while less widely used than ATH (less than 5% by mass of total fire retardant market consumption) works in the same way as ATH, only it decomposes at temperatures approximately 100 °C higher (see Table 2).

The higher decomposition temperature of calcium hydroxide (~430 °C) suggests that it may perform well with polymers of higher thermal stability. In practice, however,

**Table 2** Mineral fillers with potential fire retardant applications and corresponding decomposition data

| Mineral filler | Decomposition onset/°C | Enthalpy of decomposition/ kJ kg$^{-1}$ | Volatile content/% w/w | | |
|---|---|---|---|---|---|
| | | | $H_2O$ | $CO_2$ | Total |
| Aluminum hydroxide, (ATH) $Al(OH)_3$ | 180–200 | 1300 | 34.5 | 0 | 34.5 |
| Magnesium hydroxide, (MDH) $Mg(OH)_2$) | 300–320 | 1450 | 31 | 0 | 31 |
| Calcium hydroxide, (CDH) $Ca(OH)_2$ | 430–450 | 1150 | 24 | 0 | 24 |
| Hydromagnesite, $Mg_5(CO_3)_4(OH)_2.4H_2O$ | 220–240 | 1300 | 20 | 36 | 56 |
| Huntite, $Mg_3Ca(CO_3)_4$ | 400–420 | 980 | 0 | 50 | 50 |
| Hydromagnesite and huntite as 60:40 mixtures, (HMH) | 220–240[a] | 990 | 11 | 43 | 51 |
| Nesquehonite $MgCO_3.3H_2O$ | 70–100 | 1750 | 39 | 22 | 61 |
| Magnesium carbonate subhydrate, $MgO.CO_{2\ (0.96)}H_2O_{(0.30)}$ | 340–350 | Not available | 9 | 47 | 56 |
| Boehmite (AlO(OH)) | 340–350 | 560 | 15 | 0 | 15 |

[a] Decomposition begins as the hydromagnesite decomposes but the decomposition occurs over a temperature range from 220 to 750 °C (Hollingbery and Hull 2010)

calcium hydroxide does not perform well, due to the high thermal stability of the carbonate, which forms exothermically, in preference to the oxide (Rothon 2003).

## Hydromagnesite and Huntite Mixtures

Naturally occurring mixtures of hydromagnesite ($Mg_5(CO_3)_4(OH)_2.4H_2O$) and huntite ($Mg_3Ca(CO_3)_4$), some of which are sold as UltraCarb®, have similar potential as FRs to ATH or MDH. Commercially extracted natural reserves of hydromagnesite and huntite (HMH) mixtures are already sufficiently pure and do not need chemical processing or precipitation of the final product. This makes production of fine particle size mixtures of huntite and hydromagnesite much less energy intensive. The only by-product is a small quantity of dolomite, $MgCa(CO_3)_2$, a mineral closely related to huntite, $Mg_3Ca(CO_3)_4$, that occurs naturally in the mixture and is removed during the grinding process.

## Carbonates

Nesquehonite ($MgCO_3.3H_2O$) has the properties of an effective fire retardant mineral filler but is not commercially produced for this purpose due to its low decomposition temperature (70–100 °C); it would decompose during processing.

Hydromagnesite (basic magnesium carbonate) can be formed from nesquehonite and has greater thermal stability (decomposition onset at approximately 220–240 °C). It finds its main fire retardant and smoke suppressant applications in elastomers, although its use is limited by its platy morphology and its increased cost compared to ATH (Rothon 2003). Magnesium carbonate subhydrate ($MgO.CO_{2\ (0.96)}H_2O_{(0.30)}$) has higher decomposition temperatures still (340–350 °C) and is capable of withstanding processing temperatures of up to 300 °C. Its application as a fire retardant is, however, limited: despite showing oxygen index results equivalent to ATH, its decomposition is too slow to perform effectively in ignitability tests (Rothon 2003).

### Boehmite

Boehmite AlO(OH) and nanoboehmite have recently shown (Zhang et al. 2010) potential as fire retardant additives, although nanoboehmite is also believed to act in the gas phase as a free radical trap, since its endotherm and heat capacity contributions are too small to justify its wider use as an absorber of heat. Boehmite is an intermediate decomposition product of ATH. ATH undergoes its largest endothermic stage in the formation of boehmite, while the endotherm of the final decomposition stage of boehmite to alumina is smaller; thus, endothermic decomposition is unlikely to be the principal fire retardant action of boehmite.

## Mode of Action

The most important fire retardant effects of mineral fillers can be summarized as follows:

1. Endothermic decomposition, absorbing heat and therefore keeping the surrounding polymer cooler.
2. Production of inert diluent gases. Flaming reactions require a critical concentration of free radicals to be self-sustaining. If this concentration falls sufficiently, for example, by the release of water or carbon dioxide, flame extinction will occur.
3. Accumulation of an inert layer on the surface of the decomposing polymer, shielding it from incoming radiation, and acting as a barrier to oxygen reaching the fuel, flammable pyrolysis products reaching the gas phase, and radiant heat reaching the polymer.
4. Incorporation of any noncombustible filler reduces the flammability of a polymer, by reducing the total amount of fuel, the rate of diffusion of oxygen into, and fuel from, the polymer bulk while increasing the heat capacity, thermal conductivity, reflectivity, and emissivity.

These effects are discussed in detail in section "Fire Retardant Effects of Mineral Fillers." First, however, a summary of the two fundamental thermal analysis techniques, thermogravimetry (TGA) and differential scanning calorimetry (DSC), is given to contextualize the decomposition data used to illustrate the fire retardant effects of these materials.

## Thermal Analysis Techniques

### Thermogravimetry

"Thermogravimetry is a technique in which the mass of a test specimen is measured as a function of temperature or time, while the test specimen is subjected to a controlled temperature program." (ISO 11358 1997) Thermogravimetric analysis (TGA) is the most commonly used method for investigating the thermal decomposition processes of polymers.

Experiments can be performed isothermally (at one temperature) or dynamically (using a variable or fixed heating rate). In isothermal experiments the sample is rapidly heated to the desired temperature, usually by insertion into a preheated furnace, and the weight of the sample is monitored during the course of thermal decomposition. In practice, the sample does not heat instantaneously, so errors arise where the selected temperature is high enough for significant decomposition to occur within the first few minutes. Dynamic TGA subjects the sample to temperature programmed heating. A commonly used heating rate for investigating fire behavior is 10 °C $min^{-1}$; this is considered a compromise as it is low enough to attain thermal equilibrium within the sample but high enough to reflect the dynamic processes occurring in a fire. Alternatively, a variable heating rate, for example, heating at 10 °C $min^{-1}$ to 400 °C, followed by 1 °C $min^{-1}$ heating to 410 °C and then back to 10 °C $min^{-1}$, can be used to focus on a particular step. A further modification is high-resolution TGA, in which the changes in sample mass are used to slow the heating program, to get better resolution of individual thermal events. As isothermal TGA is falling into disuse, it is common to refer to "dynamic TGA" simply as TGA.

The results of TGA experiments may be presented as sample mass, usually as a percentage of total mass as a function of temperature (or time, for isothermal TGA), or may be presented as the differential, showing the peaks of mass loss (DTG). Both formats have their advantages – the mass versus temperature plot gives direct information about sample composition, the percentage of nonvolatiles, etc., while it is much easier to see small differences in peak decomposition temperatures from DTG curves, and allows easy quantification of the maximum rate of mass loss (or fuel production, which is proportional to heat release rate in fire science). Figure 1 shows the TGA and DTG curves for ATH in nitrogen at a heating rate of 10 °C $min^{-1}$, showing two decomposition stages: the first, occurring between 200 and 300 °C represents the main mass loss from water; the second, more gradual, mass loss corresponds to the slow decomposition of boehmite, resulting in a residue of alumina.

### Differential Thermal Analysis and Differential Scanning Calorimetry

These techniques quantify the energy required, or released, during temperature programmed heating. Originally, differential scanning calorimetry (DSC), invented

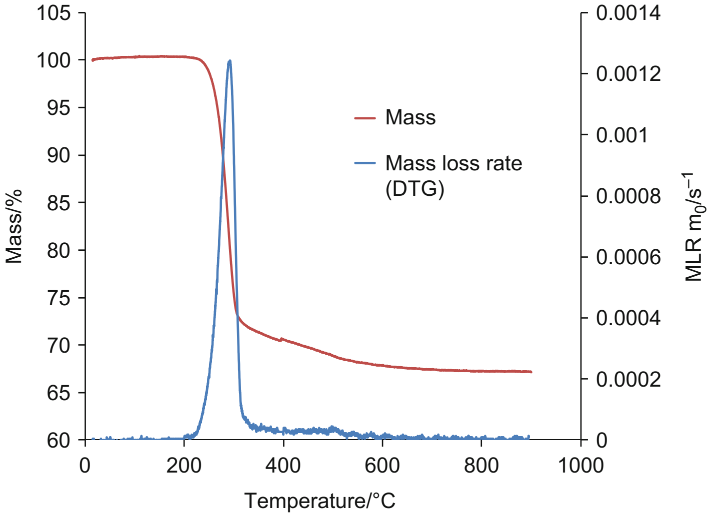


**Fig. 1** TGA and DTG curves for ATH decomposition in nitrogen at 10 °C $\text{min}^{-1}$

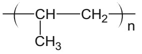
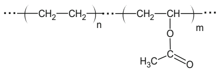
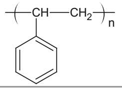
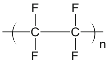
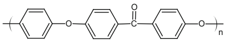
by Perkin-Elmer, was deemed by the International Conference on Thermal Analysis (ICTA) to describe only the technique where a quantifiable amount of energy, as an electric current, was supplied to the sample (or reference) to maintain the sample and reference temperatures equal, now known as *power compensation DSC*.

In differential thermal analysis (DTA), the temperature of the sample is compared to the temperature of a reference (usually a matching empty crucible) during programmed heating (or cooling). Raw DTA data is recorded as temperature difference (between the sample and reference pans) as a function of temperature. Prior calibration using materials of known heat capacity, such as sapphire disks, together with software converts the temperature difference into energy units, to make the results comparable to power compensation DSC. Thus, calibrated DTA became known as *heat flux DSC*. Now it is recognized that both techniques provide the same information and are both classed as DSC (Laye 2002). Data is reported as a differential, showing endothermic (heat to sample) or exothermic (heat from sample) processes. DSC provides useful information about the thermal decomposition of both mineral fillers and polymeric materials.

## Fire Retardant Effects of Mineral Fillers

It is necessary to ensure that the decomposition of the mineral fillers intended for use as fire retardants occurs within a temperature range similar to that of its host polymer. Table 3 shows typical melting and decomposition temperatures of some common polymers – this is important information for selecting an effective fire retardant for the particular polymer matrix. The “processing window” lies between the melting

**Table 3** Decomposition temperatures of some common polymers

| Polymer | Structure | Melting range/°C | Decomposition onset/°C |
|---|---|---|---|
| Polyethylene (PE) | $-\!\left(CH_2-CH_2\right)_n\!-$ | 115–135 | 370–415 |
| Polypropylene (PP) |  $-\!\left(\underset{CH_3}{\underset{\mid}{CH}}-CH_2\right)_n\!-$ | 130–170 | 350–390 |
| Poly(ethylene-co-vinyl acetate) (EVA) |  | 75–100 | 300 |
| Polystyrene |  | 230–240 | 275–364 |
| Polycaprolactam/Polyamide 6 (PA 6) | $-\!\left(NHCO-(CH_2)_5\right)_n\!-$ | 225–235 | 435 |
| Poly(tetrafluoro ethylene) (PTFE) |  | 327 | 470–510 |
| Poly(ether ether ketone) (PEEK) |  | 334 | 570 |

point and decomposition temperature; the filler must not decompose within the processing window.

The polymers listed in Table 3 demonstrate a considerable range of melting and decomposition temperatures. Comparing these with the decomposition temperatures of the mineral fillers in Table 2, it could be said that ATH, MDH, hydromagnesite, and HMH mixtures tend to be suitable for most of these materials. Due to its low cost, ATH is a popular choice, but for those polymers that are processed above its decomposition temperature, MDH and HMH mixtures would be more suitable. For polymers that decompose at higher temperatures, for example, PEEK and PTFE, fillers such as ATH and MDH would undergo decomposition too early and be unable to interfere with the decomposition of the polymer matrix. These polymers would be better suited to mineral fillers with higher decomposition temperatures, although few are in common use.

The fire retardant effects of mineral fillers can be illustrated using ATH as an example. ATH decomposes to form alumina ($Al_2O_3$) with the release of water. It breaks down endothermically forming water vapor, diluting the radicals in the flame, while the residue of alumina builds up to form a protective layer.

$$2\ Al(OH)_3(s) \overset{180-200\,^{\circ}C}{\rightarrow} Al_2O_3(s)\ +3\ H_2O(g)$$

$$\Delta H\ =\ +1.3\ kJ\ g^{-1}$$

Organic polymers have heat capacities (Stoliarov et al. 2009) ranging from 0.9 to 2.1 J $K^{-1}g^{-1}$, thus the decomposition enthalpy of a fire retardant mineral filler is a factor of 1000 larger – the decomposition enthalpy of 1 g $Al(OH)_3$ is equal to the heat (q) required to raise the temperature of a mass (m) of 1.5 g of low density polyethylene (LDPE) from ambient temperature to decomposition (400 °C) ($\Delta\theta$), assuming constant heat capacity (c) during heating ($q = m\,c\,\Delta\theta$, so $q = 1.5 \times 2.3 \times 375 = 1.29$ kJ). ATH is also an effective heat conductor and acts to reduce local hotspots, which are responsible for starting fires (Table 4).

## Quantifying the Fire Retardant Effects

The decomposition data of the mineral fillers in Table 2, together with the average values of heat capacities of the filler, its residue, and its gaseous decomposition products have been used to estimate the heat absorption by the filler (% Filler), the residue (% Residue), the evolved water vapor and carbon dioxide (% Gas), and the decomposition endotherm (% Decomposition Endotherm) shown in Table 5.

The figures generally show broad similarities – in all cases, the greatest contribution comes from the endothermic decomposition. The decomposition temperature clearly affects the relative contributions of the heat capacity of the filler and those of the residue and gas. It can be seen that in some cases, e.g., $Al(OH)_3$, and $MgCO_3.3H_2O$, the heat capacities of the gas phase products exceed that of the condensed phase, where for others, e.g., $Mg(OH)_2$ and $Ca(OH)_2$, the solid phase contribution is greater. Comparing aluminum and magnesium hydroxide, it is

**Table 4** Fire retardant effects of mineral fillers

| Effect | How quantified |
|---|---|
| Diluting polymer in condensed phase | Heat capacity of the filler prior to decomposition |
| Endothermic decomposition of filler | Heat of decomposition |
| Presence of inert residue | Heat capacity of the residue after decomposition |
| Presence of diluent gases | Heat capacity of the diluent gases |

**Table 5** Relative contribution of heat absorbing effects for potential mineral filler fire retardants (Hull et al. 2011)

| | Relative contribution fire retardant effects | | | |
|---|---|---|---|---|
| | % Filler | % Endotherm | % Residue | % Gas |
| Aluminum hydroxide | 9 | 55 | 13 | 23 |
| Magnesium hydroxide | 19 | 56 | 9 | 15 |
| Calcium hydroxide | 29 | 55 | 5 | 11 |
| Nesquehonite | 1 | 58 | 12 | 29 |
| Hydromagnesite | 10 | 56 | 14 | 21 |
| Huntite | 20 | 58 | 9 | 13 |
| Ultracarb[a] | 14 | 57 | 12 | 18 |
| Boehmite | 18 | 46 | 20 | 15 |

[a] Ultracarb is the trade name for HMH mixtures containing hydromagnesite and huntite at a ratio of around 60:40

evident that the difference between their relative effects arises from the higher decomposition temperature of $Mg(OH)_2$, giving a larger contribution to the heat capacity of the undecomposed filler, but a smaller contribution from the heat capacity of the residue and the heat capacity of the (greater volume of) water vapor released by the $Al(OH)_3$ – even though the energy for such a release is similar for both fillers. Where two separate decomposition processes occur, such as in nesquehonite, which loses water at 100 °C and carbon dioxide at 450 °C, the heat capacity of the intermediate $MgCO_3$ has been included in the residue contribution, together with MgO. The low decomposition temperature of nesquehonite and the high volume of volatiles make this an interesting candidate material for polymers with very low (~100 °C) decomposition temperatures. For the hydromagnesite, huntite, and Ultracarb mixture, which is often proposed as an alternative to $Al(OH)_3$, it can be seen that the higher decomposition temperature of huntite gives a greater filler contribution, and overall Ultracarb is intermediate between aluminum and magnesium hydroxides.

As the data have all been calculated in energy units, the contribution to the individual fillers may also be compared in absolute terms. Figure 2 shows the energy absorption per gram of each of the processes undergone by the filler.

The higher decomposition temperature of magnesium hydroxide and particularly the greater contribution of the filler increase its energy absorbing capacity by about 250 J $g^{-1}$, compared to aluminum hydroxide, while the lower endotherm and smaller volatile heat capacity of calcium hydroxide also indicates inferior potential as a fire retardant. The large endotherm and higher vapor heat capacity of nesquehonite suggest its potential as a superior fire retardant additive, except that it decomposes at such a low temperature (onset of decomposition occurs between 70 and 100 °C).

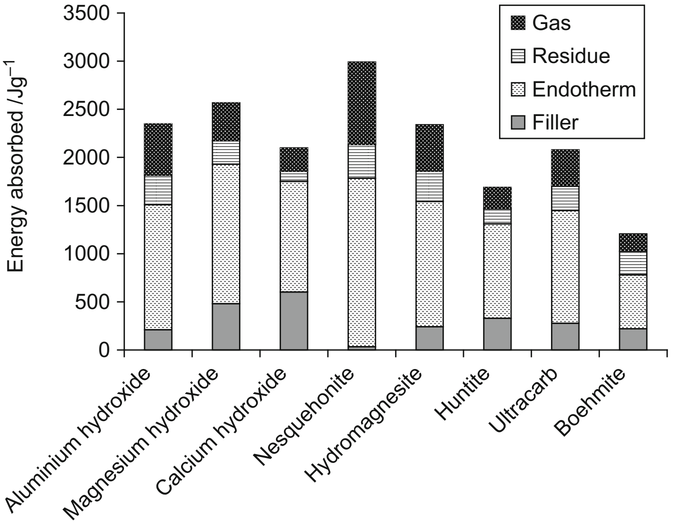


**Fig. 2** Absolute estimation of heat absorbed by potential fire retardant mineral fillers

The behavior of hydromagnesite is very similar to that of aluminum hydroxide, where the smaller endotherm and vapor heat capacity of huntite reduce the apparent fire retardant potential of the Ultracarb mixture below aluminum hydroxide. In practice, the Ultracarb mixture is often found to outperform either hydromagnesite or aluminum hydroxide as a fire retardant. This has been ascribed to the platy morphology of huntite, reinforcing the barrier properties of the residual layer (Hollingbery and Hull 2010). The much lower energy absorbing capacity of boehmite, together with reports (Laachachi et al. 2009) of its successful application as an additive fire retardant, suggest that other mechanisms must also be operating.

It is evident from Fig. 2 and Table 5 that endothermic decomposition accounts just over half of the fire retardant effect for the mineral fillers considered. For the example of LDPE and $Al(OH)_3$ considered earlier, the total heat absorbed by 1 g of filler could otherwise have heated almost 4 g of LDPE to its decomposition temperature.

## Other Considerations

### Afterglow

Afterglow, or incandescence, is a phenomenon that can considerably reduce the effectiveness of fire retardants and their performance in certain regulatory tests. Aluminum and magnesium hydroxide have been found to reduce the temperatures at which incandescence occur and the onset temperatures of incandescence have been shown to decrease with increased loadings of ATH or MDH (Delfosse et al. 1989). MDH, or rather its decomposition product, magnesium oxide, promoted incandescence to a greater extent than aluminum oxide at all loadings investigated (20 to 65% w/w) in EVA. Observations during the same experiments found that, in cases where incandescence occurred, the residue was present as a white ash, free from carbonaceous matter. The overall conclusion was drawn that the incandescence was a result of catalytic oxidation of carbonaceous residues on the freshly formed metal oxide surfaces following decomposition of ATH and MDH. Magnesium oxide is known to have a greater catalytic effect than aluminum oxide, which correlates with the observations of enhanced incandescence in the presence of MDH compared to ATH. The phenomenon of afterglow has been shown to increase the yield of toxic carbon monoxide from burning EVA-ATH (Hull et al. 2002).

### Smoke Suppression

Smoke is condensed phase particulate matter that causes visual obscuration. Typically it is comprised of carbonaceous (soot) particles and liquid droplets. Smoke is a product of incomplete combustion. Soot particles absorb heat and emit it as infrared radiation, usually increasing the propensity for horizontal and downward flame spread. One of the attractive features of mineral filler fire retardants is their low smoke production. The mechanism of smoke suppression by MDH in several polymers has been investigated and reported (Rothon and Hornsby 1990). It has been found that the presence of MDH in these polymers reduced both the rate of smoke production and the volume of smoke produced. Smoke is only released during combustion processes when carbonaceous products escape the flame without oxidation. The reactions below are representative of some of those that result in the oxidation of carbon:

1. $2\,C + O_2 \rightarrow 2\,CO$
2. $C + O_2 \rightarrow CO_2$
3. $C + H_2O \rightarrow CO + H_2$
4. $C + CO_2 \rightarrow 2\,CO$

A variety of metal oxides, including aluminum oxide and magnesium oxide that are formed as a result of ATH and MDH decomposition, respectively, are known to catalyze these oxidation reactions. When incorporated into polymers, these mineral fillers achieve low-smoke burning and additionally only release their inert endogenous gases ($H_2O$ and/or $CO_2$), therefore not contributing to the propagation or sootiness of the flame.

### Ethylene-vinyl Acetate-Mineral Filler Composites

The polar amorphous nature of poly(ethylene-co-vinyl acetate) (EVA) allows it to tolerate the high loadings of mineral fillers that are needed to produce a fire retardant effect (up to 70% by weight). EVA and mineral filler composites are particularly prevalent in the electric cable industry for meeting “halogen-free” requirements. The global market for halogen-free cable compounds is approximately €400 million, of which EVA-metal hydroxides is around €300 million.

The thermal decomposition mechanism of virgin EVA is well documented: chain stripping of the acetate side groups releases acetic acid at ~300 °C and subsequent polyene decomposition occurs at ~400 °C and above. In the presence of mineral fillers that decompose to metal oxides, it has been shown by thermogravimetry that the microscale decomposition of the polymer composite is not simply an additive decomposition of the individual polymer and filler components. Figure 3 shows the TGA curves for the individual components of an EVA-ATH compound (~27% VA EVA at an ATH loading ~70%), together with the theoretical curve, obtained by adding the TGA curves of the individual components in proportion to their mass in the compound.

The early delay in mass loss observed in the experimental curve compared to that of the theoretical curve has been attributed to the catalytic conversion of acetic acid, stripped from the EVA, to acetone by the metal oxide that forms from the filler’s decomposition. This has been corroborated with gas analyses both on the microscale (Witkowski et al. 2012; Yen et al. 2012) and the bench scale (Ngohang et al. 2014), and demonstrated by pyrolysis modeling (Hewitt et al. 2016). In the past, acetone was produced commercially by passing acetic acid over heated calcium oxide. The same catalytic properties are possessed by aluminum and magnesium oxides; such behavior has an important effect on the fire behavior of EVA-ATH or EVA-MDH as this conversion delays the release of fuel.

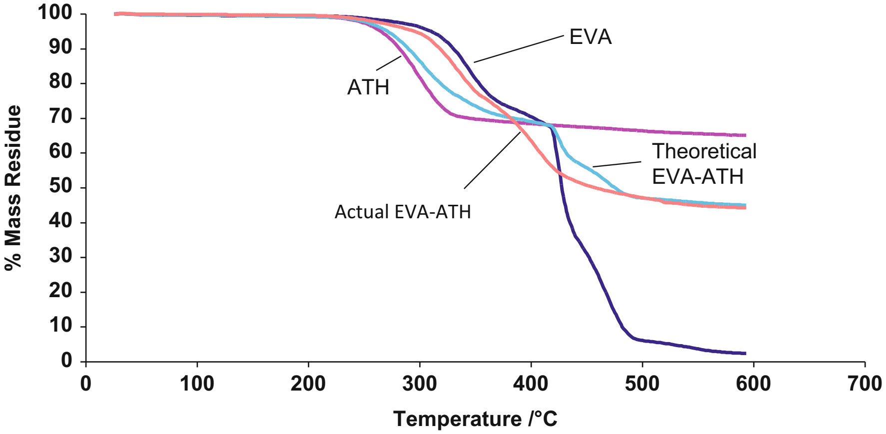


**Fig. 3** TGA curves of the individual components of an EVA-ATH compound (~27% vinyl acetate EVA at an ATH loading of ~70%) together with the theoretical curve obtained by adding the TGA curves of the individual components in proportion to their mass in the compound.

## Applications

In general, fire retardants are more expensive than their host polymers and are only added in order to meet regulatory requirements. If a particular polymer is used in a high-risk situation (mass transport, electrical and electronic, upholstered furniture, or certain construction applications) and it is too flammable, fire retardants may be incorporated to ensure that regulatory criteria are met.

The mid-1970s saw a surge in the commercial use of mineral fillers, due to legislation passed in the USA that required carpet backing to be of low flammability. ATH was found to be highly suitable for this purpose and its use has since infiltrated a multitude of other applications. In Europe, most of the market's ATH is incorporated within polyolefins, due to the demand for "low smoke and fume" (LSF) electric cables, particularly in nondomestic buildings (in domestic buildings "PVC cables" are most common, although actually comprised of roughly equal portions of PVC, chalk, and plasticizer). Magnesium compounds, including MDH, were introduced into the plastics and polymers market in the late 1980s (Janshekar et al. 2011). The Western European ATH market in 2010 was valued at $232 million and that for magnesium compounds was $34 million (Janshekar et al. 2011).

Due to its relatively low decomposition temperature, ATH is limited to polymers that can be processed below 200 °C. Magnesium compounds present an attractive alternative and offer a wide range of applications and processing temperatures. Use of MDH is expected to increase as polypropylene replaces PVC in the automotive industry, where high temperatures require thermally stable materials. Hydromagnesite and huntite mixtures are used in a range of PVC compounds for cable and building products.

**Table 6** End uses and applications for polymer – mineral filler composites

| Polymer | Mass of ATH/1000 tonnes | End use |
|---|---|---|
| Polyolefins (e.g., Polyethylene)<br>Polypropylene<br>Poly(ethylene-co-vinyl acetate) EVA | 72 | Sheathing for electric cables |
| Epoxies | 3.6 | Electronics, e.g., circuit boards |
| Poly(vinyl chloride) PVC | 46 | Building and construction, e.g., window frame |
| Polyurethane | 5 | Foams: insulation, upholstered furniture |
| Polyesters | 63 | Electrical, household, and automotive applications |
| Polyacrylates | 35 | Artificial marble |
| Nonplastic materials | 29 | Direct use of ATH in rubber and latex, paints, coatings, adhesives, sealants textiles, papers, cellulosics, wood, and laminates |

There are four types of ATH products on the market. Prices are given per kilogram based on value in 2010 (Janshekar et al. 2011).

Coarse – particle size = 40–80 μm, \$0.60–0.70 $\text{kg}^{-1}$
Ground – particle size = 2.5–20 μm, \$0.50–1.00 $\text{kg}^{-1}$
Precipitated – particle size = 0.8–2.5 μm, \$1.15–1.70 $\text{kg}^{-1}$
Surface treated – e.g., silane, stearic acid – \$1.72–2.40 $\text{kg}^{-1}$

The selection of ATH type is based on the cost and performance requirements. Ground ATH tends to be selected when the performance to price ratio is advantageous over other fire retardant solutions, or where regulations require low smoke production. About half of ground ATH is used in thermosets, one fifth is used in carpet backings, another fifth goes into coatings and plaster, and the rest is used in paints and cable applications (Janshekar et al. 2011). Precipitated ATH is mainly used in the wire and cable industry, although its use in thermosets and rubber flooring is on the rise. The commercial use of surface treated ATH is small due to the high cost; however, it finds use in applications requiring increased water resistance (e.g., bathtubs made from unsaturated polyester or acrylic polymers) or particularly high loadings (Table 6).

## Test Methods

Polymer flammability has no specific meaning; the flammability of a polymer is often defined by the method used to measure it (Nelson and Brindley 2000); flammability has been described as the ease with which a substance will ignite

(Quintiere 1997) but is also used to indicate the rate of fire growth after ignition: flammability is a function of both gas and solid phase chemistry (Zhang 2004). Fire tests are crucial to the development, screening and evaluation of materials with improved fire safety. Techniques employed to measure the ignition and burning behavior of a polymer are numerous. Some examples of fire tests are shown in Table 7, together with the individual fire properties they can quantify (Patel et al. 2012).

It can be seen from Table 7 that no single test covers all the parameters describing fire safety behavior, but many address more than one parameter. When selecting a test method, it is necessary to determine the end use of the product, and the likely fire scenarios. Aside from materials' development, in fire testing, there are generally two end purposes:

- To meet a regulatory requirement
- To demonstrate that the material being tested will perform adequately in a specific fire scenario (Babraukas 2000).

Understandably, manufacturers will optimize their materials in order to pass regulatory tests, and it is incumbent on the regulators to ensure that their tests continue to be appropriate to the types of fire retardant technologies being deployed.

## Limiting Oxygen Index

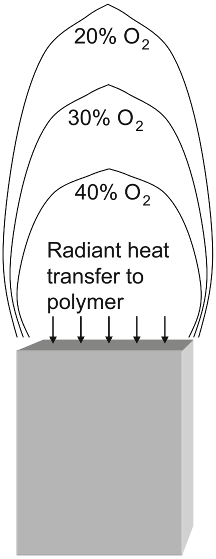
In the limiting oxygen index test (LOI) a flame is supplied to a strip of sample, typically 2 mm × 4 mm × 150 mm, in an atmosphere of known oxygen concentration. The LOI is the lowest concentration able to support downward flame propagation. It is essentially an ease of extinction test – a flame will only propagate down the polymer sample if the radiant heat transferred from the flame to the polymer is sufficient to vaporize enough fuel to replace it. As the oxygen concentration is decreased, the flame is diluted by nitrogen, increasing in size, and also reducing the radiant heat transferred to the polymer, until it is so large, the concentration of the flame propagating free radical species falls below a critical threshold, and the flame goes out. This is illustrated in Fig. 4 for three oxygen concentrations. If the test is run in high oxygen concentrations, a small, very intense white flame is observed.

The endothermic decomposition of the filler and the heat capacity of both the filler and its residue will all increase the amount of heat needed to vaporize the same amount of fuel, while the presence of gas phase flame diluents (water or carbon dioxide) will also tend to swell the flame, and reduce its temperature, reducing the proportion of heat transferred back to the polymer. Therefore, the different contributions to fire retardant behavior will all contribute to the increase in LOI, and thus be indistinguishable. However, the incorporation of any filler material in easily depolymerizable host polymers (which drip, improving their LOI) will increase the LOI.

**Table 7** Common fire tests and parameters assessed

| | Radiant ignition Test (ISO 5657) | Glow wire test (IEC 60695-2-10 to 13) | Small-flame ignitability test (ISO 11925) | UL-94 (IEC 60695-11-10) | Cone calorimeter (ISO 5660) | Laterally induced flame test (ISO 5658) | Limiting oxygen index (ISO 4589–2) | Smoke density chamber (ISO 5659) | Steady state tube furnace (ISO 19700) |
|---|---|---|---|---|---|---|---|---|---|
| Ignitability | x | x | x | | x | x | | | |
| Rate of flame spread | | | x | x | | x | | | |
| Rate of heat release | | | | | x | | | | |
| Ease of extinction | | | | | | | x | | |
| Smoke production | | | | | | | | x | x |
| Effluent toxicity | | | | | | | | | x |

**Fig. 4** The LOI test showing the swelling of the flame and consequent decrease in radiant heat transfer to the polymer with oxygen concentration decreasing from 40% to 20%.



Rothon (2003), Ashley and Rothon (1991), and Hornsby and Watson (1990) have reported a lack of correlation of LOI to other tests when applied to mineral fillers which they attribute to the key structural role played by the filler residue in the LOI. In particular, significant inexplicable differences were observed in the LOI, for example, between calcium carbonate and glass beads, or when the residue was tapped off the tip of the burning polymer, although in both instances little difference was observed in the UL94 tests.

Rothon (2003) observed that although the oxygen index test appears fairly well understood, its relevance to other tests is not well founded, and these other tests are themselves poorly understood in terms of filler effects. He attributes the difference to the smaller portion of heat fed back to the polymer in the LOI from the flame, shown in Fig. 4, compared to other tests.

In addition, correlations were usually worse with very fine mineral filler particle sizes. This was attributed to sintering of the particles, providing a more resilient residue structure, capable of shielding (by reemission) the polymer from much of the flame’s radiation.

Work on ATH has shown the strong reversibility of the dehydration reaction, such that, with larger particle sizes water released inside the particle recombines with the reactive surface of the freshly formed alumina (Souza et al. 2000). If escape of water is hindered sufficiently (for example, by the high viscosity of the polymer melt), it has been found that partial decomposition product boehmite is formed nearer the middle of the particles. This effect increases with particle size (Sobolev and Woychesin 1987).

## Bunsen Burner Test UL 94

The UL 94 (Underwriters' Laboratory) tests use a small (~15 mm) Bunsen burner type flame to ignite the endmost inch (25 mm) of a 6 in. (150 mm) strip of plastic material, either horizontally oriented (for the lowest HB classification) or vertically oriented, for the higher V-2, V-1, and the highest V-0 classifications). If flaming travels to the other end of the test strip, a failure is recorded. In the vertical test, if flaming extinguishes within 10 s, the V-0 classification is achieved, if it continues for 30 s, V-1 is achieved, unless there are flaming drips, which lower the classification to V-2.

Although widely regarded as the simplest of flammability tests, the UL 94 horizontal and vertical tests involve several interacting physical processes which are inadequately reflected in the final classification of HB, V-2, V-1, and V-0. As the flame propagation is either horizontal or vertically upward, flame dilution, and hence flame dilation is likely to have a smaller effect than energy absorption through endothermic decomposition or solid phase heat capacity, since a greater portion of the heat of combustion is fed back to the polymer, than in the LOI test. Unlike the LOI, dripping can be disadvantageous in the UL 94 test; flaming drips limit the classification to V-2 at best. Solid phase fillers and residues will almost always reduce dripping. Endothermic decomposition with release of water or carbon dioxide must coincide with fuel release to be effective in flammability reduction – in the UL 94 test, once the first flame is extinguished, it is followed by the second 10 s application – after which the endothermic water loss is exhausted, and the heat capacity of the protective residue may make the most important contribution.

## Cone Calorimetry

The cone calorimeter (ISO 5660) is a widely used technique for physically modeling flaming combustion penetrating into the bulk of a polymeric material. The sample (100 mm × 100 mm) is subject to uniform irradiation from the conical heater, typically with a flux of 25, 35, or 50 $\mathrm{kWm^{-2}}$, in the presence of a spark igniter. The effluent is drawn into a hood, and the oxygen ($O_2$) consumption is precisely determined. For most materials containing carbon, hydrogen, oxygen, and nitrogen, the heat release may be calculated as 13.1 kJ per g $O_2$ consumed.

Results from the cone calorimeter increasingly dominate reports of the efficacy of fire retardant systems, although it features in few regulatory requirements. A detailed description of its use for assessment of fire retardant behavior has been given elsewhere (Schartel and Hull 2007). Unlike the LOI, the effects of dripping are negligible, since the solid/liquid sample is contained within a foil tray. The key flammability parameters obtained from cone calorimetry are the time to ignition (TTI) and the heat release rate per unit area (HRR). As flame spread can be viewed as a series of repeated ignitions, surface spread of flame is likely to be controlled by the time to ignition. The overall heat release rate $(\dot{Q})$ is the most important parameter controlling the fire growth rate. In the cone calorimeter and other standard protocols, only the heat release rate per unit area (HRR) is measured, since surface spread of flame is prevented by the small sample size (100 × 100 mm). However, uncontrolled fires spread across surfaces as well as penetrating into them, and the overall heat release rate $(\dot{Q})$ is the product of the heat release rate per unit area (HRR) and the burning area (A). If the speed of flame spread is assumed constant ($v_f$) and the fire spreads as a growing circle (of radius r), the heat release rate will increase in proportion to the square of time (Celzard et al. 2011).

$$\dot{Q} = A \times \mathrm{HRR} = \pi r^2 \times \mathrm{HRR} = \pi v_f t^2 \text{ so } \dot{Q} \propto t^2$$

Fire safety engineers frequently refer to this as a "$t^2$ fire." Thus a major limitation of cone calorimeter data is that the only indication it gives of flame spread rate is through the time to ignition parameter.

The time to ignition will be a function of the time taken for the surface temperature to reach the critical value for ignition. This depends on the thermal inertia of the material (the product of heat capacity, thermal conductivity, and density); on the absorption of radiation, dependent on the absorptivity and emissivity of the sample; all of which will change on incorporation of a filler, though only the heat capacity and the decomposition endotherm of the filler, contributing to the heat capacity, have been included in this simplified analysis.

After ignition, the heat release rate per unit area increases to a peak value (pHRR), an important parameter controlling fire growth, provided the fuel has significant thickness, and the rate of burning increases as it penetrates into the bulk of the material. At the pHRR, adjacent flammable articles are most likely to have their own critical heat fluxes for ignition exceeded, and thus ignite, contributing to the conflagration. However, this mode of burning is essentially penetrative, with the flame front moving towards the fuel above the gas-polymer interface. In this case, the physical presence of the filler residue will exert a greater influence on the burning behavior (seen as a dramatic reduction of pHRR) through its heat capacity, its absorption and emission of radiation, and its physical blocking of the route from fuel to flame. Thus a polymer containing a mineral which formed a coherent residue would be expected to show a HRR curve like that of a char forming material (such as wood) rather than that of a normal thermally thick burning (Schartel and Hull 2007). This is shown in Fig. 5. In this case the endothermic release of diluent gas may be counterproductive, encouraging greater flow of the protected fuel through the filler residue towards the surface, as the filler decomposes and gas release from below disrupts the protective layer.

In a study in the effect of nanoparticulate fillers, Schartel and Weiβ (2010) concluded that their major effect as fire retardants was to absorb and reemit radiation, and this effect increased with increasing surface temperature (following Stefan's Law) $\propto T^4$. While the conclusions of Schartel's work are controversial, the capacity of fine or ultrafine particles to reach high temperatures, where they become highly

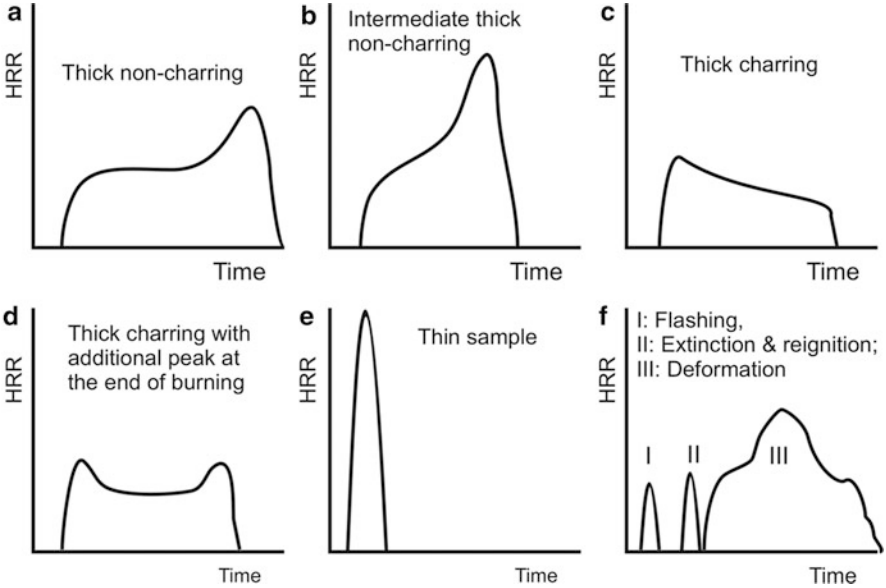


**Fig. 5** Idealized heat release curves for a range of sample types and behaviors

effective radiation shields (as absorbers and reemitters), has an obvious bearing on the present work. However, other sources cite different reasons for the particle size effect (Hughes et al. 1993).

It is worth noting that while the burning behavior of polymers containing mineral fillers will be modified, not all these effects will be evident in the cone data. It has been observed that the particle size effect, evident in the LOI and UL 94, is less evident in the cone calorimeter (Herbert 1994). The time to ignition will be delayed, and the peak heat release rate may be delayed and smaller then if the same mass of polymer was burned in the absence of the mineral filler, but the total heat released and hence the effective heat of combustion will not be reduced by the heat absorbing effects of the filler (typically twice the decomposition endotherm). This arises through the use of oxygen depletion calorimetry, which relates the heat release to the oxygen consumption as 13.1 kJ of heat released per gram of oxygen consumed. Any endothermic effects, which would be seen by a thermometric device, or in a real fire, will not be observed using oxygen depletion calorimetry. For example:

For a PE-ATH mixture (33.3:66.6%), the effective heat of combustion (EHC) for PE is 43 kJ $g^{-1}$; in this mixture, the cone calorimeter would record an EHC value of 14.3 kJ $g^{-1}$ ($43 \times 0.33$). However, the actual EHC would be that recorded by the cone *minus* the endothermic effects of the mineral filler, in the case of ATH, 2.3 kJ $g^{-1}$ ($14.3–2.3 = 12.0$ kJ $g^{-1}$) (from data in Fig. 2). This results in an error of approximately 16%.

This is an artifact of the technique and corrections need to be incorporated into measurement of total or effective heat of combustion, wherever oxygen depletion calorimetry is used to assess fire performance of materials containing endothermically decomposing mineral fillers. However, the delay in the time to ignition and the flattening of the heat release rate curve will still be apparent in cone calorimeter tests on polymers fire retarded with mineral fillers.

### Microscale Measurement of Heat Release

Microscale combustion calorimetry (MCC) (Lyon and Walters 2004) evaluates the combustibility of milligram samples by separately reproducing the solid state and gas phase processes of flaming combustion by controlled pyrolysis of the sample in an inert gas stream, followed by high temperature oxidation of the volatile pyrolysis products. Oxygen consumption calorimetry is used to measure the heat of combustion of the pyrolysis products. The maximum amount of heat released per unit mass per degree of temperature ($\mathrm{J\ g^{-1}\ {}^{\circ}C^{-1}}$) is a material property that appears to be a good predictor of “flammability.” The heat release capacity (HRC) and total heat release (THR), obtained by MCC, are related to the char yield and the heat of complete combustion of the volatiles. It takes no account of physical effects, such as dripping, wicking, and sample thickness, or chemical effects such as flame inhibition, because the conditions force pyrolysis and combustion to completion. However, varying the combustion temperature or oxygen concentration results in incomplete combustion as occurring in real fires. The THR results have been correlated to LOI; HRC and char residue to LOI; and HRC and THR with peak heat release rate (pHRR) in the cone calorimeter. It has been used as a screening test for efficacy of flame retardant additives (Lyon et al. 2007). As in the cone calorimeter, the use of oxygen depletion to measure the heat release will mask any effect of endothermic decomposition of the filler, although the filler may have a small effect in reducing the peak heat release rate.

## Environmental Sustainability

Sustainability generally refers to processes or products capable of being continued with minimal long-term effect on the environment. The International Union for Nature Conservancy (IUNC) define sustainability as something that improves the quality of human life while living within the carrying capacity of supporting ecosystems. In terms of fire retardant polymers, meeting these requirements is highly dependent on the existing practices and processes used during manufacture, and particularly during end-of-life processing. Given the dependence of polymer manufacture on petrochemicals, the environmental problems associated with halogenated flame retardants, the environmentally damaging manufacturing process of many fire retardants, and the incompatibility of fire retardant polymers with polymer recyclate, improvement in any of these areas could be claimed to increase the sustainability.

The sustainability requirements of an ideal fire retardant polymer can be identified.

1. The polymer would be derived from sustainably farmed biobased sources.
2. The polymer would be of inherently low flammability or incorporate a fire retardant whose manufacturer is clean and environmentally sustainable. This could be a naturally occurring material such as hydromagnesite-huntite (HMH) (Hollingbery and Hull 2010), deoxyribose nucleic acid (DNA), starch, or lignin, which would not pose problems of biodegradability or incompatibility in landfill.
3. The fire retardancy should be maintained through the end-of-life processing, such that the material can be readily reused.

In general, mineral filler fire retardants avoid the problems of halogenated flame retardants (which can be persistent, bioaccumulative, and toxic (PBT) when released into the environment). Moreover, their action does not adversely affect the smoke or toxicity from the burning polymer, and no special end-of-life processing is required. However, the world's most widely used fire retardant, aluminum hydroxide (ATH), uses very large amounts of energy in the extraction of aluminum from bauxite, and the process generates equal volumes of ATH and toxic red sludge, for which there is currently no viable remediation strategy. Thousands of tonnes of this highly alkaline toxic red sludge escaped in Hungary in 2010 causing 10 deaths. From 2016, European manufacturers are prohibited from dumping this sludge in the sea, and must identify uses for it.

## Conclusions

Mineral filler fire retardants represent one of the most important classes of fire retardant additive, exceeding all others by weight, if not by value. This is partly because they are available at relatively low cost, and need to be used at high loadings, but also because they provide the most effective, sustainable solution. As "fillers" they can enhance a material, providing structural integrity to the polymer, as described elsewhere in this volume, and if they are cheaper than the host polymer, may also reduce the unit cost.

Unlike halogenated flame retardants, whose selection only requires compatibility with the host polymer and a decomposition temperature around that of the polymer, mineral filler fire retardants also place other demands on formulators, arising from unwanted changes in physical, mechanical, and electrical properties, and particularly compatibility at high loadings.

A simple model has been described to quantify the relative contributions to the fire retardant effects of mineral fillers. The model is clearly not the end of the story but allows simple physical phenomena to be quantified in order to isolate more complex chemical and rheological phenomena. For example, the predicted similarity in performance between HMH and ATH in EVA is not observed in practice in the cone calorimeter, where the platy nature of the huntite reinforces the residue, reducing the main peak of heat release rate (Hollingbery and Hull 2012).

All fire retardant formulations require careful screening and evaluation. In many cases, the results of small- or bench-scale tests cannot be directly correlated to the behavior of real unwanted fires. It is essential to fully understand the characteristics of the test methods being employed when formulations are being optimized and to understand their relationship to the large-scale test. In particular, the use of oxygen depletion calorimetry (in the cone calorimeter (ISO 5660), microscale combustion calorimeter (ASTM D 7309), the single burning item test (EN 13823), and the bunched vertical wire cable test (IEC 60332–3) means that the beneficial effect of endothermic dehydration is not accounted for in the total heat release calculation.

The future drivers in fire retardant development are likely to focus on sustainability – although this has yet to be clearly defined, and many developers claim advances in sustainability while only focusing on a single aspect. With time, product specifiers will become more precise about their sustainability requirements, and it will be more difficult to hide behind overhyped claims, or “greenwash.”

In conclusion, mineral filler fire retardants are an essential tool for reducing the flammability of synthetic polymers and in many cases are capable of doing so without adverse effects on the environment or toxicity of the fire effluent. The greater expense of developing suitable formulations is largely offset by the difficulties competitors face in trying to reverse engineer them in order to copy them.

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# Thermally Conductive Additives

# 18

Joerg Ulrich Zilles

## Contents

## Abstract

Metals are by far still the most important materials in heat management with extremely high intrinsic heat conductivities (aluminum metal in the range of 200 W/m K). Their severe drawbacks on the other side are their high price, their high density (weight), and their high electrical conductivities.

Thermoplastics and thermosets are widely used in E&E (electric and electronic) applications. Their low thermal conductivity in the range of only 0,2–0,4 W/(m K) is unfortunately linked to their chemical structure.

Materials for thermal management in direct contact with heat sources have to transport heat by conduction as fast and effectively as possible away from them. Literature and experiments reveal that for effective removal of heat, heat

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conductivities exceeding 1–2 W/m K already drastically reduce temperature at the contact area between heat source and heat sink.

Since polymers offer complete freedom of design (but offering only heat conductivities in the range of 0,2–0,4 W/m K) in contrast to metal, using appropriate additives to increase their insufficient heat conductivity will be the future in integrated heat sink/housing design for LEDs, electric motors/engines, as well as for luminaires and other electronic parts. To achieve this, new rules of design, recipes, compounding, and molding have to be applied to the polymers.

Heat conductive additives for polymers differ heavily in price and performance. Performance must never be measured by heat conductivity alone but especially for housings, parts under mechanical stress or heat sinks also mechanical properties have to be taken into account. For electrically insulating solutions, alumosilicate shows equilibrated properties; heat conductivities of 2–3 W/m K can be achieved. Adding hexagonal boron nitride to an alumosilicate/PA compound can increase heat conductivities even further without deterioration of mechanical properties and with only moderate effect on the price.

The use of thermally conductive plastics creates a whole series of important advantages. Besides the benefits of lightweight construction, the use of plastics offers the possibility of producing complex geometries quickly and cost efficiently by means of injection molding or casting technologies. This new development will influence heavily forthcoming solutions in electronics, electrical devices, automotive industry, e-mobility, and like trends.

**Keywords**

Heat conductivity • Minerals • Additives • Heat management • Thermal conductivity

## Definition

Thermal conductivity of a matter is its property to conduct heat from one place to the other. Thermal conductivity is measured in watts per meter kelvin W/(m K).

## Introduction

Thermoplastics and thermosets are widely used in E&E (electric and electronic) applications. Their low thermal conductivity in the range of only 0.2–0.4 W/(m K) is linked to their chemical structure. Metals are by far still the most important materials in heat management; their only drawbacks are their high price and their high electrical conductivities, the latter being inevitably linked to the metal properties, on which their high intrinsic heat conductivity is also based. When being used in combination with electrical components with high energy density (processors, light-emitting diodes, electric motors, batteries, electronics, etc.), new requirements of an efficient dissipation of heat while maintaining electrical insulation properties of housings like integration of heat management/heat sinks are requested. The use of thermally conductive plastics creates a whole series of important advantages. Besides the benefits of lightweight construction, the use of plastics offers the possibility of producing complex geometries quickly and cost efficiently by means of injection molding or casting technologies. This new development will influence heavily forthcoming solutions in electronics, electrical devices, e-mobility, and like trends.

## Theory

Generation of heat is inevitably linked to the use of electricity and the resistances involved. Typically, heat is an unwanted side effect that has to be kept within certain limits due to the choice of materials used and usability of the object itself. Heat reduces, for example, the lifetime of electronics in general based on the Arrhenius formula

$$k = A \cdot e^{-(EA/RT)}$$

The Q10 rule of thumb is mostly also applied to the deterioration of electronics by different failure modes, stating that an increase of 10 °C doubles the deterioration velocity. Same is true for the oxidation or degradation rates of polymers, lacquers, adhesives, etc. This means that lifetime of materials like electronics is cut by half if operating temperature rises by 10 °C on the long run.

Therefore, heat management is an integral part of the construction of electronics, luminaires, electrical parts (especially in mid- and high-voltage application), parts for combustion engines, electric motors, and other mechanical machines nowadays. Lifetime estimates for LEDs, for example, can only be guaranteed if proper heat transport from the hotspot to air (or alternative cooling systems in high-power luminaires) takes place.

### Mechanisms of Heat Transport

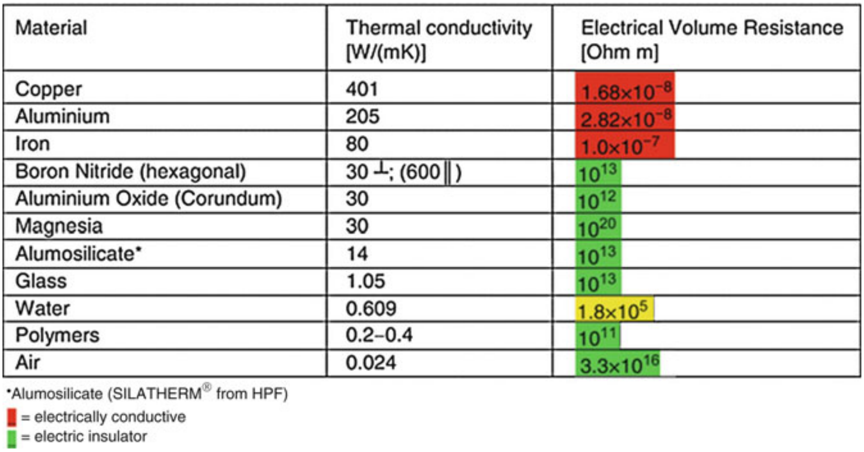
Materials for thermal management in direct contact with heat sources have to transport heat by conduction (heat transfer from one solid to another, also known as diffusion heat transfer) as fast and effectively as possible away from them.

Heat transfer by conductivity is described by Fourier's law:

$$Q = kA\,dT/d$$

$Q =$ heat transfer (W)
$A =$ heat transfer area (m$^2$)
$k =$ thermal conductivity of the material (W/(m K))
$dT =$ temperature difference across the material (K)
$d =$ material thickness (i.e., path between cool and hot side) (m)

**Table 1** Heat conductivities and electrical volume resistance of different materials



| Material | Thermal conductivity [W/(mK)] | Electrical Volume Resistance [Ohm m] |
|---|---|---|
| Copper | 401 | $1.68 \times 10^{-8}$ |
| Aluminium | 205 | $2.82 \times 10^{-8}$ |
| Iron | 80 | $1.0 \times 10^{-7}$ |
| Boron Nitride (hexagonal) | 30 ⊥; (600 ∥) | $10^{13}$ |
| Aluminium Oxide (Corundum) | 30 | $10^{12}$ |
| Magnesia | 30 | $10^{20}$ |
| Alumosilicate* | 14 | $10^{13}$ |
| Glass | 1.05 | $10^{13}$ |
| Water | 0.609 | $1.8 \times 10^{5}$ |
| Polymers | 0.2–0.4 | $10^{11}$ |
| Air | 0.024 | $3.3 \times 10^{16}$ |

*Alumosilicate (SILATHERM® from HPF)

🟥 = electrically conductive

🟩 = electric insulator

Table 1 shows a selection of coefficients of heat conductivity for different materials at room temperature.

Heat – for reasons above – has to be conducted away from the heat source by some kind of heat sink or housing with high surface area to transfer heat effectively to the final destination (which typically is the air surrounding us). Heat release has to be passed by convection (heat transfer from a solid to a moving fluid) to a pool of matter being large enough to take up all the energy released by the heat source during long-term operation.

Heat transfer by convection is described by Newton's law of cooling:

$$Q = h_c \ A \ \ dT$$

$Q$ = heat transferred (W)
$A$ = heat transfer area of the surface ($m^2$)
$h_c$ = convective heat transfer coefficient of the process ($W/(m^2 \ K)$)
$dT$ = temperature difference between the surface and the bulk fluid (K)

Air as a fluid is the most common final destination of that heat. (Finally also, radiation of every heated part is a direct mechanism of partially releasing heat but less effective when talking about cooling because it can only be influenced by color and texture of the emitter.)

Heat transfer coefficients of media in free or forced convection conditions are as follows:

| | |
|---|---|
| Air-free convection | 5–25 $W/(m^2 \ K)$ |
| Air-forced convection | 10–200 $W/(m^2 \ K)$ |
| Water-free convection | 20–100 $W/(m^2 \ K)$ |
| Water-forced convection | 50–10,000 $W/(m^2 \ K)$ |

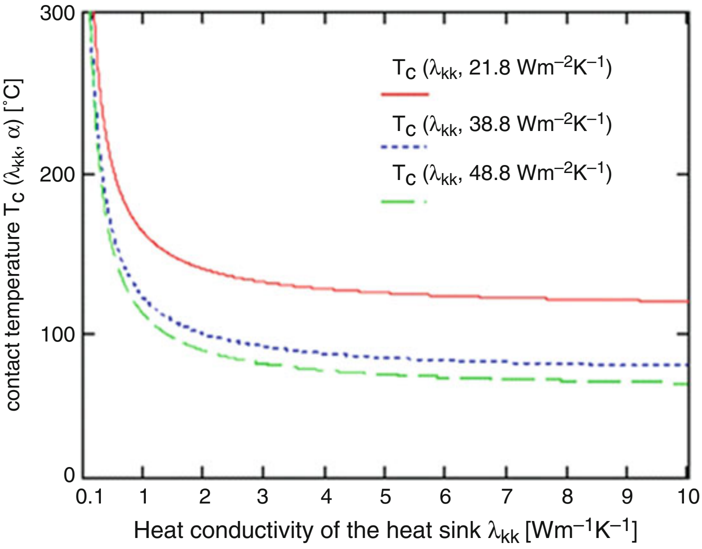


**Fig. 1** Contact temperature in dependence of heat conductivity and convection regimes (Heinle 2012)

Figure 1 (Heinle 2012) shows a graph revealing that for effective removal of heat by a heat sink in the regime of free to forced convection of air, heat conductivities of the heat sink exceeding 1 W/m K already drastically reduce temperature at the contact area between heat source and heat sink.

Since polymers offer complete freedom of design (but offering only heat conductivities in the range of 0.2–0.4 W/(m K)) in contrast to metal, using appropriate additives to increase their insufficient heat conductivity will be the future in integrated heat sink/housing design for LEDs as well as for luminaires and other electronic parts. To achieve this, new rules of design have to be applied making use of the advantage of creating large surface areas for effective heat transfer to the air as well as reducing the thickness of material in direct contact with the heat source (since velocity of heat transport through the polymer compound material is slower than in metals).

## Heat Conductive Thermoplastic Polymer Compounds in Comparison

To compare different heat conductive fillers in polyamide, they were compounded at the same heat conductive additive concentration of 65% w/w in the polymer matrix (HPF The Mineral Engineers 2014a). Only hexagonal boron nitride gave mechanically completely unstable compounds (no continuous material but unstable aggregates). Therefore, additive concentration had to be reduced to 55% here, being the maximum concentration possible, resulting in a material being processable.

Additives were compounded into PA6 by an extruder (Leistritz Co., ZSE27 MAXX). Moldings were produced from those compounds by means of injection molding (Demag Co., Ergotech 100/420-310): multipurpose test bar (ISO 3167 type A); sheet 80 mm * 80 mm * 2 mm.

Test specimens required for measurement of thermal conductivities were cut mechanically from the sheets. The thermal properties of injection-molded parts vary, depending on whether they are measured in flow direction or in perpendicular direction for this purpose. In order to take this into account, the measurements were performed as follows: To measure perpendicularly to extrusion direction (Y-direction), cutting of disks with d = 2.7 mm was performed with the sheets in central position. For determination of the thermal conductivity in injection direction (X-direction), six bars each with a length of 12.7 mm and a width of 2 mm had to be cut out, which, for the purpose of measurement, were then rotated through 90° while clamped together in a specimen holder. Results are shown in Table 2.

Figure 2 shows a comparison of relative properties of PA compounds filled with different heat conductive additives.

It becomes clear that heat conductive additives differ heavily in price and performance. Performance must never be measured by heat conductivity alone, but especially for housings or heat sinks also, mechanical properties have to be taken into account. Alumosilicate shows the most equilibrated properties; heat conductivities of 2.3 W/(m K) (y-direction, 75% by weight additive concentration in the compound) can be achieved. It has already been reported that adding of hexagonal boron nitride to an alumosilicate/PA compound can increase heat conductivities without deterioration of mechanical properties and with only moderate effect on the price.

Table 3 shows that heat conductivity in the region of 2.3 W/(m K) is achievable with alumosilicate maintaining excellent mechanical properties. Therefore, use of the material not only as heat sink but also as exterior housing with integrated heat sink function is possible (HPF The Mineral Engineers 2014a).

## Heat Conductive Thermoset Polymer Compounds Based on Epoxy Resin

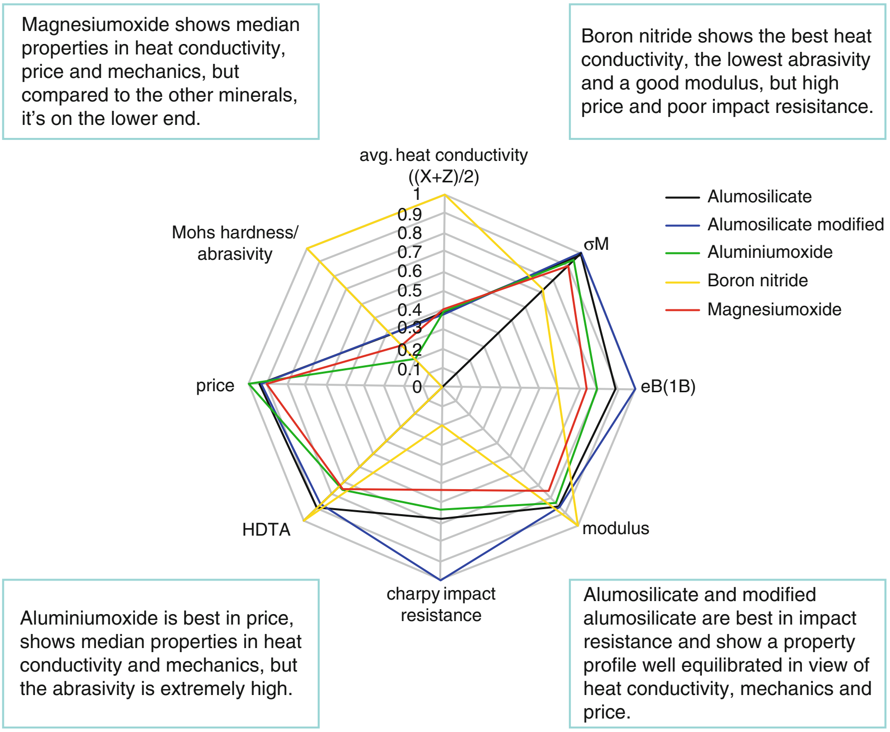
In addition to the thermoplastic system, different grain sizes and surface-treated types of the alumosilicate were tested in a thermoset application (HPF The Mineral Engineers 2014b).

An epoxy resin system (resin: ARALDITE CY 184, hardener: ARADUR HY 1235, accelerator: DY 062) has been filled with different grades of alumosilicate additive and tested regarding thermal conductivity and mechanical properties. The compound was mixed under vacuum at 60 °C. Conditions of the curing process were 2 h at 100 °C and 16 h at 140 °C post cure. For each sample, five specimens (12.7 × 12.7 × 2 mm) were analyzed.

For the determination of thermal conductivity of filled epoxy resin, a NETZSCH LFA 447 NanoFlash according to ASTME-1461, DIN 30905, and DIN EN 821 was used.

**Table 2** Heat conductivity and mechanical data of PA compounds filled with different heat conductive additives, alumosilicate is SILATHERM® from HPF

| Product in PA | Avg. heat conductivity ((X + Y)/2) W/(m K) | $\sigma_B$ [MPa] | $\varepsilon_{B(tB)}$ [%] | Modulus [MPa] | Charpy impact resistance [kJ/m$^2$] | HDTA [°C] | Price (€/kg) | Mohs hardness/ abrasivity |
|---|---|---|---|---|---|---|---|---|
| 65 % Alumosilicate* | 1.26 | 93.7 | 3.7 | 10,000 | 42.2 | 142.5 | 2.6 | 5 |
| 65 % Aluminum oxide | 1.23 | 88.8 | 3.3 | 9,640 | 39.1 | 119.8 | 1 | 9 |
| 55 % Boron nitride | 3.17 | 68.1 | 2.5 | 11,800 | 10.4 | 161.9 | 50 | 2 |
| 65 % Magnesia | 1.28 | 84.7 | 3.1 | 8,910 | 31.6 | 120.0 | 5 | 6 |



Magnesiumoxide shows median properties in heat conductivity, price and mechanics, but compared to the other minerals, it's on the lower end.

Boron nitride shows the best heat conductivity, the lowest abrasivity and a good modulus, but high price and poor impact resisitance.

Aluminiumoxide is best in price, shows median properties in heat conductivity and mechanics, but the abrasivity is extremely high.

Alumosilicate and modified alumosilicate are best in impact resistance and show a property profile well equilibrated in view of heat conductivity, mechanics and price.

**Fig. 2** Relative properties of PA compounds filled with different heat conductive additives

In the course of the experiments, it turned out quickly that a maximum filling degree makes a significant contribution to increasing thermal conductivity. Although the goal of the developments was to increase the filing degree, at the same time easy processability (casting) remained always in focus.

With a new special surface treatment (SST) in combination with the perfect grain size distribution, an equilibrated compound in view of thermal conductivity, processability, and mechanical data could be developed (Table 4).

## Viscosity

In order to ensure that the EP/alumosilicate compounds exhibit good flow abilities, viscosity measurements were performed with the following conditions (Fig. 3):

HAAKE Rheostress 6000
Searle Geometrie
Temperature of 60 °C and shear rate of 0.1–300 (1/s)

Due to a special surface coating, developed for epoxy resin systems, a viscosity reduction and good process ability for casting are achieved. The system shows good

**Table 3** Heat conductivity in PA compounds filled with alumosilicate (SILATHERM® from HPF) heat conductive additive in dependence of filler concentration (HPF The Mineral Engineers 2014a)

|  |  | Tensile properties |  |  |  |  | Charpy impact resistance |  | Izod impact resistance |  | Heat deflection | Heat conductivity |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Additive | Additive concentration [%] | Tensile strength [MPa] | Yield at tensile strength [%] | Tensile break [MPa] | Yield at break [%] | Modulus [MPa] | Unnotched $[kJ/m]^2$ | Notched $[kJ/m]^2$ | Unnotched $[kJ/m]^2$ | Notched $[kJ/m]^2$ | HDT A [°C] | x-direction [W/(m K)] | y-direction [W/(m K)] |
| Alumosilicate | 65 | 92.2 | 2 | 92.2 | 3.4 | 11,100 | 37.81 | 2.93 | 30.62 | 3.45 | 150.49 | 0.9 | 1.5 |
| Alumosilicate | 70 | 93.7 | 1.5 | 93.7 | 3 | 13,500 | 30.69 | 3.18 | 24.05 | 3.72 | 165 | 1.3 | 1.8 |
| Alumosilicate | 75 | 94.7 | 1.1 | 94.7 | 2.5 | 16,300 | 24.25 | 2.85 | 20.09 | 3.7 | 172.7 | 1.3 | 2.3 |

**Table 4** Description and filling ratio of alumosilicate (SILATHERM® from HPF) additives in EP compounds (HPF The Mineral Engineers 2014b)

| Overview of the products tested | | | | |
|---|---|---|---|---|
| Additive | Surface treatment | Medium grain size $d_{50}$ (μm) | Filling degree (% vol.) | Filling degree (wt%) |
| Alumosilicate* 008 EST | Epoxy-silane | 30 | 47.00 | 72.50 |
| Alumosilicate* 008 SST* | Special coating | 30 | 52.20 | 76.50 |
| Alumosilicate* 007 EST | Epoxy-silane | 29 | 50.20 | 75.00 |
| Alumosilicate* 007 SST* | Special coating | 29 | 55.80 | 79.00 |
| Alumosilicate* 007 SST* | Special coating | 29 | 58.85 | 81.00 |

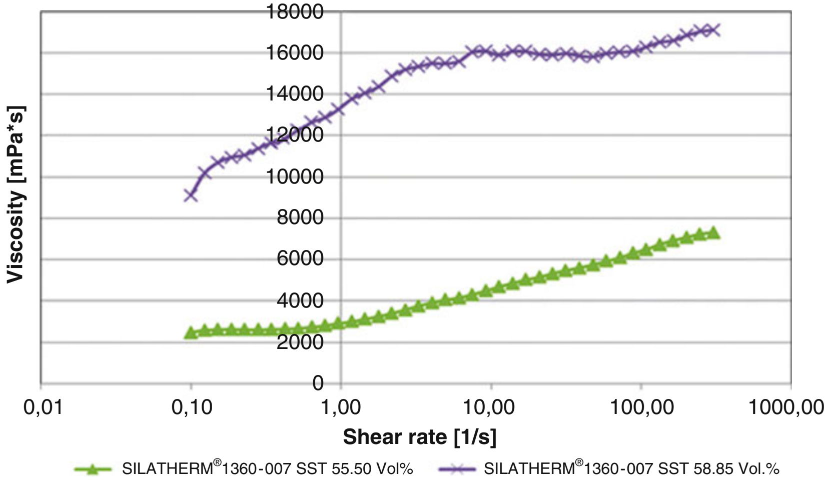


**Fig. 3** Viscosity of two different additive loadings in EP dependent on shear rate (HPF The Mineral Engineers 2014b)

flow ability up to a filling degree of 58.85% vol. with a thermal conductivity of 2.0 W/m K (Fig. 4).

## Electrical Properties

In order to analyze the electrical properties, the loss factor (tan δ) and the permittivity ($\varepsilon_r$) were determined before and after water storage in accordance with IEC 60250. The specimens were stored 100 days at 50 °C. Before water storage, all specimens had excellent values of tan δ lower than 0.05 and a permittivity $\varepsilon_r$ lower than 6.

After 100 days of water storage, all specimens showed a loss factor higher than 0.1. The permittivity increased to more than 15. Due to the dielectrical properties,

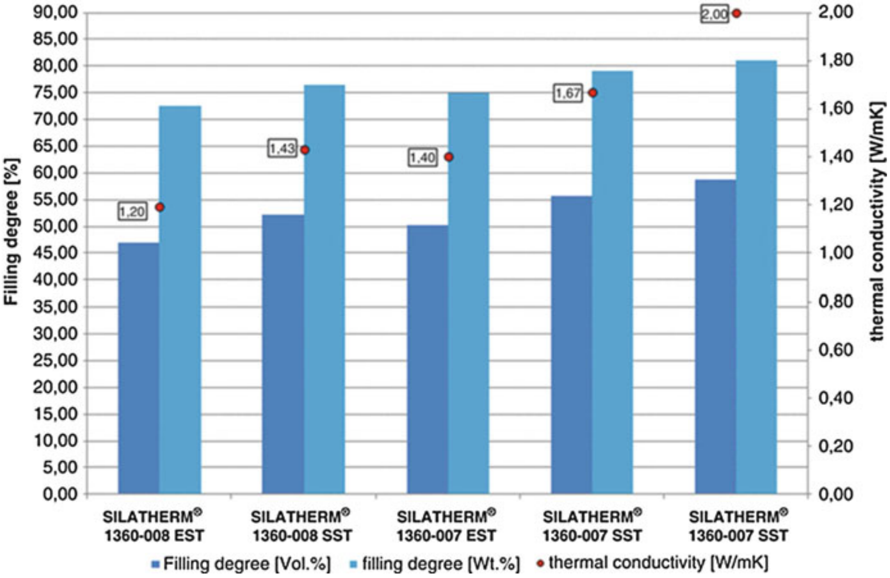


**Fig. 4** Heat conductivity of alumosilicate filled EP depending on volume/mass-concentration of additive (HPF The Mineral Engineers 2014b)

alumosilicate is not recommended for outdoor (subjected to direct weathering) but for indoor applications only.

### Mechanical Properties

The mechanical properties were characterized in accordance with ISO 178 (three-point bending test) and ISO 179 (impact strength). Due to the high filling load, all specimens showed a high stiffness and a loss of flexibility:

By use of the alumosilicate additive in casting resins, thermal conductivities up to 2.0 W/(m K) could be achieved. For the purpose of comparison, unfilled epoxy resin has a thermal conductivity of only 0.2 W/(m K).

The filling degree can be increased up to 58.85% vol. providing good flow ability and casting process ability at the same time when using the alumosilicate with a special surface coating (SST) (Table 5).

## Comparison of an Aluminum Heat Sink with an EP/Alumosilicate Compound Heat Sink of the Same Geometry

Based on the alumosilicate additive, a heat sink in the same geometry as an aluminum heat sink was produced and compared to each other (Zilles 2014).

To each heat sink, a metal block as substitute for an electronic part was glued with heat conductive glue, and both assemblies were put onto a hot plate heated to 100 °C

**Table 5** Mechanical properties of EP compounds with thermal conductive additive (alumosilicate is SILATHERM® from HPF) (HPF The Mineral Engineers 2014b)

| Filler | Filling degree (vol%) | E-Modulus (MPa) | Tensile strength (MPa) | Elongation at break (%) | Impact strength (kJ/m$^2$) | Heat conductivity (W/(m K)) |
|---|---|---|---|---|---|---|
| Alumosilicate* 008 EST | 46.93 | 16,100 | 127 | 0.92 | 9.31 | 1.20 |
| Alumosilicate* 008 SST* | 52.20 | 20,680 | 119 | 0.65 | 7.34 | 1.43 |
| Alumosilicate* 007 EST | 50.16 | 15,500 | 118 | 0.86 | 6.84 | 1.40 |
| Alumosilicate* 007 SST* | 55.79 | 18,050 | 113 | 0.70 | 4.56 | 1.67 |
| Alumosilicate* 007 SST* | 58.85 | 19,010 | 107 | 0.63 | 5.46 | 1.91 |

**Fig. 5** Experimental setup of heat sink comparison

isolated versus the surroundings. Figure 5 shows the setup with the EP/alumosilicate heat sink at the front.

Measurements of temperatures took place at the metal substitute for the electronics as a direct indicator of the heat dissipation by the heat sink as well as on the lower part of the heat sink by an infrared camera (Figs. 6, 7, and 8).

Experiments were performed under different convection conditions:

Full free convection of air with approx. 5 W/(m$^2$ K) (closed environment)
Free convection of air with approx. 25 W/(m$^2$ K) (open environment)
Forced convection of air with approx. 100 W/(m$^2$ K) (fan blowing onto heat sink)

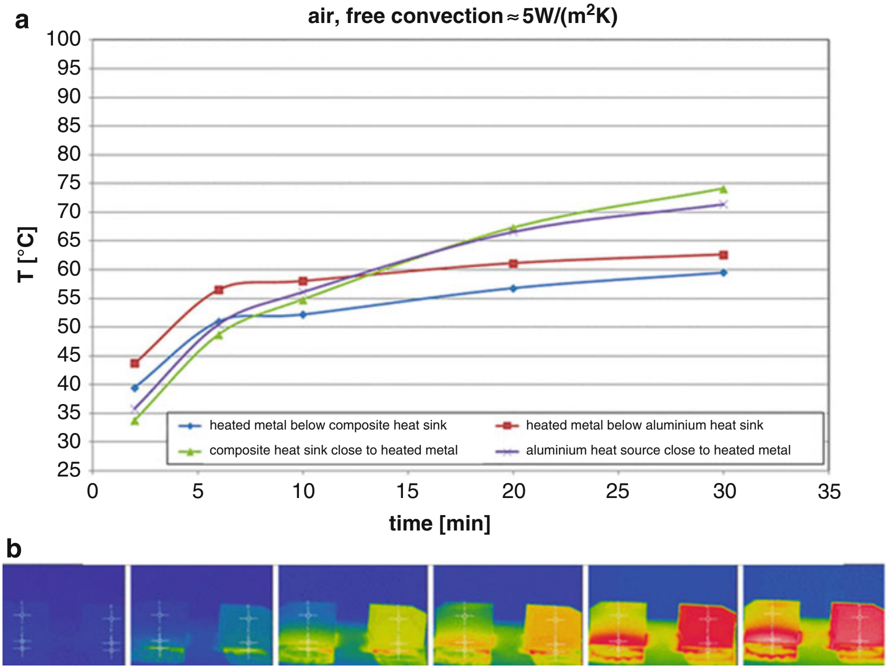


**Fig. 6** (**a**, **b**) Temperature over time of polymer composite and aluminum heat sink, respectively, their metal support (as substitute for the electronics to be cooled) under free convection (approx. 5 W/($m^2$ K))

In the regimes of free air convection, the composite heat sink shows the same performance as the aluminum metal heat sink, keeping the metal block (the "electronics") at the same temperature.

In the regime of forced convection, the composite heat sink keeps the "electronics" at 37 °C, whereas the aluminum heat sink keeps it at 32 °C; nevertheless, it should be kept in mind that the "electronics" were heated to 100 °C by the hot plate from below.

Finally applying new rules of construction of heat sinks made from plastics like reducing the thickness of material in direct contact with the heat source (since velocity of heat transport through the compound material by nature is slower than in metals), even more improvement is achieved as shown in Fig. 9 in comparison with Fig. 8.

Here, the metal plates as replacement for electronic parts kept cool both at the same temperature and at about room temperature.

Besides thermal conductive properties of the compound and the aluminum heat sink proving similar coefficients of thermal expansion but much lower mass of the composite heat sink, the potential of mass reduction in heat management when

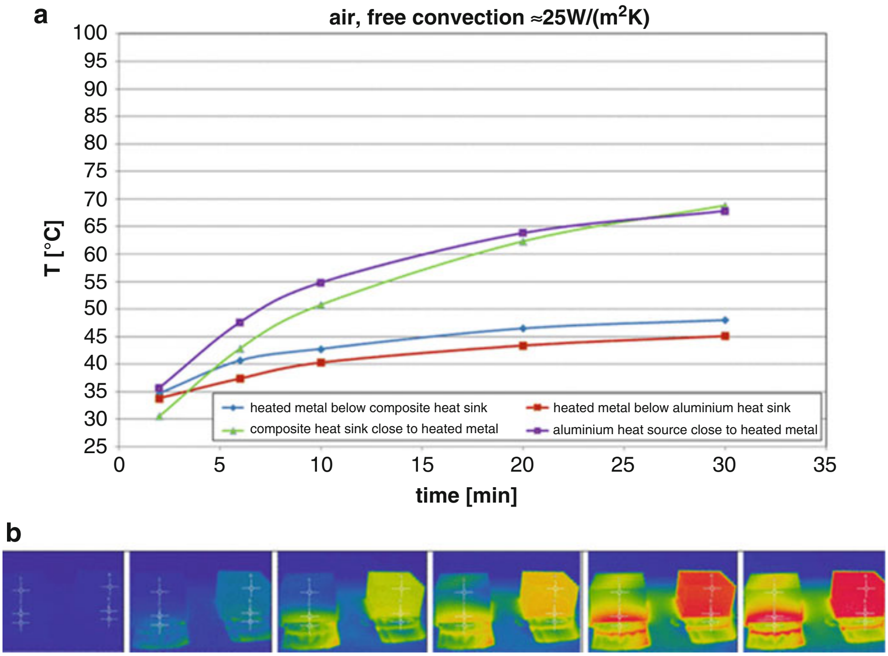


**Fig. 7** (**a**, **b**) Temperature over time of polymer composite and aluminum heat sink, respectively, their metal support (as substitute for the electronics to be cooled) under free convection (approx. 25 W/($m^2$ K))

switching from metals to plastic compound materials should be emphasized. Table 6 shows physical data of compound versus aluminum heat sink in comparison.

## Limits of Heat Conductivity in Plastics

Since a mechanism of heat conductivity in electrical insulators is driven by the ability of materials to conduct phonons (and NOT electrons), percolation is typically not observed and thermal conductivity is governed by the amount of heat conductive additive, its intrinsic thermal conductivity, the thermal conductivity of the polymer matrix (which is to some extent governed by its crystallinity), and the presence – or, better, absence – of interfacial gaps in the setup which are the most critical barrier for heat transfer.

Heinle (2012) describes in his work excellently the limits of thermal conductivity of composites with examples from literature.

He states that although carbon nanotubes have an intrinsic thermal conductivity of 3,000 W/(m K) (along their tubular axis), they cannot compensate – at commercially feasible level of addition in the range of below 10% – the volume effect of the polymer matrix. When adding up to 10% of CNT, an epoxy compound does not

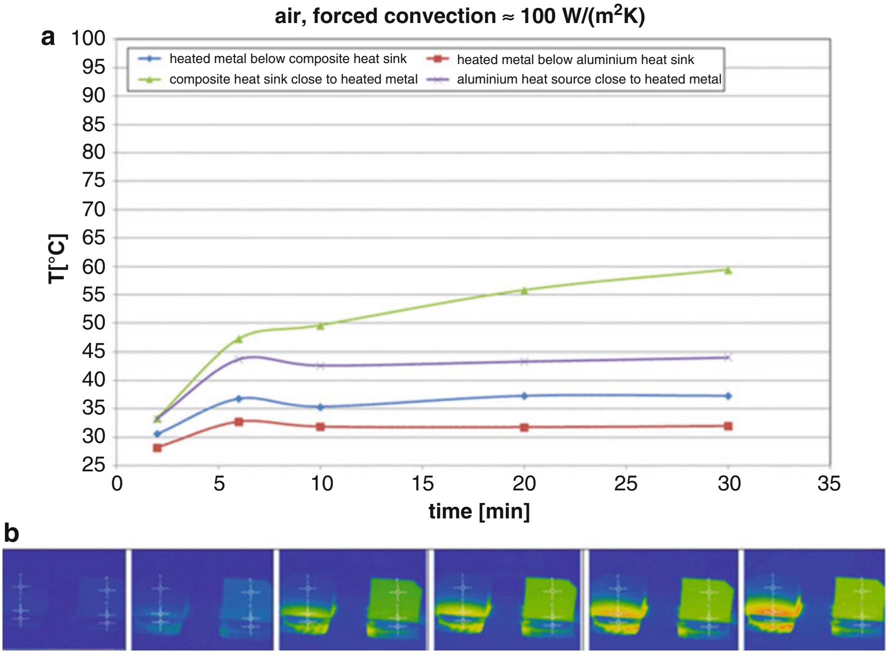


**Fig. 8** (**a**, **b**) Temperature over time of composite and aluminum heat sink respectively their metal support (as substitute for the electronics to be cooled) under forced convection (approx. 100 W/($m^2$ K))

exceed a thermal conductivity of 0.5 W/(m K). Typically, thermal conductivities of 1–20 W/(m K) can be achieved in composites when using high additive concentrations of metals, ceramics, or graphite. Highest thermal conductivities cited here are using graphite or copper platelets or filaments in the range of 30–60% by weight. These compounds are not electrical insulators.

Figure 10 demonstrates the current state of the art of thermally conductive compounds; Fig. 11 summarizes the current commercially available solutions in thermoplastics.

Typically also here, compounds with high thermal conductivity also show electrical conductivity. Electrical insulating materials of the same polymer matrix show significantly lower thermal conductivity in comparison with those with high electrical conductivity.

Taking this into account, he states that the inevitable high addition rate of thermally conductive additives causes strong drawbacks on the mechanics of polymers. This is due to the fact that percolation – as in electrically conductive systems the sufficient condition for maximum thermal conductivity – is not enough to achieve good thermal conductivity. Higher additive concentrations are necessary here because heat conductivity in electrically insulating systems is governed by the mass proportion of the higher heat conductive material in the compound.

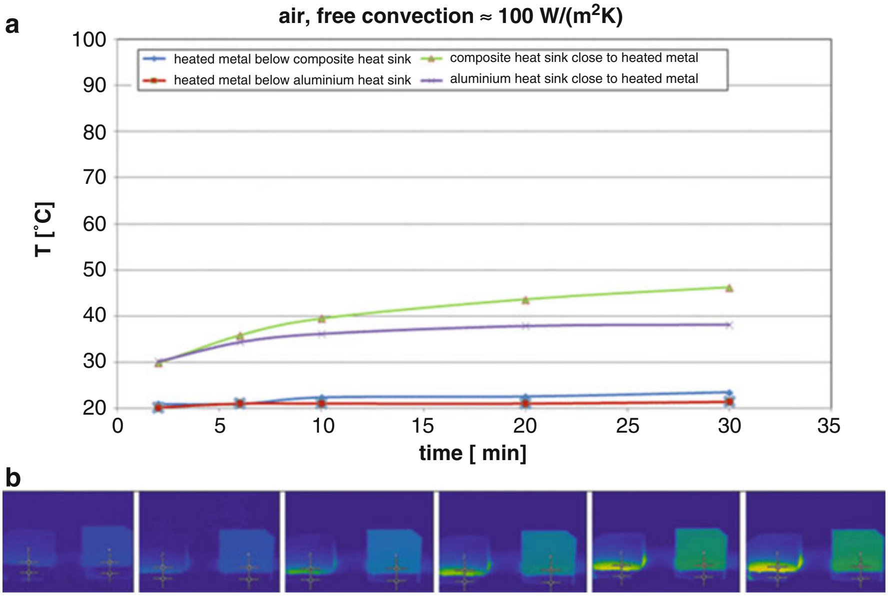


**Fig. 9** (**a**, **b**) Temperature over time of composite and aluminum heat sink, respectively, their metal support (as substitute for the electronics to be cooled) under forced convection (approx. 100 W/($m^2$ K)) with reduced material thickness on the composite heat sink base

**Table 6** Physical data of compound versus aluminum heat sink in comparison (alumosilicate is SILATHERM® from HPF)

| Thermal conductive material forming the heat sink | Additive concentration (vol%) | Additive concentration (wt%) | CTE (10–6 1/K) -20–100 °C | Mass of heat sink (g) |
|---|---|---|---|---|
| Alumosilicate*/EP compound | 58.85 | 81.00 | 25 | 62 |
| Aluminum | – | – | 23 | 88 |

The balancing of thermal conductivity and mechanical properties using computer simulation of inject mold processes, additive orientation, and distribution is the major subject of the Ph.D. study cited (Heinle 2012).

## Thermal Conductive Adhesives

Thermal conductive adhesives are usually based on epoxy – or silicone – resins.

Due to their higher degree of cross-linking, epoxy resins exhibit higher thermal conductivities in comparison with silicone resin-based ones. But when mechanical

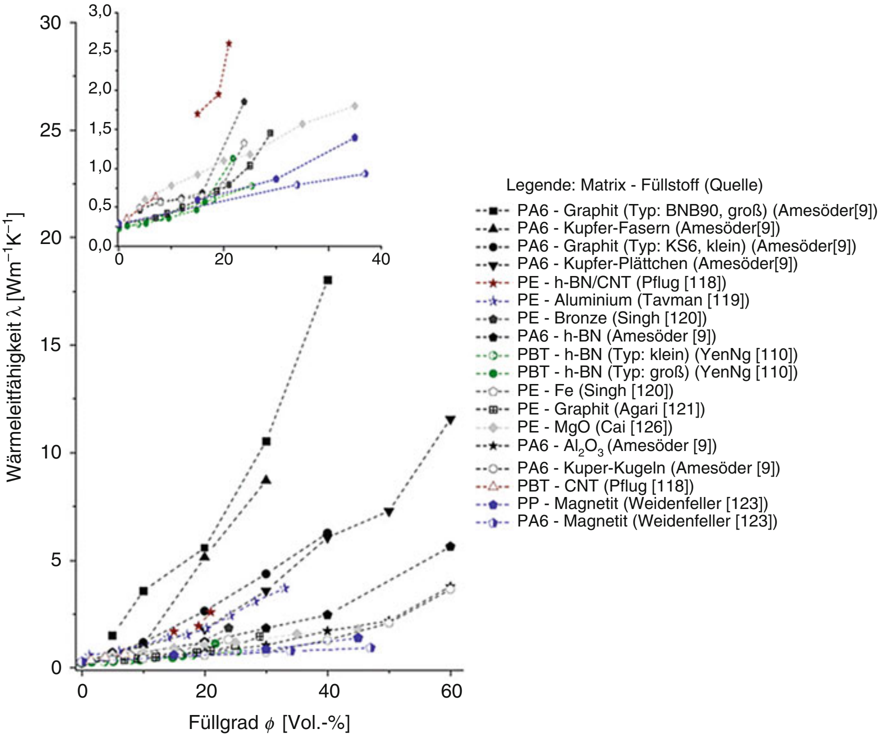


**Fig. 10** Dependence of thermal conductivity on filling ratio of various thermally conductive additives in various matrices (Heinle 2012)

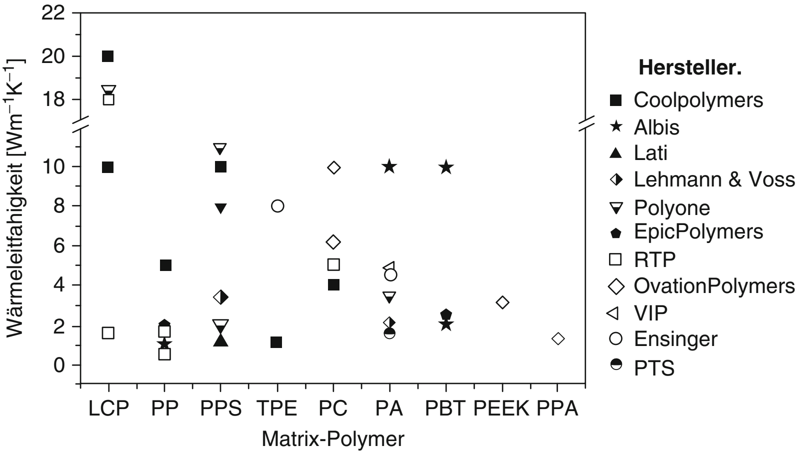


**Fig. 11** Commercial available thermally conductive compounds in various thermoplastics matrices (Heinle 2012)

stress has to be distributed, silicone resins typically show more advantageous behavior.

Thermal conductivities are governed by solid fillers/additives, since the resins show only little thermal conductivity (epoxy in the range of 0.2–0.35 W/(m K) and silicone resin in the range of 0.15–0.32 W/(m K)). Most common additives are aluminum oxide, boron nitride, aluminum (metal), and silver oxide. Additionally, literature mentions aluminum nitride and silver. Metallic additives like silver or aluminum show extraordinarily high heat conductivities, but electrical conductivity also is high, so they cannot be used whenever electrical insulation is necessary.

Typical thermal conductive additive concentration ranges from 60% to 75% by weight of the cured adhesive. Higher concentrations increase thermal conductivities but also reduce the cohesion in the adhesive. Also, a high concentration of polymer is not favorable since the high coefficient of thermal expansion (CTE) in those resins can lead to CTE mismatch, which also can be the reason for adhesive failure.

The higher the intrinsic thermal conductivity of the additive, the higher it increases heat conductivity of the adhesive when comparing same concentrations. Anyhow, this relationship is not linear since also particle shapes (and their anisotropic effects) govern thermal conductivity.

Below a film thickness of 100 μm, thermal conductivity becomes a function of film thickness itself. The lower the film thickness, the poorer the heat conductivity. Adhesion processes and film thickness have to be optimized to yield perfect adhesion paired with optimum performance in view of thermal management. This is why the absolute number of thermal conductivity of adhesives is not relevant – except the higher the better – but the effective heat resistance/conductivity has to be measured directly on the affordable film thickness and geometry in the real-life system.

Heat resistivity describes the temperature difference that is created when heat passes through the object. The reciprocal of heat resistivity is thermal conductivity. Heat resistivity is calculated whenever resistivities occur in series, like heat transmittance to a heat sink, heat transport within the heat sink, and finally heat transmittance to the air.

$$R_{th} = \frac{l}{\lambda \cdot A}$$

$R_{th}$ absolute heat resistivity (K/W)
$l$ path length (m)
$A$ cross section area (m$^2$)
$\lambda$ thermal conductivity (W/m K)

A comparison of data sheet values often leads to unsatisfactory results since here – most of the time – thermal conductivities for the volume of the adhesives are listed. Relevant for the application are actual thermal conductivities achieved on a real-life adhesive bond.

**Table 7** Data of commercially available adhesives for E&E applications

| Supplier | Adhesive type | Adhesive class | Additive | Particle size (µm) | Additive concentration (Gew.%) | Adhesive layer thickness | Viscosity (mPa*s) | Thermal conductivity (W/m K) |
|---|---|---|---|---|---|---|---|---|
| Lumi Tronix | Artic silver premium | 2 K-epoxy | Silver oxide | No data | 62–65 | “Trowel in thin layers” → paste | No data | 7.5 |
| 3 M | TC-2.707 | 2 K-epoxy | Aluminum | No data | 50 | No data | 100,000 | 0.72 |
| Polytec PT | Polytec TC 301 | 1 K-epoxy | Aluminum | <30 | No data | No data | 43,000 (84 rpm, 23 °C) | 3 |
| Polytec PT | Polytec TC 420 | 2 K-epoxy | Aluminum oxide | <50 | No data | No data | 22,000 | 1 |
| Polytec PT | Polytec TC 430 | 2 K-epoxy | Boron nitride | <20 | No data | No data | 13,000 (84 rpm, 23 °C) | 1.7 |
| EPO-TEK | EPO-TEK 930-4 | 2 K-epoxy | Boron nitride | <20 | No data | No data | 12,000–17,000 (20 rpm, 23 °C) | 1.67 |
| EPO-TEK | EPO-TEK H65-175MP | 1 K-epoxy | Aluminum | <20 | No data | No data | 80,000–120,000 (2.5 rpm, 23 °C) | 0.79 |
| DOW CORNING | TC-2035 | 2 K-silicone | Surface treated aluminum oxide | No data | 93 | Minimum 50 µm possible | 130,000 | 3.3 |
| DOW CORNING | 1-4173 | 1 K-silicone | Surface treated aluminum oxide | No data | 85 | No data | 61,000 | 1.8 |

## Range of Thermal Conductivities

Thermal conductivities of epoxy adhesives can be grouped into five general segments:

1. Very high: >4.0 W/(m K) (new technologies)
2. High: >2.0 W/(m K) (typically filled with silver)
3. Ordinary: 0.7–2.0 W/(m K) (aluminum and boron nitride filled)
4. Low: <0.7 W/(m K) (no functional additives mentioned)
5. Epoxy resin: 0.2–0.35 W/(m K)

A comparison of different thermal conductive adhesives is given in Table 7.

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# Carbon Black for Electrically Conductive Polymer Applications

# 19

Michael E. Spahr, Raffaele Gilardi, and Daniele Bonacchi

## Contents

**Abstract**

Carbon black is incorporated into polymers for permanent electrostatic discharge protection, explosion prevention, and polymer applications that require electrical volume resistivities between 1 and $10^6$ Ω cm. Typically, the so-called conductive carbon black is used since grades that belong to this specialty carbon black family impart electrical conductivity to polymers at lower critical volume fractions than conventional carbon black. Hence, conductive carbon black materials influence to a lower degree the mechanical properties of the resulting conducting polymer compound.

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Conductive carbon black grades are produced by furnace black processes and by specially designed processes like the ENSACO® process or are obtained as by-products from the gasification of hydrocarbons; these processes are based on the thermal-oxidative decomposition of hydrocarbons. In contrast, acetylene black being another conductive carbon black is formed during the exothermic decomposition of acetylene to carbon black and hydrogen occurring above 800 °C in the absence of oxygen.

Conductive carbon black grades show a large carbon black structure indicated by a high void volume. The void volume can be characterized by the oil absorption number (OAN) being above 170 mL/100 g of carbon for typical conductive carbon black. The oil absorption number at a given compression state (COAN) is attributed to the difference in sensitiveness of the carbon black structure toward compression observed between different carbon black grades. Therefore, the COAN indirectly indicates the resistance of the carbon black structure toward shear stress as well as the ability of carbon black to form a conductive network and maintain it in the polymer compound.

Usually the critical carbon black volume fraction at which the polymer compound becomes electrically conductive is decreasing with increasing COAN. The steplike transition from the insulating to the conducting state, which occurs at the critical carbon black volume fraction when incorporating carbon black into the polymer, can be described by a percolation mechanism. The amount of carbon black required to make a polymer compound conductive is, besides the carbon black type, influenced by the polymer type and polymer properties like crystallinity, viscosity, and surface tension. Due to the occurrence of shear stress during the dispersion of the carbon black in the compounding process as well as during the finishing process to the final polymer article, both compounding and finishing have to be considered as well when determining the amount carbon black required for a conductive polymer compound. Statistical, thermodynamic, and structure-oriented percolation models are the best applicable to describe at a theoretical scientific level the formation of the conductive carbon black network in the polymer matrix and to calculate the percolation from the insulating to the conducting state.

**Keywords**

Conductive polymer composites • Carbon black • Carbon black structure • Carbon black dispersion • Compound processing • Electrical conductivity • ESD protection • Percolation

## Definition

Carbon black is incorporated in polymers for permanent electrostatic charge protection, explosion prevention, and polymer applications that require electrical resistivities below $10^6$ Ω cm. At the critical volume fraction of the carbon black grade, the carbon black-polymer compound percolates from an electrically insulating to a conducting domain. The capability of a carbon black material to impart electrical conductivity to a polymer compound depends on its ability to establish and maintain in the insulating polymer matrix a conductive network in which the electronic charge carriers move mainly by a tunneling mechanism. Conductive carbon black fillers impart electrical conductivity to polymers at lower critical volume fractions than conventional carbon blacks and hence influence to a lower degree the mechanical properties of the resulting conducting polymer compound. The key property of this family of special carbon black grades is a high carbon black structure, i.e., a high void volume. High-structured carbon black materials are preferred fillers to make polymers conductive as they allow high polymer concentrations to be maintained while establishing the conductive network. Besides the carbon black properties, also the polymer properties and the processing of the carbon black-filled polymer compound influence the critical volume fraction and insulator-conductor transition. Statistical, thermodynamic, and structure-oriented percolation models are the best applicable to describe at a theoretical scientific level the formation of the conductive carbon black network in the polymer matrix.

## Introduction

Polymers are usually electrically insulating with electrical surface resistivities of above $10^{12}$ Ω cm. However, some polymer applications require lower electrical resistivity which can be achieved by dispersing special additives above a threshold concentration into the polymer matrix. Such polymer composites are classified according to their electrical volume or surface resistivity in ranges determining the final application of the polymer compound (Norman 1970; Funt et al. 1993; Markarian 2008). Polymer compounds within a surface resistivity range of $10^{10}$–$10^{12}$ Ω $\text{sq}^{-1}$ achieved by the addition of organic antistats provide low static decay rates required in antistatic applications. Antistats are widely used in packaging such as films, thermofused containers, and PET bottles in all of which they reduce the attraction of dust or help to keep surfaces separate. Electrostatic dissipation at faster static decay occurs within a surface resistivity range of $10^{6}$–$10^{10}$ Ω $\text{sq}^{-1}$. The optimum surface resistivity range of polymer compounds used for permanent electrostatic discharge (ESD) protection spans from $10^{6}$–$10^{9}$ Ω $\text{sq}^{-1}$ and is required, e.g., for packaging of electronics, trays, conveyor belts, casings, containers or hoses for flammable or explosive substances, and antistatic flooring. Conductive polymer materials are classified in the surface resistivity range of $10^{1}$–$10^{6}$ Ω $\text{sq}^{-1}$ which is above the range of $10^{-1}$–$10^{-5}$ Ω $\text{sq}^{-1}$ being typical for metals. Conductive polymer composites are used for electromagnetic interference (EMI) shielding applications that require surface resistivities lower than 10 Ω $\text{sq}^{-1}$ and in self-limiting switches and heaters. Electrically conducting polymer compounds with volume resistivities below $10^{3}$ Ω cm are used in the jacketing, insulator, and conductor shielding of power cables. Used in these shielding layers around the conductor, they prevent partial discharge at the interface between the insulation layers and conductor and eliminate any field stress by homogenizing the electrical field around the conductor. In addition they smooth out any sharp edges at the conductor surface. Specific conductive carbon black-polymer composites are positive temperature coefficient (PTC) materials that, when heated, become resistive at a defined temperature.

Carbon black is electrically conductive; most carbon black grades have an electrical volume resistivity in the range of $10^{-1}$–$10^{2}$ $\Omega$ cm. Carbon black therefore imparts conductivity to polymers (Funt et al. 1993). High carbon black concentrations are required with conventional carbon blacks to achieve good electrical properties, and this reduces certain composite mechanical properties and ease of processing while increasing the costs. Generally special carbon black grades, so-called conductive carbon blacks, are used which allow to reach the final resistivity level in filled polymer composites at lower concentration than conventional carbon black grades. Over the past few decades, static dissipative and conductive polymer composites have become part of the polymer world, and conductive carbon black remains the major conductive filler, due to the fact that in most cases conductive carbon black grades offer the best performance as well as the most economical solution. Conductive carbon blacks are specialty blacks that represent only about 1% of the global annual carbon black production estimated at about 11 Mio. tons (calendar year 2012). About 50% of the conductive carbon black volumes are used for power cables, 36% for plastic, and 14% for rubber compounds. Alternative more recent conductive additives used for ESD protection application are inherently dissipative polymer (IDP) materials. Although metal powders are intrinsically more conductive than carbon black, they are less frequently used in conductive polymer composites. Some conductive metal powders or fibers of steel, aluminum, and copper have the tendency to oxidize to form an electrically insulating layer on their surface. Noble metals like gold and silver powders are economically not feasible for most conductive polymer applications. Nevertheless, metal-coated polymers (MCP) or metal powder-filled polymer composites are applied, in particular for EMI shielding.

## Conductive Carbon Black Properties and Manufacture

A general overview about the primary and secondary properties of carbon black, typical related analysis methods, and the principles of the carbon black manufacturing processes are given in the cross-reference Carbon Black as Polymer Filler or in other reviews (Medalia 1982; Hess and Herd 1993; Kühner and Voll 1993; Probst 1993; Taylor 1997; Wang et al. 2004). The section below focuses on the main material characteristics of conductive carbon black, reviews the intrinsic conductivity and conductivity mechanism of carbon black, and describes the specific manufacturing processes of conductive carbon black grades used at an industrial level.

## Material Characteristics Describing Conductive Carbon Black

The microstructure of conductive carbon black can range from paracrystalline primary particles consisting of concentrically arranged continuous layers of hexagonally arranged carbon atoms to primary particles containing small graphitic or turbostratic domains. In Fig. 1 HRTEM images compare the microstructure of an acetylene black indicating small graphitic domains with a planar arrangement of the carbon layers with the microstructure of ENSACO® 250G showing distorted carbon layers that are concentrically arranged within the particle around the growth center or nucleus.

Characteristic feature of the conductive carbon black family is the large carbon black structure formed by more or less spherically shaped primary carbon particles with an average diameter of typically several tens of nanometers. The coalesced primary particle units are coated by continuous carbon layers that in this manner bind them by strong covalent bonds to rigid aggregates as it is indicated for ENSACO® 250G by the transmission electron microscope (TEM) image in Fig. 1a. The major fraction of aggregates in conductive carbon black contains a multitude of primary particles arranged in three-dimensionally branched particle chains, fibrous, or grape-like shapes that can have sizes of up to several hundred of nanometers. The aggregates form agglomerates which are held together physically. The carbon black structure of a typical conductive carbon black, ENSACO® 250G, is illustrated by transmission electron microscope (TEM) and scanning electron microscope (SEM) images in Fig. 2.

The complexity of the arrangements of the carbon black particles, aggregates, and agglomerates results in a relatively high void volume and the possibility to establish

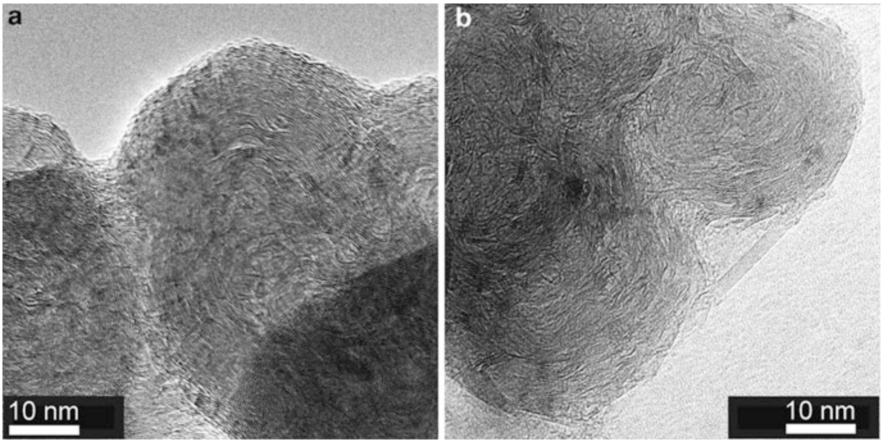


**Fig. 1** HRTEM images of typical primary particles for ENSACO® 250G (**a**) and acetylene black (**b**)

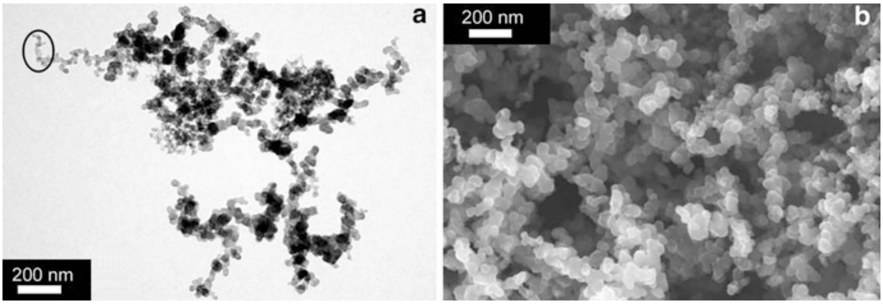
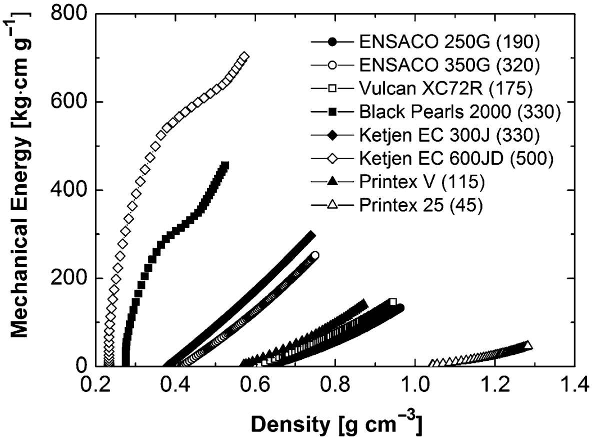


**Fig. 2** Mechanical work required to compact carbon black grades with different levels of carbon black structure in equal pressure increments from 1 to 5 kN cm$^{-2}$ at the corresponding compression density of the sample. The numbers given in brackets in the graph legend indicate the OAN of the corresponding carbon black grade in mL (100 g carbon)$^{-1}$

and maintain a carbon network in polymer compounds. The void volume is a measure to compare the structure of carbon blacks. The void volume depends on the size and shape of the aggregates, the aggregate agglomeration, and the porosity of the primary particles. Therefore, the carbon black structure can be considered as the sum of a number of accessible voids by unit weight given by (i) the inter-aggregate space, (ii) the interstices within the aggregates, and (iii) the porosity of elementary particles. The higher structure level of the carbon black is, the higher is the volume of the voids. Dibutyl phthalate absorption (DBPA) today replaced by oil absorption number (OAN) (ASTM D2414) is employed to measure the void volume and thus the average structure level of carbon black. The OAN is higher the more complex the carbon black structure is. Carbon black grades with an OAN of above 170 mL/100 g are specified as conductive carbon black.

The carbon black structure is very sensitive to the state of compression of the carbon black. Important stages during carbon black production and processing that can cover a broad range of compression states are the (1) carbon black powder after the gas separation step in the manufacturing process, (2) compacted carbon black flakes or pelletized carbon black, and (3) the polymer compound. The compressed oil absorption number (COAN) measured by ASTM D3493 at a given compression state is attributed to the difference in sensitiveness of the carbon black structure toward compression observed for different carbon black grades. Therefore, the COAN can indirectly indicate the resistance of the carbon black structure toward shear stress during the compounding process as well as its ability to form a conductive network and maintain it in the polymer compound. A similar concept takes into account the mechanical resistance of carbon black to compression by measuring the decrease of void volume with increasing compaction pressure at a given weight (ASTM D6086). Probst et al. suggested that the mechanical work being necessary to compact carbon black is ruled by electrostatic surface charges contained in the carbon black aggregates (Grivei and Probst 2003). These electrostatic surface charges are responsible for the aggregate agglomeration which

**Fig. 3** TEM images indicating the different level of porosity in the primary particles of *extra-conductive* ENSACO™ 350G (Image **a**, BET SSA of 770 m$^2$ g$^{-1}$) and *ultra-conductive* carbon black (Image **b**, BET SSA of 1400 m$^2$ g$^{-1}$)



consequently is reversible and depends on the interaction with the physical environment. Figure 3 shows the mechanical compaction energy calculated from the volume changes achieved by incremental pressure increases at the corresponding compression density of the carbon black samples. Higher structured carbon blacks require significantly higher mechanical work to achieve a given volume density. With a model based on the electrical interpretation of the mechanical properties, it was possible to calculate a superficial charge carrier concentration in the range of $10^{16}$ cm$^{-3}$ increasing with the OAN of the carbon black materials. Intrinsic electrical resistivity values calculated with this model were found to be consistent with values obtained from measurements of the pure carbon black at high pressure (see also following section). These results supported the possible relationship between the resistance of the structure to mechanical stress and the electrical behavior of carbon black governed by electrostatic surface charges ruling the carbon black agglomeration.

The surface area is, besides the OAN, the other secondary carbon black property used to describe conductive carbon black. The specific surface areas calculated from nitrogen isotherms (ASTM D6556) according to the Brunauer, Emmett, and Teller model (BET SSA) of conductive carbon black grades can largely vary from low-surface-area ENSACO® carbon black grades or acetylene black (45–75 m$^2$ g$^{-1}$) to *supra-conductive* carbon black grades (ca. 200 m$^2$ g$^{-1}$), *extra-conductive* carbon black (ca. 800 m$^2$ g$^{-1}$), and *ultra-conductive* carbon black (above 1200 m$^2$ g$^{-1}$). The porosity can be neglected in the low-surface-area carbon black grades for which the BET SSA increases with the primary particle size. For carbon black above ca. 150 m$^2$ g$^{-1}$, pores in the primary particles contribute to the BET SSA. A further increasing BET SSA is created mainly by an increasing porosity of the primary particles. The TEM images of the high-surface-area ENSACO® 350G and *ultra-conductive* carbon black in Fig. 4 indicate the existence of a significant amount of pores in the primary particles. For the latter carbon black material, the large pores hollowed the primary particles that almost completely lost the typical spherical character.

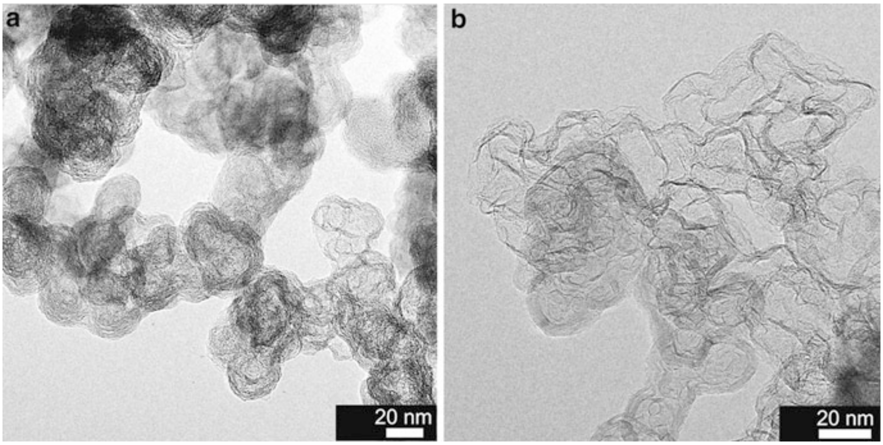


**Fig. 4** TEM (**a**) and SEM (**b**) images indicating the high carbon black structure of ENSACO® 250G consisting of agglomerates of carbon black aggregates with branched shape. An example of one aggregate is indicated by the *circle*

Table 1 lists a selection of commercial conductive carbon black grades categorized according to their OAN in *conductive* carbon black, *extra-conductive* carbon black, and *ultra-conductive* carbon black and gives their main properties.

## Intrinsic Electrical and Thermal Conductivity of Carbon Black

Carbon black materials are semiconducting with intrinsic electrical resistivity values between $10^1$ and $10^{-2}$ Ω cm. Figure 5 shows the electrical resistivity of carbon black grades under compression at the corresponding compression density of the sample. For all carbon black types, the intrinsic electrical resistivity is decreasing with increasing applied pressure. A certain electrical resistivity level is usually achieved at lower volume density of the carbon black material the higher its structure is. Elevated resistivity values at high compression density observed for some of the carbon black materials could be explained by the microstructure or the high volatile content.

The influence of the particle size on the intrinsic conductivity of carbon black does not seem to be established, but porosity plays a role once the porosity level is very high: *Ultra-conductive* carbon black composed of hollow particles shows a higher intrinsic electrical conductivity as it could be expected from its specific volume. On the contrary, the high carbon black structure of conductive carbon black causes high specific volume and consequently low intrinsic conductivity (Probst 1993). Voet et al. showed that for most carbon black grades, the logarithm of the resistivity is a function of the cube root of the specific volume, the limiting element being the interparticle distance (Donnet and Voet 1976). It was concluded

**Table 1** Physical properties of commercial conductive carbon black grades (according to supplier information)

| Carbon black grade | Medium particle diameter [nm] | BET SSA [$m^2\ g^{-1}$] | Iodine absorption number [$mg\ g^{-1}$] | OAN [$mL\ (100\ g)^{-1}$] | Volatiles [%] |
|---|---|---|---|---|---|
| Conductive carbon black | | | | | |
| Vulcan XC 72R (N472) | 30 | 250 | 255 | 175 | 1.5 |
| ENSACO 250G | 35 | 65 | 82 | 190 | 0.1 |
| Acetylene black granules | 35 | 65 | 93 | 160 | 0.01 |
| Conductex 7055 Ultra | 42 | 55 | 50 | 170 | 1 |
| Extra-conductive carbon black | | | | | |
| Ketjenblack EC300J | 40 | 800 | 790 | 365 | 0.4 |
| ENSACO 350G | 30 | 770 | 860 | 320 | 0.2 |
| Printex XE2 | 35 | 1000 | 1075 | 380 | 1 |
| Black pearls 2000 | 12 | 1475 | 1050 | 330 | 2 |
| *Ultra-conductive* carbon black | | | | | |
| Ketjenblack EC600JD | 34 | 1400 | 1050 | 495 | 0.5 |

that the resistivity of the carbon black is an exponential function of the average particle distance at prevailing pressure and that the predominant conduction mechanism is electron tunneling.

At very high compression, most carbon blacks approach the same limiting level of conductivity. With increasing pressure, since the aggregates becoming more tightly packed and pressed against each other, and with very low contact resistance, the conduction mechanism is considered to be by direct contact and therefore more graphitic in nature (Hess and Herd 1993). In this regime, due to the mostly concentric nature of the superficial carbon layers in the carbon black particles, most of the contacts are between graphitic basal planes. The electronic conductivity along the graphite basal planes in the chemical structure of graphite is four orders of magnitude higher than perpendicular to them. This explains the higher intrinsic electrical resistivities found for carbon black compared to graphite powders usually having a higher probability of contacts between prismatic edges. Surface oxides and impurities absorbed at the carbon black surface significantly increase the electrical resistance. Due to these reasons, heat-treated carbon black materials show a resistivity minimum at about 1200 °C when all surface oxides are completely desorbed from the surface. Above this temperature, the layers show an increased tendency to form

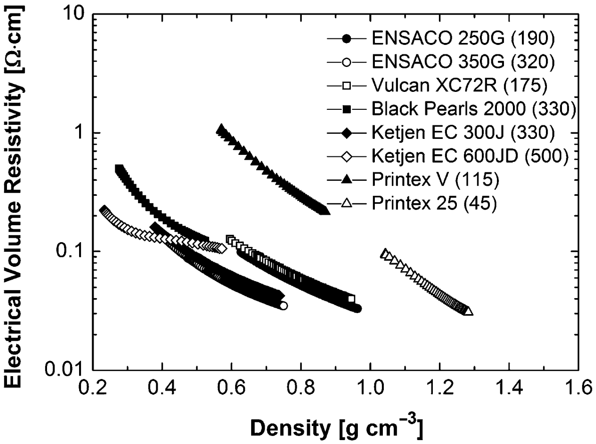


**Fig. 5** Electrical volume resistivity obtained from two-point electrical resistivity measurements of pressed carbon black samples at the corresponding compression density. The carbon black samples were compacted by increasing the pressure in equal increments from 1 to 5 kN cm$^{-2}$ with two brass pistons that at the same time acted as sensing electrodes for the electrical resistivity measurement. The numbers given in brackets in the graph legend indicate the OAN of the corresponding carbon black grades in mL (100 g carbon)$^{-1}$

around the aggregates a continuous encapsulating shell consequently causing an increase of the electrical contact resistance.

Compared to graphite powders, carbon black materials show significantly lower level of thermal conductivity ranging from 0.1 to 0.5 W (mK)$^{-1}$. Graphitic materials therefore would be preferred usually as carbon filler if a high thermal conductivity was required. The electrical and thermal conductivity of graphitic carbons is described in more details elsewhere in this encyclopedia (▶ Chap. 20, "Graphitic Carbon Powders for Polymer Applications").

## Manufacture of Conductive Carbon Black

Conductive carbon black grades can be obtained via both manufacturing process principles, the oxygen-free thermal decomposition and the thermal-oxidative decomposition of hydrocarbons (Kühner and Voll 1993; Taylor 1997; Wang et al. 2004). The creation of highly branched aggregates of small primary carbon black particles and the stabilization of these structures are key features in the manufacturing process. Their achievement in the oil-furnace process usually is accompanied by a significant reduction of the process yield. Conductive furnace blacks are produced by co-injecting preheated oil feedstock and air in a closed flow reactor creating a turbulent flame. The most important process stages influencing the carbon black properties are the atomization and vaporization of the oil droplets in the reactor, the partial combustion and pyrolysis of the atomized feedstock in the turbulent flame, and the secondary reactions between the carbon black particles and the components of the reactor off-gas. The carbon black structure formed in the reactor is largely dependent on the formation and concentration of solid primary particles being determined by the concentration of feedstock vapor and reactor temperature (Kühner and Voll 1993). Low feedstock/air ratios increase the concentration of feedstock vapor and reactor temperature and therefore cause small primary particle sizes and large carbon black structures. To stop the particle growth and moreover to avoid carbon black loss occurring at these temperatures due to the Boudouard and water-gas reaction with $CO_2$ and $H_2O$ gas, respectively, being both present in the reactor, a cooling step and subsequently the separation from the tail gas are performed. These stages are followed by the reaction of the carbon black with oxygen upon the first contact with air and a densification and eventual pelletization step.

The production process of acetylene black is based on the exothermic decomposition of acetylene to carbon black and hydrogen occurring above 800 °C in the absence of oxygen. Once the reaction is started, the acetylene decomposition reaction autogenously provides the energy required for the cracking of acetylene to carbon followed by the synthesis of the carbon black:

$$n\mathrm{C_2H_2} \rightarrow 2n\mathrm{C} + n\mathrm{H_2} + \mathrm{Energy}$$

The high synthesis temperatures above 2000 °C being typical for the acetylene black production give rise to a relatively high graphitization degree of the primary particles that show low surface area. The high-surface-area gasification blacks are by-products from the production of synthesis gas based on the incomplete combustion of hydrocarbons. Hereby, the preheated oil feedstock reacts with air and vapor at relatively high temperatures to form synthesis gas ($H_2/CO$) and a carbon black by-product that is separated by filters or extraction. The process has no flexibility in producing different grades or changing the carbon black properties as the carbon black production is not the main purpose.

Acetylene black and conductive furnace black were the only conductive carbon black grades available on the market until the mid-1970s when the gasification black products like Ketjenblack EC300J and Philblack XE-2 (later name: Printex XE-2), known as *extra-conductive* carbon black and both being by-products from the Shell gasification process, became available. In the early 1990s, the low-surface-area, high structure ENSACO® carbon black grades were introduced together with the *extra-conductive* high-surface-area ENSACO® 350 carbon black being all manufactured out of a specifically designed process for conductive carbon black by IMERYS (IMERYS Belgium, ex-MMM Carbon).

The development of new conductive carbon additives for polymers has been ongoing since more than three decades. The major effort has been made to decrease the required carbon black concentration with no deterioration of the level of conductivity of the carbon black-filled polymer compound. The family of the *extra-conductive* carbon blacks is the result of this effort. Oxidative aftertreatment of those *extra-conductive* carbon blacks made another step in this direction. Aftertreated *extra-conductive* carbon blacks, also called *ultra-conductive* carbon blacks, generate in some polymers sufficiently high conductivities at concentrations below 2 wt%. Other development directions have been:

1. High purity: low sulfur, low grit, and low metal content.
   This trend was mainly pushed by the power cable industry. With increasing voltage, higher purity for conductor shields has been demanded. However, purity also has been beneficial for other numerous plastic applications, e.g., plastic films and reduced degradation of sensitive plastics (like alkaline catalyzed hydrolyzation).
2. Stability of the conductivity, i.e., resistance to shear occurring in the extrusion process to prepare conductive polymer compounds.
3. Very high conductivities for specific applications.
4. Reduced viscosity for conductive compounds.
5. Reduced or increased positive temperature coefficient (PTC) effect.

## Carbon Black-Polymer Composites

### The Insulator-Conductor Transition

Carbon black-filled conductive polymer compounds have been studied extensively since the 1970s, and the results are published in numerous technical articles and patents. Several reviews give an overview about the phenomenological aspects that have to be considered when creating conductive polymer compounds with the help of carbon black fillers (Probst 1993, 2009; Huang 2002; Davidson 2010). The incorporation of conductive particles into a polymer matrix fundamentally modifies the electrical and dielectrical behavior as well as the mechanical properties. The electrical resistivity decreases, typically abruptly by several orders of magnitude, at a critical conductive particle concentration at which the polymer composite becomes electrically conductive. Electrical resistivity curves show with increasing concentration of conductive particles three consecutive distinct zones, an insulation zone, a percolation zone, and a conduction zone, respectively (Fig. 6). Three parameters describe the percolation from the insulating to the conducting domain: the critical concentration or critical carbon volume fraction at which the percolation occurs (percolation threshold), the slope of the percolation, and the ultimate electrical resistivity level.

In carbon black-filled polymer compounds, the percolation threshold and slope from the insulating to the electrically conducting domain and the ultimate resistivity level are influenced by the carbon black type, the polymer type, as well as the mixing/compounding and finishing process. These variables will be elucidated in the following sections.

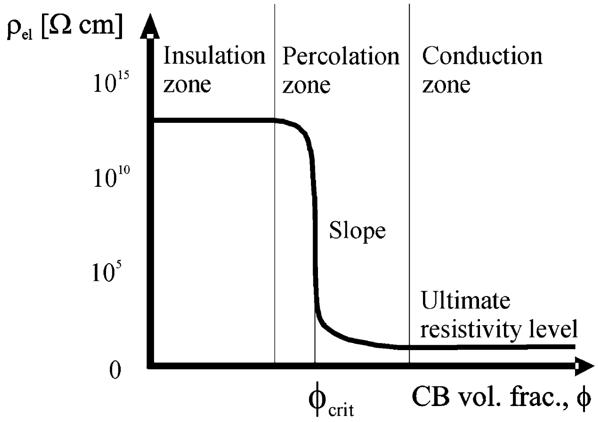


**Fig. 6** Schematic representation of the electrical resistivity of a polymer compound as a function of the conductive particle filler concentration

## Carbon Black Properties, Critical Carbon Black Concentration, and Mechanical Compound Properties

Carbon blacks are electrically conductive and impart electrical conductivity to the typically insulating polymer. Generally, conductive carbon black grades are preferred as they allow reaching the percolation at lower concentration than conventional carbon black and therefore influence to a lower degree the mechanical properties of the resulting polymer compound. The capability of a carbon black to impart electrical conductivity to a polymer compound depends on its ability to establish and maintain a conductive network in the insulating polymer matrix. Hereby, the carbon black aggregates assemble continuous paths that allow the transport of electrical charges through the polymer matrix. The key property of conductive carbon black is the high carbon black structure, i.e., the high void volume. Conductive carbon black can accept high polymer levels while maintaining the carbon black network. The higher the OAN and COAN of the carbon black grade, i.e., the higher the carbon black structure and the ability to maintain the carbon black structure under the influence of mechanical stress like compression and shear forces occurring during the compounding process, the lower is the carbon black concentration required to make the polymer compound conductive. At the percolation threshold, all carbon black materials show quite a constant total volume calculated from the product of COAN and volume fraction of the carbon black grade. This underlines the fact that all carbon black materials can achieve a low electrical resistivity level, but the selection is based on other criteria as well, for example, mechanical properties and dispersion. In addition, the carbon black surface should be free of any organic residue or chemical groups that could deteriorate the electrical contacts or act as electron traps. The quality and number of carbon black interparticle contacts as well as the carbon black microstructure mainly influence the ultimate resistivity level. Figure 7 illustrates the electrical volume resistivity as a function of the carbon black loading in polypropylene for several examples of commercial conductive carbon black grades. The percolation threshold decreases with increasing

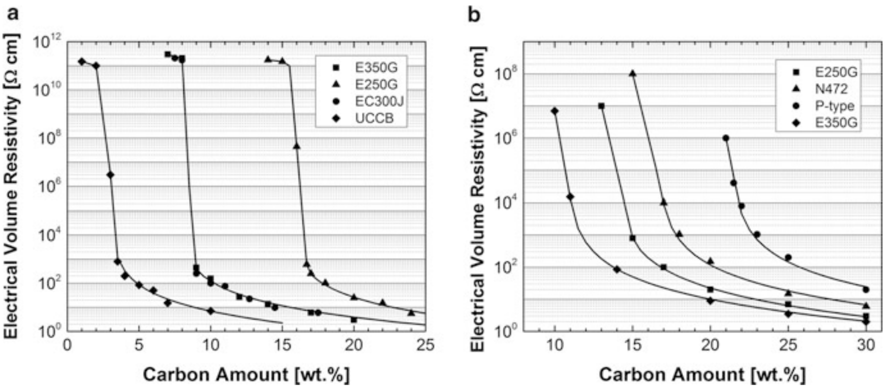


**Fig. 7** Electrical volume resistivity of carbon black compounds at different carbon black loadings. (**a**) ENSACO® 350G (E350G, OAN = 320 mL (100 g)$^{-1}$), ENSACO® 250G (E250G, OAN = 190 mL (100 g)$^{-1}$), Ketjenblack EC300J (EC300J, OAN = 330 mL (100 g)$^{-1}$), and ultra-conductive carbon black (UCCB, OAN = 560 mL (100 g)$^{-1}$) in high-density polyethylene (compounding by twin-screw extruder, compound processing by injection molding); (**b**) ENSACO® 350G (E350G, OAN = 320 mL (100 g)$^{-1}$), ENSACO® 250G (E250G, OAN = 190 mL (100 g)$^{-1}$), VULCAN® XC72R (N-472, OAN = 175 mL (100 g)$^{-1}$), and P-type carbon black (P-type, OAN = 100 mL (100 g)$^{-1}$) in low-density polyethylene (compounding by twin-screw extruder, compound processing by compression molding at 2 min/170 °C)

OAN of the carbon black grades indicating the influence of the carbon black structure on carbon black concentration at which the compound becomes conductive.

A proper selection of a conductive carbon black is made in such a way that other performance criteria, especially the mechanical properties, are met while the compound is electrically conductive. With the addition of carbon black into thermoplastics at low loadings, usually an increase of the tensile and flexural modulus, i.e., the stiffness and rigidity of the resulting polymer compound, can be observed. At high carbon black concentration, the tensile strength decreases again. The tensile elongation at break generally decreases, but much variety can be observed depending on the polymer grade and especially the dispersion quality. Also the impact properties typically decrease when incorporating carbon black in the polymer due to the increased brittleness of the resulting polymer composite. The increase of the melt viscosity and stiffness accompanied with the incorporation of carbon black in a polymer are drivers to minimize the carbon black content in a conductive compound.

However, a low critical volume fraction is not always equivalent to best performance. Low-surface-area conductive carbon black ENSACO® 250G achieves in a high-density polyethylene (HDPE) compound at equal electrical resistivity level a higher fluidity and similar mechanical properties compared to extra-conductive carbon black ENSACO® 350G, as summarized in Table 2. The reason for this behavior could be found in the lower surface area of ENSACO® 250G together with the higher achievable dispersion degree. For many carbon black grades, the

**Table 2** Melt flow index and mechanical properties of ENSACO® 250G and ENSACO® 350G containing compounds of HDPE with adjusted carbon black loadings resulting in the same level of electrical volume resistivity

| | Pure HDPE (Hostalen GD 7255) | HDPE/ ENSACO® 350G | HDPE/ ENSACO® 250G |
|---|---|---|---|
| Carbon loading [wt%] | 0 | 17.5 | 25.0 |
| Electrical volume resistivity [Ω cm] | $>10^{11}$ | 7.3 | 6.9 |
| Melt flow index at 190 °C/5 kg [g (10 min)$^{-1}$] | 11 | 0.89 | 2.46 |
| Tensile modulus [MPa] | 886 | 1234 | 1259 |
| Stress at yield [MPa] | 23.40 | 31.13 | 31.10 |
| Strain at yield [%] | 10.2 | 7.7 | 7.4 |
| Flexural strength at conventional deflection [MPa] | 18.85 | 28.87 | 29.36 |
| Flexural modulus [MPa] | 943 | 1364 | 1547 |
| Impact strength [kJ m$^{-2}$] | 8.89 | 5.41 | 5.49 |

melt viscosity of corresponding polymer compounds at the same weight percent carbon loading is highly dependent on the BET SSA. In high-surface-area carbon blacks, the DBP absorption or OAN usually follows the surface area mostly created by the particle porosity and is also related to the melt viscosity (Fox 1982). The critical pigment volume concentration (CPVC) of a carbon black grade is a function of its OAN and apparent density, $\delta\ CB$:

$$\mathrm{CPVC} = \frac{100}{1 + (\mathrm{OAN})\dfrac{\delta_{CB}}{100}} \tag{1}$$

It can be seen that both electrical resistivity and melt viscosity show a threshold behavior at the CPVC. Both properties change as a function of the carbon loading at the critical volume fraction at which a continuous carbon network is established throughout the sample. The carbon network, once established, makes the polymer compound more rigid, as well as more conducting. The melt viscosity has an influence on the mobility of the carbon black aggregates. As described below in more detail, a high melt viscosity can significantly retard the coagulation (structuring) of the aggregates to the conductive network. In that case a higher carbon black volume fraction is needed to reach the critical concentration of carbon black in the polymer compound.

## Polymer Nature and Properties

The carbon black and polymer properties influencing the organization and stability of the conducting network are those having an impact on the coagulation of the

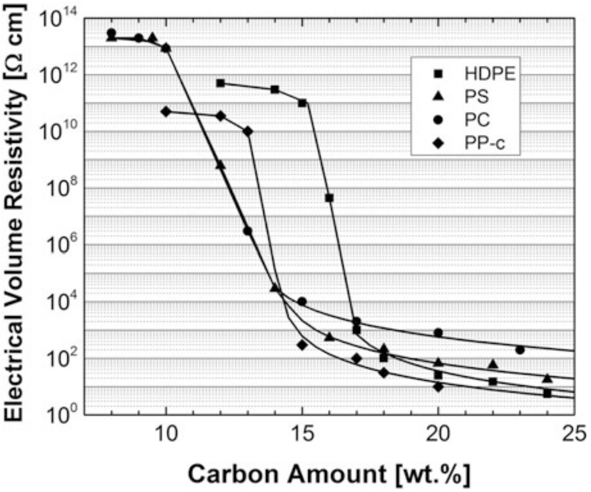


**Fig. 8** Electrical resistivity of ENSACO® 250G/polymer compounds with high-density polyethylene (*HDPE*), polystyrene (*PS*), polycarbonate (*PC*), and polypropylene copolymer (*PP-c*) as polymer component as a function of the carbon black concentration (compounding, twin-screw extruder; processing, injection molding)

carbon black aggregates and improving or inhibiting their mobility. The percolation threshold is determined by a balance of the interactions between the carbon black aggregates and the interaction between the carbon black aggregates and the polymer molecules. If the interactions between the carbon black aggregates are stronger, the carbon black agglomerates tend to stick together in the melt-mixing process typically used to prepare the compounds and the carbon black agglomerates are difficult to disperse. If the interactions between the carbon black aggregates and the polymer prevail, the carbon black aggregates are dispersed separately without contact and the formation of conductive paths is retarded until a higher concentration of carbon black is provided. Miyasaka et al. (1982) proposed to consider the surface tension of carbon black and polymer component as a parameter to quantify these interactions. They found that the percolation concentration increases with increasing polymer surface tension due to the stronger interaction between carbon black filler and polymer matrix. Figure 8 illustrates with examples of ENSACO® 250G/polymer compounds the influence of the polymer on the electrical compound resistivity.

The crystallinity of polymer is another parameter influencing the percolation threshold. For amorphous polymers, the carbon black particles are uniformly dispersed in the polymer matrix, and high electrical conductivity is achieved when the carbon black concentration reaches the percolation threshold. In crystalline polymers the carbon black is mostly ejected from the crystalline regions during the crystallization of the polymer in the cooling process and concentrated in the amorphous regions leading to a decrease of the critical volume fraction of the carbon black. As mineral fillers or glass fibers do not incorporate the carbon black, the carbon black is concentrated in the polymer phase and a similar effect can be observed. The increase of the molecular weight of the polymer always causes an increase in percolation concentration as high-molecular-weight polymers make it more difficult to wet the carbon black surface and slow the formation of the conducting network. The increase

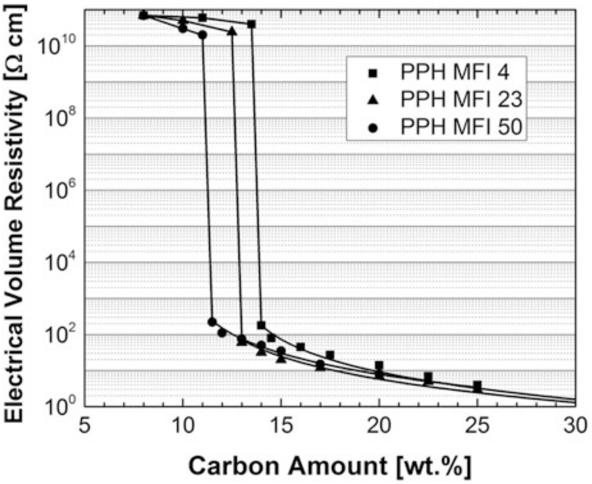


**Fig. 9** Electrical resistivity of ENSACO® 250G at different weight percentages in polypropylene homopolymers (*PPH*) with MFI of 4, 23, and 50 g (10 min)$^{-1}$ (MFI measured at 190 °/5 kg, compounding, twin-screw extruder; processing, injection molding)

of molecular weight increases the melt viscosity, i.e., decreases the melt flow index (MFI), which moves the percolation threshold to higher carbon black concentration, as illustrated in Fig. 9. A plasticizer lowers the melt viscosity and therefore the percolation concentration should be lower. Plasticizers may also intervene in the mixing and finishing process by reducing or increasing the shear energy involved. Some of them intervene in the coagulation process of the carbon black and thus influence the percolation threshold. In elastomers the chemical cross-linking system could significantly influence the electrical resistivity of the carbon black-elastomer composite.

Recently, multiphase polymer blends are considered as technical solutions to achieve a sufficient electrical conductivity in the polymer compound at low loadings of conductive carbon black. The phase separation in these polymer blends and selective distribution of the carbon black into one phase can lead to conducting polymer compounds at lower carbon black filler content which can provide better compound processability and avoid poor mechanical properties caused by high filler loading. The percolation threshold depends strongly on the phase morphology and the distribution of carbon black in the polymer blend. The carbon black distribution in a blend of two immiscible polymers occurs in different proportions depending upon its affinity to the polymer components and the compound processing. The carbon black could be distributed predominantly in one continuous phase or located preferentially at the interface of the two polymer phases. The first case includes a multiple percolation effect: The polymer phase predominantly containing the carbon black becomes conductive after the carbon black concentration reaches the percolation threshold in this phase. With increasing volume fraction of the carbon black-rich phase, the phase changes from a dropwise domain into a continuous structure, and the polymer mixture becomes conductive. The decrease of the percolation threshold in a crystalline polymer can be considered as the result of a multiphase system: The amorphous phase is enriched with carbon black, while the crystalline phase contains

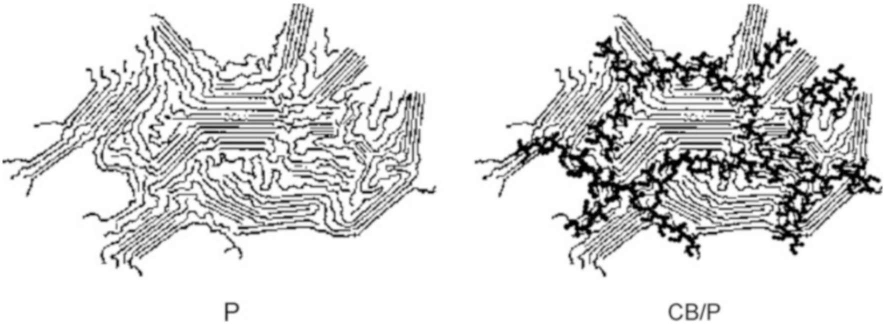


**Fig. 10** Schematic representation of a crystalline polymer (*P*) segregating the carbon black in the continuous amorphous domain of the carbon black-polymer composite (*CB*/*P*)

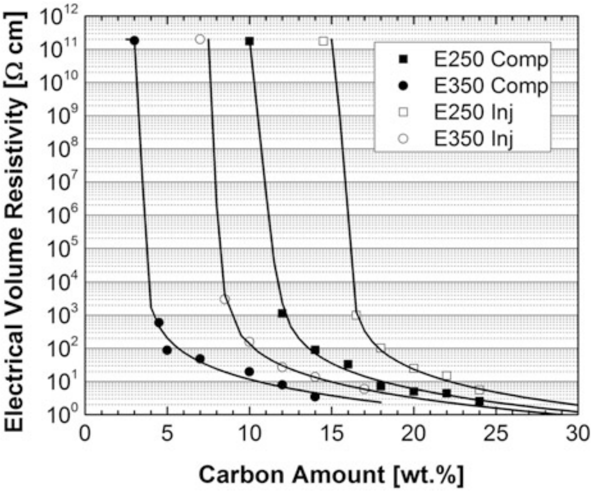
no or only small amounts of carbon black. Since the amorphous phase is the continuous domain, the crystalline polymer compound becomes conductive at lower overall carbon black concentration as shown in the schematic drawing of Fig. 10.

## Compound Processing

The dispersion of the carbon black in the polymer matrix can have significant effects on the compound resistivity and therefore is the most important stage in the preparation of conductive polymers. Hereby, extrusion mixing, typically performed by corotating twin-screw extruders, is the most important technique to disperse carbon black in polymers. Other major mixing equipments are kneaders, internal intensive batch mixers, two-roll mills, and intensive dry mixers. Usually it is preferred to add the carbon black to the molten polymer, e.g., by the split-feed technology in twin-screw extruders, as it avoids carbon black compaction and, consequently, poor dispersion. Compounding conductive carbon black means incorporating materials with extremely low bulk density and therefore high filler volume into the polymer. Controlled compression or pelletizing is applied to facilitate the feeding or incorporation process of the carbon black filler. In the early stage of mixing, polymer penetrates into the interstices between the particle aggregates. A high carbon black void volume supports this process and makes the dispersion of highly structured carbon black easier than the dispersion of lower structured carbon black. In addition, a low carbon black specific surface area facilitates the occurring wetting process of the carbon black surface by the polymer. The best property combination for carbon black as far as dispersion is concerned is given by a high carbon black structure and a low BET SSA. All mixing types allow generation of predominantly high shearing forces which are responsible for the dispersion of the carbon black agglomerates. Carbon black agglomerates are mainly based on weak electrical interactions of the aggregates and as such are sensitive to shear. The shearing forces disentangle to a certain degree the agglomerates into aggregates and consequently have an impact on the final structure (agglomerate size) in the compound. Perfect dispersion is achieved when the agglomerates are separated into discrete aggregates with surfaces that are completely covered with polymer. This structure breakdown increases the electrical resistivity of the compound with increasing mixing time. In the first stages of the mixing process, the electrical compound resistivity rapidly decreases as electrical pathways are established between the carbon black agglomerates but reaches an optimum when further mixing gradually increases the resistivity due to the structure breakdown and the related increase of the gap between primary particle aggregates. In addition, especially highly viscous polymer matrices and high-shear mixing processes can generate very high shearing forces acting on carbon black and may cause an over-shearing effect which leads to the compression, to the deformation, and finally to the breakage of the carbon black aggregates. In such case an extended mixing time would increase the electrical volume resistivity. The contrary effects of the shearing forces on the formation of the carbon black network in the polymer matrix result in an optimum mixing time that depends on the specific process and formulation. A very careful and consistent mixing procedure ensures good conductivity and a homogeneous mix and avoids over- and under-dispersion. The breakdown of the carbon black structure usually can be partially recovered in the filler-polymer network by a rearrangement of the carbon black aggregates and polymer molecules occurring after mixing or finishing. This restructuring called coagulation or flocculation is mainly controlled by the carbon black aggregate and polymer interactions as well as the aggregate mobility. Carbon black and polymer surface tension as well as melt viscosity influence coagulation. Consequently, specific surface area and specific superficial energetic sites of the carbon black as well as polymer nature and MFI play an important role. Mixing can also reduce the polymer crystallinity and hence move the percolation threshold to higher carbon black concentration.

The finishing processes may also influence the polymer compound properties. Finishing techniques such as extrusion, injection, film blowing, thermoforming, and calendering influence the compound properties to a different degree and change the conductive properties of the resulting carbon black-filled polymer specimen. Hence, the total compounding and finishing process has to be considered when formulating the recipe. Figure 11 shows the electrical volume resistivities of bars containing ENSACO® 250G/HDPE compounds at different loadings. The higher percolation threshold of the injection molded bars can be explained by a sum of different effects taking place. The nonuniform shear flow during mold filling, i.e., higher shear near the mold surface, leads to polymer segregation and lower carbon black concentration at the surface-near regions of the sample bar. This effect together with decreased polymer crystallinity at the surface of the compound specimen is the reason for the so-called skin effect observed in the case of the injection molding process. In addition, the higher shearing forces of the injection molding compared to the compression molding can cause overall higher structure breakdown of the carbon black as well as higher reduction of polymer crystallinity. Typically the influence of shear on the electrical properties during finishing is reduced at lower electrical compound resistivities corresponding to higher carbon black concentration and is

**Fig. 11** Electrical volume resistivity of ENSACO® 250G/HDPE and ENSACO® 350G/HDPE compound bars at different loadings produced by compression (*Comp*) and injection (*Inj*) molding (compounding by twin-screw extruder, 220 °C)



higher near the percolation threshold where small changes in carbon black structure or concentration have larger impact on the electrical conductivity. Compounding at higher concentrations causes higher structure breakdown due to the higher shearing forces required. Consequently, the structure suffers less in further breakdown when additional shear is applied during finishing. In elastomer compounds shear could also occur during service of the finished parts, hence increasing its resistivity by dynamic deformation. Resistivity plateaus reached at a certain number of deformations indicate maximum structure breakdown linked to the COAN. Recovery of the conductivity is possible quantitatively by relieving the compound thermally.

## Conduction Mechanisms in Carbon Black-Polymer Composites

Random dispersion of carbon black in an electrically insulating polymer matrix changes, above a critical carbon black volume fraction, the resulting polymer compound from an insulator to a conductor. At this percolation threshold, a sudden change in the dispersal state of conducting particles, the coagulation of conducting primary aggregates to a conducting network, facilitates the electronic conduction through the polymer-filler composite. The total electrical resistance of a compound is the sum of all aggregate resistances, *Ra*, and inter-aggregate resistances, *Re*,

$$R = \sum_{i=0}^{n} R_{a,j} + \sum_{i=1}^{n} R_{e,i} \tag{2}$$

of the conducting network and depends, beyond the percolation threshold, on the microstructure and surface of the carbon black as well as the polymer type. In general, conductive carbon black-polymer composites have semiconducting character. As the polymer can only affect $R_e$ in Eq. 2, it influences the electrical contacts between the aggregates. In fact, a conduction mechanism through real physical contacts between the carbon black particles in the conducting network without any influence of the polymer, as it is found in the case of carbon fibers and graphite, can only be found for carbon black primary particles larger than 300 nm. In this case, the electrical compound conductivity increases with temperature (Carmona 1988, 1989; Probst 1993).

Most of the carbon black grades have smaller primary particle sizes, and their polymer composites like in the case of direct particle contacts have semiconducting character. However, thin polymer films between the carbon black particles form discontinuities in the conducting network being responsible for a tunneling mechanism of the charge carriers (Sichel et al. 1982). The probability for electron tunneling decreases with an increasing gap width. The electrical resistivity $\rho_{el}$ therefore decreases with decreasing particle distance (polymer film thickness) and at the same time depends on the electrical field $E$ and the temperature $T$ according to the following expression:

$$\rho_{el} = \rho_{el}^{0} \ e^{-\frac{T_1}{T+T_\mathrm{e}}\left(1-\frac{E}{E_0}\right)^2} \tag{3}$$

where $T_1$, $T_0$, and $E_0$ are constants and $\rho_{el}^{0}$ is carbon black concentration dependent. The influence of the temperature is attributed to thermal fluctuations lowering the inter-aggregate gap and modulating the potential barrier. A higher electrical field can excite electrons and maintain a higher kinetic and potential energy level required for the tunneling of electrons. The theory of fluctuation-induced tunneling can qualitatively account for the temperature, the electrical field, and the pressure dependences of the electrical polymer compound resistivity.

Also the positive temperature coefficient (PTC) phenomenon can be explained by this theory. The PTC stands for an increase of the electrical resistance when the temperature increases. In the case of a carbon black-polymer compound, the PTC is based on the higher thermal expansion of polymer matrix than the conductive network. With increasing temperature the higher thermal expansion of the polymer increases the gap between the particle aggregates in the conductive network. The potential barrier increases and the electrical compound resistivity increases. The opposite mechanism explains the possible negative temperature coefficient (NTC), the increase of the electrical resistance of a high-temperature conductor when the temperature is decreased. Some polymer blends, based on the concept of double percolation and two-step percolation, gave access to PTC and NTC compositions with balanced performance as well as improved processability and reproducibility. Mixtures of carbon black grades could cause a sharper resistivity change with temperature than a single carbon black at loadings near the percolation range. The PTC or NTC effect could lead to new specific technical features or could be problematic: A sharp resistivity increase or decrease could be used, e.g., for switch applications. In contrast, in a semiconductive cable compound, it would be preferable to avoid significant changes in electrical resistivity with temperature.

Above the percolation threshold, the electrical resistivity of carbon black compounds reaches values that are often 1–2 orders of magnitude higher than that of compressed pure carbon black in air. However, the thickness of the polymer film between the carbon black aggregates decreases with higher loadings and decreasing carbon black-polymer interactions. Grivei and Probst showed that for very high carbon black loadings as well as carbon black-polymer interactions that are negligible or do not affect the interparticle contacts, the ratio between the electrical resistivity of the carbon black under high compression in air and the electrical compound resistivity based on the same carbon black at the corresponding volume fraction becomes unity, indicating a conduction mechanism by direct contact (Grivei and Probst 2003).

## Percolation Models

Since the 1970s the insulator-conductor transition occurring during the incorporation of conductive particles in an insulating polymer matrix has been the subject of extensive research. Related activities have developed mathematical models that explain on a scientific level the network formation as well as the behavior of the electrical resistivity near the percolation threshold (Carmona 1988, 1989; Lux 1993). The models being the most applicable to carbon black-filled compounds are the statistical and thermodynamic percolation models (Probst 1993; Huang 2002). Due to the assumptions made therein, all models have their limitations that have to be considered when predicting percolation curves from the properties of different carbon black and polymer types (Balberg 1998, 2002; Rubin et al. 1999; Carmona and Ravier 2002).

The statistical model proposed by Kirkpatrick and Zallen treated conduction in a composite of an insulator filled with conductive spherical particles as a theoretical percolation problem. They approached the problem by starting with a regular finite array of points and randomly assigning bonds between the points until a cluster of connected particles spans the relevant boundary of the array and percolation occurs. They assumed that conduction through the compound bulk is controlled by conduction over a number of paths of randomly formed particle chains. With increasing number of particles, the number of continuous chains or conductive paths through the compound increases. The local effect is largest where the first chains have formed. The total resistance for any chain consists of the sum of individual resistances at each contact point. If these individual resistances remain constant, the electrical resistivity $\rho_{el}$ of a composite at a filler volume fraction $\phi$ follows the expression

$$\rho_{el} = \rho_{el}^{0}(\phi - \phi_{crit})^{?t} \qquad (4)$$

where $\phi\ crit$ is the critical volume fraction of carbon black filler, $\rho_{el}^{0}$ is a scaling factor corresponding to the compound resistivity at the percolation threshold, and the exponent t is a geometrical factor being 1.5 for three-dimensional systems but commonly about two for real carbon black-polymer composites for carbon black volume fractions above the percolation threshold.

Aharoni and Janzen developed the concept of average number of contacts between filler particles, c being the product of a contact probability, p, and a maximum number of contacts a particle can have with its neighbors, C. Janzen calculated based on the statistical model of Kirkpatrick and Zallen the critical average contact number at the percolation threshold $c_{crit} = 1.5$ and concluded with

$$c = \frac{\phi}{(1-\phi)} \tag{5}$$

and with the carbon black density ρ and the compressed DPB absorption, v in (mL $g^{-1}$), for the critical volume fraction:

$$\phi_{crit} = \frac{1}{1+\rho\ \eta\left(\frac{C}{c_{crit}}\right)} \tag{6}$$

Based on his assumption that the maximum number of contacts C = 6, Eq. 7 becomes

$$\phi_{crit} = \frac{1}{1+4\rho\ \eta} \tag{7}$$

Equation 8 predicts a decreasing critical volume fraction with increasing compressed DBP absorption being considered to correspond to the carbon black structure in the polymer compound. Although the relation predicts the critical volume fraction of many carbon black grades satisfactorily, the experimental values of $\phi_{crit}$ for very low structured carbon blacks usually having large particle sizes are higher than predicted. For these carbon blacks, also the values obtained for the geometrical factor t are much higher than 2.0. For carbon black types with very high structures and small particle sizes, the experimental values of $\phi_{crit}$ are lower. An explanation could be that the statistical percolation models do not consider the geometrical form of the aggregates as well as the filler-filler and filler-polymer interactions. Balberg took into account the spatial geometrical and electrical properties of the carbon black-polymer composites and proposed to introduce the tunneling conductance mechanism into the statistical percolation theory (Balberg 1998, 2002; Rubin et al. 1999). This tunneling-percolation model showed a better agreement with the experiments.

The thermodynamic percolation models emphasize the importance of interfacial interactions and consider the percolation phenomenon as a phase separation process. Sumita et al. took into account the overall interfacial free energies in the compounds. They assumed that the interfacial excess energy in the compound is increasing with increasing carbon black particles from an interfacial free energy *K 0* at the start of the mixing process at a linear rate *c* up to an overall mixture-independent free energy, *g**, at which the network formation begins. This can explain the experimental finding that a greater value of specific free energy is accompanied by a lower volume percolation concentration and vice versa. The model also considers the melt viscosity of the polymer, η, which if high in value has an inhibiting influence on the coagulation process, the mixing time, *t*, and the diameter of the carbon black particles, *R*. The final equation has the form

$$1 - e^{\left(-\frac{ct}{\gamma_c}\right)} + K_0 e^{\left(-\frac{ct}{\gamma_P}\right)} \tag{8}$$

where $\gamma_c$ and $\gamma_P$ are the surface tension values of the carbon black particles and the polymer, respectively. The dynamic boundary model of Wessling et al. introduced additional assumptions on the basis of the nonequilibrium thermodynamics and a formation mechanism of the conducting network. Below the percolation, the particles are covered by a stabile absorbed polymer layer and are distributed nonhomogeneously in the polymer matrix in the form of flat agglomerates. Near the critical volume fraction with increasing particle number creating compression forces, the absorption layers are partially destroyed and the particles come closer until they are in electrical contact at a distance of 10 nm or less. In this way two-dimensional conductive islands are formed that coagulate to a three-dimensional network in a subsequent phase separation process by the interfacial energies at the carbon black particles and the absorption polymer/polymer boundaries.

Many experimental findings are in agreement with the argument that percolation is a phase separation like the abrupt increase of the tensile strength and compound hardness. However, some assumptions seem rough for a general thermodynamic explanation of the percolation phenomenon of carbon black-polymer composites. The highly structured geometry of the carbon black particle aggregate, the aggregate agglomeration, the compound inhomogeneities like isolated particle clusters, the temperature dependence of the surface energies, the different miscibility of the conducting particles with the polymer constituents of polymer blends, and the carbon black segregation in the amorphous part or crystallite boundaries of semicrystalline or crystalline polymers are examples that limit the applicability of such models.

Most recent approaches have considered inhomogeneities in the distribution of the conductive phase within the polymer compound created by the applied compounding and finishing method as only the compression molding route ensures the lack of any inhomogeneity in the distribution of the conductive phase. Structure-oriented percolation models are based on parameters which have to be determined from the microlevel structure of the composite part after the final processing step. A detailed substitution of the real compound structure by a theoretical model structure is needed for the determination of such parameters. The setup of this model structure requires suitable analytical tools and powerful image analysis techniques, but the resulting models lead to the most realistic theoretical predictions (Lux 1993; Carmona and Ravier 2002).

## Cross-References

- ▶ Carbon Black as a Polymer Filler
- ▶ Graphitic Carbon Powders for Polymer Applications

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# Graphitic Carbon Powders for Polymer Applications

# 20

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## Contents

### Abstract

Carbon is used as filler in multifunctional polymer compounds. Carbon is present in nature or can be synthetized in different forms. Due to its valency, carbon is capable of forming many allotropes. Well-known forms of carbon include diamond and graphite. In recent decades many more allotropes and forms of carbon have been discovered and researched including ball shapes such as buckminsterfullerene and sheets such as

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graphene. More extended structures of carbon include nanotubes, nanobuds, and nanoribbons. Other unusual forms of carbon exist at very high temperature or extreme pressures. Graphite is the most common allotrope and is characterized by good electrical, thermal, and lubricating properties. The term “graphitic carbon” includes various types of carbon powders with different levels of crystallinity like natural and synthetic graphite. Natural graphite from ore deposits occurs in three main forms: flake graphite, lump or vein graphite, and amorphous graphite. Synthetic graphite is manufactured from natural or petroleum carbon precursors in high-temperature processes that transfer amorphous carbon to carbon of higher structural order.

The electrically and thermally insulating character of most polymers can be changed by the addition of electrically and thermally conductive fillers like graphite powders. Graphitic carbon powders especially represent a valid filler solution for thermally conductive polymer compounds in the case that electrical insulation is not a prerequisite. For applications where high electrical resistivity is required, graphite can still be used at low concentration when the resulting graphite polymer composite has not percolated to the electrically conductive state but already shows significant thermal conductivity. The two-dimensional crystal structure and anisometric particle shape of graphite lead to anisotropic properties of the final polymer compound. The degree of anisotropy can be influenced by the graphite type, polymer type, and processing conditions. Graphitic carbon powders can also be used as solid lubricant, infrared shielding filler, and gas barriers to reduce the gas penetration through polymer films. Graphitic carbons have been poorly considered in the past as fillers for electrically conductive polymers due to the, compared to carbon black, higher impact on the mechanical properties of the resulting polymer compounds. However, the recent search for metal-free polymer compounds with good thermal conductivity and light weight has offered new opportunities to further exploit the potential of graphite-filled polymer composites in various applications. We will review the main properties of graphitic carbon powders, alongside with processing and properties of the resulting graphite-filled polymer composites and the related final applications as well as the mechanisms for lubrication, electrical, and thermal conduction obtained in graphite-filled polymer compounds.

**Keywords**
Graphite • Polymer • Thermal conductivity • Electrical conductivity • Gas barrier • Lubrication

## Definition

Graphite is the most common allotrope of carbon and is characterized by good electrical, thermal, and lubricating properties. Graphite powders are suitable fillers to improve the conductivity and tribological properties of polymer composites.

## Introduction

There is a growing interest in polymer compounds for several applications in the frame of metal replacement in automotive and other industries. The advantages of plastic parts versus metal parts are reduced weight, lower cost, design flexibility, durability (low corrosion), and shorter production times. Depending on the final application, there are different requirements in terms of mechanical properties, thermal stability, and electrical and thermal conductivity. Such requirements can be fulfilled by appropriate choice of polymer and filler types.

Carbon-based fillers are promising candidates for multifunctional polymer compounds. Carbon is present in nature or can be synthetized in different forms. Well-known allotropes include diamond, graphite, carbon black, fullerenes, and carbon nanotubes. The layered crystal structure of graphite and its morphological and surface properties explain the semimetal electrical conductivity, high thermal conductivity, lubricity, and chemical inertness. Because of its ability to delaminate under shear stress, graphite powder has been used for many years to improve the tribological properties of polymer composites. Recently, graphite is also employed at high loading in plastic composites to enhance their thermal conductivity for heat dissipation or heat exchange applications where electrical conductivity can be tolerated. Although carbon blacks are the best option to manufacture electrically conductive polymers, graphite is still used as electrically conductive additive in special applications that requires multiple functions (e.g., lubrication or thermal conductivity). Another common application of graphite is to increase the thermal insulation of EPS, due to its ability to reflect thermal radiation. The two-dimensional crystal structure of graphite associated with its flaky morphology typically leads to anisotropic properties of the final polymer compounds and, similar to other lamellar powders, can also work as gas barriers to reduce gas penetration of polymer composites.

This chapter will review the manufacturing processes and properties of graphitic carbon powders (section "Manufacturing Processes and Properties of Graphitic Carbon Powders"), the preparation of graphite-filled polymer composites (section "Graphite-Filled Polymer Composites Processing"), and the mechanism of conduction (section "Conduction Mechanisms in Graphite Polymer Composites"). Finally, in section "Properties and Applications of Graphite-Filled Polymer Composites," the properties and applications of graphite-filled polymer composites will be discussed.

## Manufacturing Processes and Properties of Graphitic Carbon Powders

### Production

Within graphite powders, one can distinguish two main families based on the origin: natural and synthetic graphite (see Fig. 1).

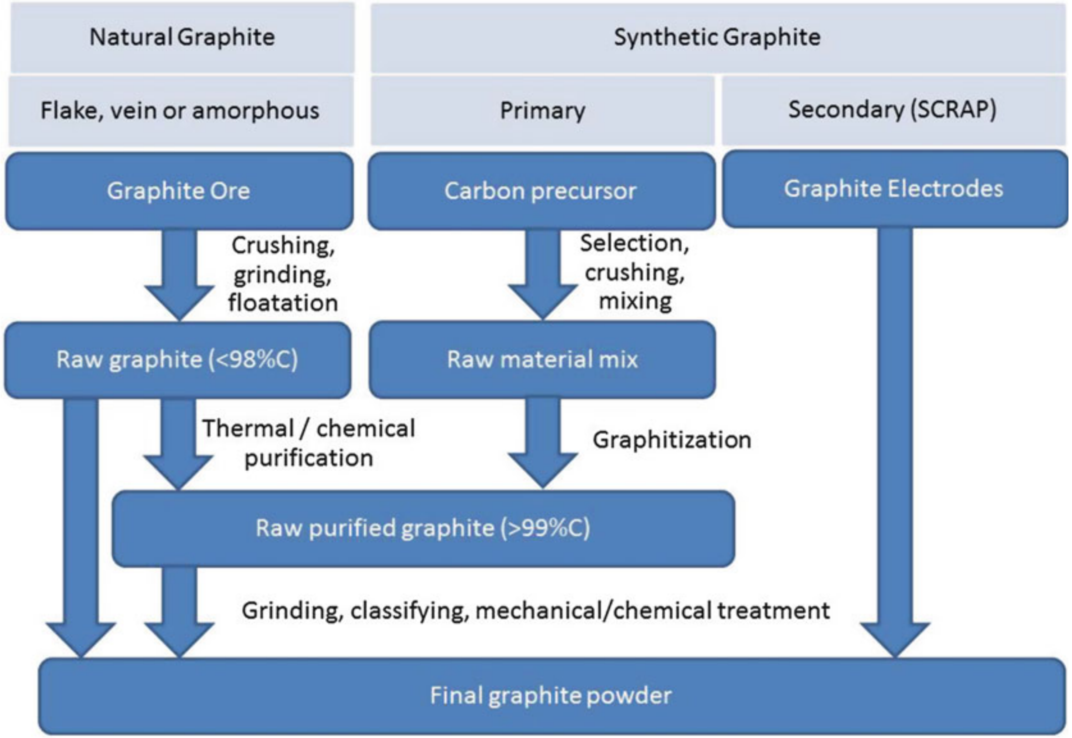

**Fig. 1** Main steps of the synthetic and natural graphite manufacturing process

Natural graphite results from the transformation of organic matter deposits subjected to strong pressures combined with high temperatures over millions of years. Ore containing sufficient graphite content (typically between 3% and 20% depending on the deposit) can be extracted from the mine, and graphite particles are then liberated by mechanical grinding. The released graphite particles are then separated from impurities by flotation in order to reach purity levels as high as 98% carbon. Higher purity levels can be achieved by subsequent chemical or thermal purification. The purified graphite powders can be then sieved to different particle size ranges or ground to fine particle size by different milling techniques. Natural graphite can be further classified into three different types:

Flake graphite occurs as isolated, flat, platelike particles with good crystallinity (see Fig. 2a). Many deposits are available in China, Brazil, Canada, and Africa. The yearly production is about 400,000 t.

Vein graphite (also called lump graphite) occurs mainly in Sri Lanka and long-term availability is questionable. Large crystals are condensed into lumps.

Amorphous graphite occurs as fine particles with low crystallinity and low purity. It is typically extracted and processed in China and Mexico and is lower in costs compared to the other types. The yearly production is about 600,000 t.

The natural graphite properties are fixed by the metamorphological processes occurring during the graphite formation. The graphite properties vary between different graphite deposits and may even vary within one deposit. Selection allows improving the consistency of natural graphite product lots.

Synthetic graphite is obtained by transformation of a carbonaceous precursor (such as petroleum coke) into graphite through an industrial process called graphitization (Franklin 1951). Graphitization is defined as a solid-state transformation of thermodynamically unstable carbon into graphite by thermal activation. The existence of graphitizable carbons, non-graphitizable carbons, and intermediates was first recognized by Franklin. With increasing heat treatment temperatures,

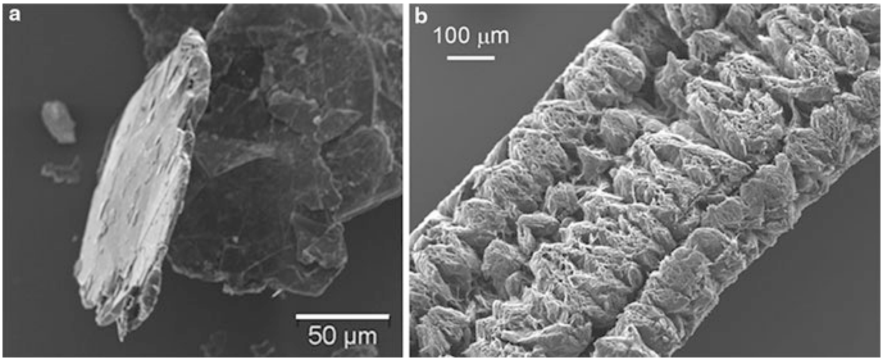

**Fig. 2** SEM picture of (**a**) natural flake graphite and (**b**) expanded graphite

graphitizable carbons go through a progressive structural ordering process. During the graphitization process, a progressive decrease of the medium $d_{002}$ interlayer spacing (c/2 value) occurs from 0.3440 nm down to the ultimate value for graphite, 0.3354 nm. The value of 0.3440 nm is the lowest value possible in a turbostratic structure. The turbostratic order of graphitic carbons was introduced by Warren and Biscoe as a roughly parallel and equidistant stacking of graphene layers but with each layer having a completely random orientation about the layer normal. According to Franklin, the degree of graphitization g of a graphitizing carbon is defined as

$$g = \frac{(0.3440 - d_{002})}{(0.3440 - 0.3354)} \tag{1}$$

Méring and Maire expanded the Franklin model for the graphitization process suggesting not only an ordering of disordered stacks of graphitic atomic layers (graphene layers) to perfect graphene layers with a 3D structure but also the healing of defects within the elementary graphite layer. According to their studies, the fundamental process of graphitization lies in the transformation of elemental layer states which are disordered and contain carbon defects to the ideal graphene layers. The transformation of disordered stacks of graphitic atomic layers into an ordered arrangement, as the graphitization was described by Franklin, is only a consequence of the internal transformation (Hess and Herd 1993).

The driving force to develop these graphitization processes has been the production of graphite electrodes used in electric arc furnaces for steel production and as anodes in the production of aluminum. The graphitization of the carbonaceous precursor is performed at temperature above 2500 °C under exclusion of oxygen. During the heat treatment, the amorphous precursor is transformed into crystalline carbon. Typically, coal tar or petroleum coke is pressed into blocks using pitch as binder and heated. During the graphitization process, the structural ordering process results in a progressive decrease of the medium $d_{002}$ interlayer spacing (c/2 value from 0.3440 nm down to the ultimate value for graphite 0.3354 nm) and concomitant increase of the crystal size (Lc and La values increase from few nm at 1200 °C to the order of 10 nm at 2000 °C and to more than 100 nm at higher graphitization temperatures).

Secondary synthetic graphite (also called “scrap graphite”) is a by-product of the graphite electrode industry and is available in large quantities (>100,000 t per year). It can be of high purity but usually has lower level of crystallinity and shows much wider property variations between different production lots compared to primary synthetic graphite.

On the other hand, primary synthetic graphite is not a by-product and is produced with a dedicated process. One of the most common batch processes is the Acheson furnace technology (Acheson 1893), where the carbon raw material is positioned between two electrodes and covered by refractory material to avoid oxidation. Electric current is passed through the carbon bulk, which acts as an electric resistance between the electrodes. In this way, temperatures above 3000 °C can be generated in the furnace (Joule effect). At the end of the graphitization process, bulk agglomerated graphite is unloaded from the furnace and further milled into powders of desired granulometry. This process allows the variation of the graphite properties to a large extent by controlling the production process parameters. This explains the multitude of primary synthetic graphite powder products with various crystallinity and morphologies being available on the market.

Expanded graphite is an exfoliated form of graphite (Herold et al. 1994). The production process is based on the thermal exfoliation of graphite intercalation compounds formed by the treatment of graphite flakes with strong acid in the presence of an oxidizing agent. The most prominent graphite intercalation compound used in industrial processes is graphite sulfate, $C_m{}^{+}HSO_4{}^{-} \cdot n\ H_2SO_4$, prepared by reacting graphite flakes with concentrated sulfuric acid and hydrogen peroxide, ammonium peroxydisulfate, and nitric or chromic acid as the oxidizing agent. Under these chemical conditions, graphite is oxidized and at the same time sulfate anions and sulfuric acid molecules are inserted between the graphite layers. Not every graphite interlayer is necessarily occupied by guest species, but intercalation compounds of different stages exist. The stage that can be achieved depends on the chemical conditions, but usually the actual composition may vary and causes the typical non-stoichiometry of these graphite salts. Other reagents that can be used are nitric acid, chloric acid, and nitric acid in acetic acid. The resulting graphite salt is isolated by filtration, washing, and drying. The expansion of the graphite salts occurs at temperatures above 300 °C. At industrial scale, this process is conducted by thermal shock, in which the material is exposed briefly to temperatures above 700 °C which cause the decomposition of the guest anions and acid molecules between the graphite layers to gaseous products that exfoliate the graphite layers. As an alternative, microwave radiations can be used for the exfoliation process. After expansion, the powder is composed by coarse "wormlike"-shaped grains (see Fig. 2b). Usually, expanded graphite cannot be used in this form due to the extremely low bulk density, and it is ground to fine particle size or compressed to graphite foils or graphite "paper." The graphite particles resulting from grinding of expanded graphite are very anisometric (high aspect ratio) and extremely effective as conductive additive at low loadings. Specially granulated expanded graphite materials have shown advantages in the incorporation into polymers using industrial feeding and mixing equipment (Gilardi and Bonacchi 2011). The largest industrial applications of exfoliated graphite are seals and gaskets from polymer-impregnated graphite foils.

## Properties

The term synthetic or natural graphite describes the origin of the graphite products. However, for the final application, the graphite material and surface properties are more important than the origin to distinguish between different graphite materials. The main categories of parameter that describe the graphite properties are purity, crystallinity, texture, particle size, and shape as well as the surface properties. As in all particle assemblies, these properties are distributive, and usually medium values are given to quantify the properties.

### Purity

The purity of graphite can vary a lot depending on the origin. Natural graphite is generally of lower purity compared to synthetic graphite. The purity of graphite is generally assessed by measuring the ash residue after combustion (ASTM C 561–91). The ash composition depends on the deposit and usually contains large quantities of silica ($SiO_2$), aluminosilicates, and other metal oxides commonly found in the Earth's crust ($Fe_2O_3$, $Al_2O_3$, CaO, etc.). High-purity graphite is generally stable in corrosive environments and has good oxidation resistance, as especially metal impurities are known to catalyze graphite oxidation. For some polymer types, high-purity graphite is required (>99.9% C) as impurities may cause degradation of the polymer matrix.

### Crystallinity

The crystal structure consists of layers of six-membered rings of $sp^2$ carbon atoms arranged in hexagonal pattern and bound together by covalent bonds; see Fig. 3. These so-called graphene layers are stacked in the crystallographic c-direction bound together by weak van der Waals forces. When mechanical pressure is applied, graphite can be easily cleaved along the graphene sheets. This characteristic of graphite is the main reason for its good lubricating properties.

By stacking, the hexagonal symmetry is maintained. This is in contrast to the turbostratic order in which the carbon layers are parallel but rotated around the crystallographic c-axis. The thermodynamically stable crystal structure is hexagonal, where every third graphene layer has an identical position to the first layer resulting in a stacking sequence A-B-A-B. A rhombohedral structure exists in which only every fourth graphene layer has an identical position to the first layer resulting in a sequence of A-B-C-A-B-C. This rhombohedral structure appears as statistical stacking defects and can be formed by mechanical deformation of hexagonal crystals by shear forces. Rhombohedral defects can be highly dispersed in the hexagonal graphite crystal or segregated to an isolated rhombohedral phase. Heat treatment completely transforms the rhombohedral into the hexagonal structure.

The degree of graphitization (crystallinity) can be measured by X-ray diffraction (XRD) using the Scherrer or Maire and Mering equations (Feret 1998) and is directly related to the interlayer distance c/2. High crystallinity is a prerequisite for good electrical and thermal conductivity, and highly intrinsically conductive graphite powders usually show c/2 values between 0.3354 and 0.3360 nm and real densities of 2.24–2.27 g/cm$^3$. Due to the layered crystal structure, graphite has strongly anisotropic properties. For example, it exhibits extremely high intrinsic electrical and thermal conductivity in the plane (up to 26,000 S/cm and 3000 W/mK), whereas perpendicular to the plane ("through plane"), the values are orders of magnitude lower.

The size of the crystals parallel to the graphite layers (La) and perpendicular to them (Lc) is important for the distinction of different graphite materials. Lc gives information about the average number of graphite layers stacked on each other in a single

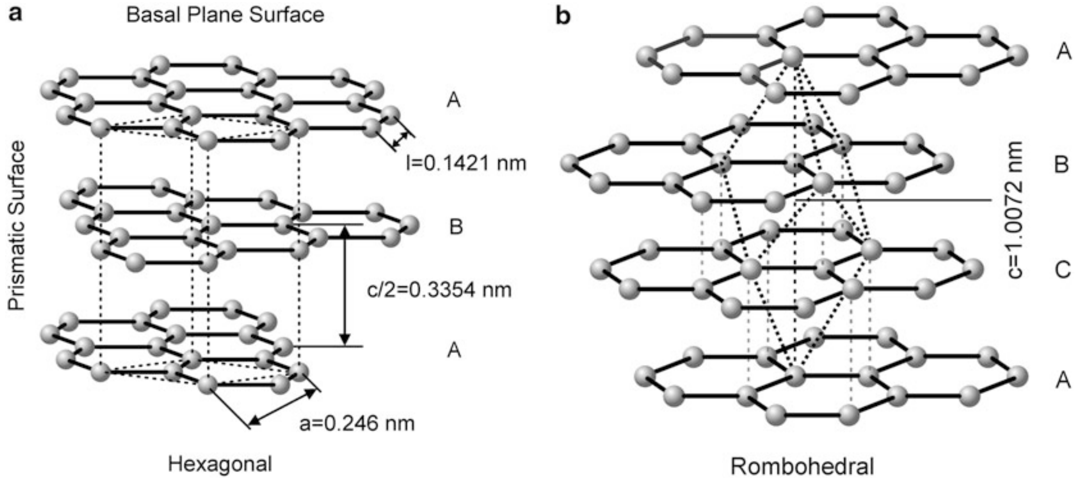

**Fig. 3** The hexagonal and rhombohedral graphite crystal structure (from Spahr 2010)

crystal and can be measured by XRD. La is more difficult to measure by XRD. As an alternative, Raman spectroscopy measurements can be used to measure the crystallinity in the direction of the graphite plane La (Tuinstra and Koenig 1970). The intensity and shape of the D- and G-band give additional information about the properties of graphite powders, like disorder and number of graphene layers (Ferrari 2007).

### Texture

Graphite powders typically consist of polycrystalline particles having the shape of platelets, which are agglomerates of intergrown single crystals. The graphite texture describes the orientation of the single crystal in the particle (mosaicity). Two extreme cases of graphite textures are schematically illustrated in Fig. 4. The first case contains few, relatively large, single crystals, which are aligned along the platelet plane and give rise to relatively strong anisotropic material properties. Such types of textures typically can be found in graphites with flaky or anisometric particle shapes. The second case contains many relatively small single crystals that are randomly oriented in the particle, giving rise to more isotropic properties. Such types of textures typically can be found in graphite materials with isometric particle shapes.

The specific (BET) surface area, which is measured by nitrogen adsorption (ISO 9277:2010), consists of surface area fractions contributed by the geometrical surface area, by the surface roughness and surface defects, as well as by the mesopores. Most of the internal porosity in the graphite particle is created by the interspaces between the crystalline domains. Smaller crystalline domains usually result in a higher porosity. The geometric surface area is related to the particle dimensions. It increases with decreasing particle size distribution. For fine graphite powders, the increase of the geometric surface area is the main reason for the increase of the specific BET surface area.

### Particle Size and Shape

The particle size can be adjusted by the conditioning process like mechanical grinding, classification, and sieving. Particle size distribution is typically measured by laser diffraction (ISO 13320:2009) for powders $<100$ μm, whereas coarser

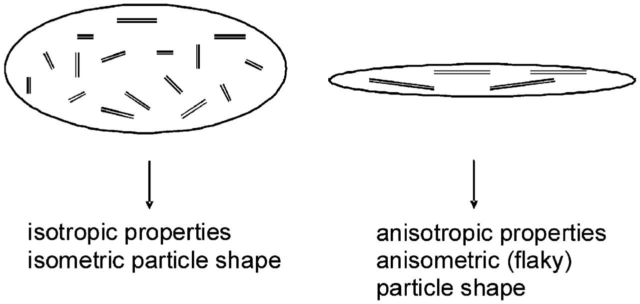

**Fig. 4** Schematic of two graphite particle models with an extremely isotropic and an anisotropic graphite texture (from Spahr 2010)

powders are analyzed by vibrating sieving. The particle shape is a consequence of the graphite type and the conditioning process and can be analyzed by optical and electron microscopes. The particle aspect ratio increases with decreasing particle thickness.

### Surface Properties

One can distinguish between two surface types in graphite: basal plane surface (the outer graphite layers of the graphite single crystal) and the edge surface (the exposed graphite layers form the higher energetic prismatic surfaces); see Fig. 3. The fraction of prismatic, basal plane surfaces is a key material parameter that correlates to different performance of graphite materials in the various applications. In particular, the surface chemistry at prismatic edges is relevant for polymer compounds. The $sp^2$ carbons terminating the graphite layers at the edges have free valences, which are typically saturated by surface groups (hydrogen, oxygen groups) and can be functionalized to improve compatibility to specific polymer types.

## Graphite-Filled Polymer Composite Processing

The production process of polymer composites can be very different depending on the polymer type and final application. The properties of the composite depend on proper dispersion of the filler in the polymer matrix. Graphite does not present any specific problem for processing and some authors reported very good processability (Wang et al. 2001). The equipment used for compounding traditional fillers such as talc, kaolin, and carbon black is normally used also for graphite. Among them, the most common processing techniques are corotating twin-screw extruder for thermoplastics and internal mixers for rubber compounds. The viscosity of the melt gradually increases, but much less than with additives like carbon black, enabling loading of up to ca. 80%. The effect of the loading on the polymer viscosity is known to depend on particle size, and smaller particles are known to increase compound viscosity much faster than large particles (Wypych 2009). High aspect-ratio graphites, such as expanded graphite, have very low apparent density resulting in very poor conveying properties. In order to overcome feeding problems, specially granulated grades have been recently developed (Gilardi and Bonacchi 2011). Once compounded, the materials follow the usual processing techniques (e.g., profile extrusion or injection molding) depending on the final application.

## Conduction Mechanisms in Graphite Polymer Composites

As mentioned in the previous sections, graphite is characterized by good electrical and thermal conductivity. Since polymers are both electrically and thermally insulating, graphite powders are suitable fillers to improve the conductivity of polymer compounds (see Fig. 5).

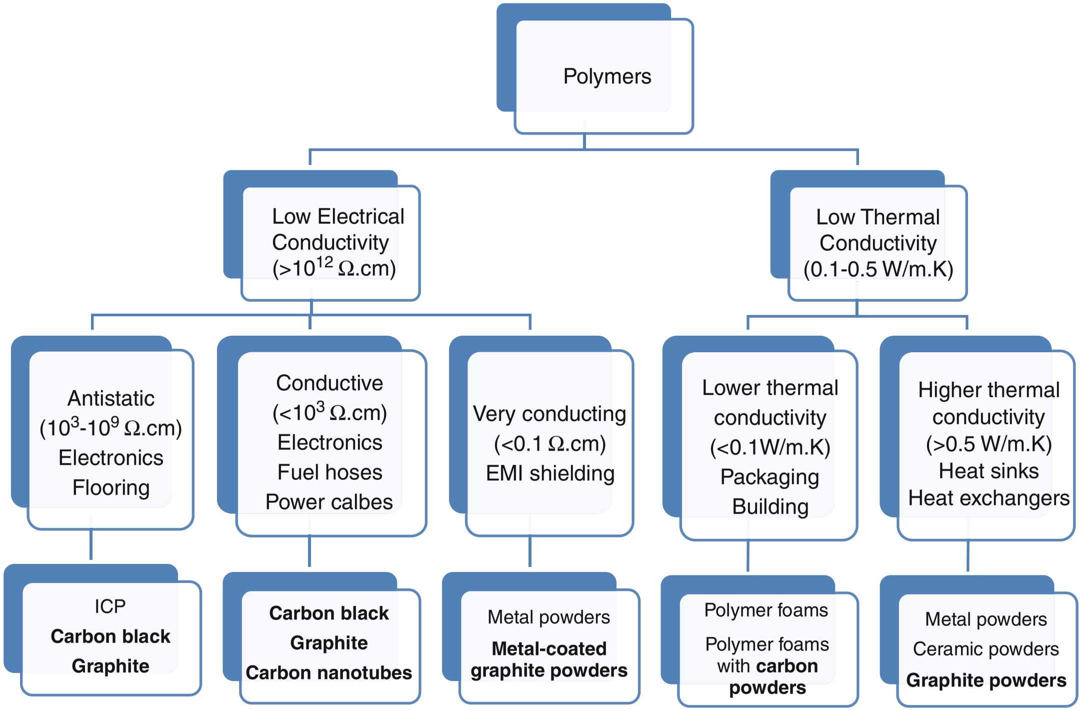

**Fig. 5** Polymers are intrinsically, electrically, and thermally insulating. Depending on the application, higher conductivity values are required that can be obtained by polymer compounds with appropriate conductive fillers

The mechanism for electrical and thermal conduction is very different. For the electrical conductivity, the percolation models of carbon black (▶ Chap. 19, "Carbon Black for Electrically Conductive Polymer Applications") are valid also for graphite and other carbon allotropes; electrical resistivity decreases sharply above the percolation threshold by several orders of magnitude. However, the electronic conduction mechanism in the conduction zone is ohmic in nature and consequently based on direct particle contacts once the conductive graphite network is formed at loadings beyond the percolation threshold. This mechanism would apply for carbon black and other carbon particles with diameters below ca. 300 nm only in the compressed dry powder form or in the polymer composite at very high loadings (Hess and Herd 1993).

For the thermal conductivity, on the other hand, the main mechanism is related to thermal vibrations of the atoms (phonons). Thermal transport requires multiple particle-to-particle paths and is a much smoother transition compared to the electrical percolation. The smoother transition is also due to the difference in conductivity between graphite and polymer matrix (typically 3 orders of magnitude for thermal conductivity compared to 20 orders of magnitude for the electrical conductivity). As shown in Fig. 6, two different regimes can be identified: electrically and thermally insulating compound below the percolation threshold and electrically and thermally conductive compound above the percolation threshold.

The thermal conductivity of polymer compounds depends on many factors: loading level, filler type, morphology and particle size distribution, and mixing and processing conditions. Several different models have been developed to predict the thermal conductivity of polymer composites. The two basic models are the "rule of mixture" (or "parallel model") and the "series model." In the rule of mixture

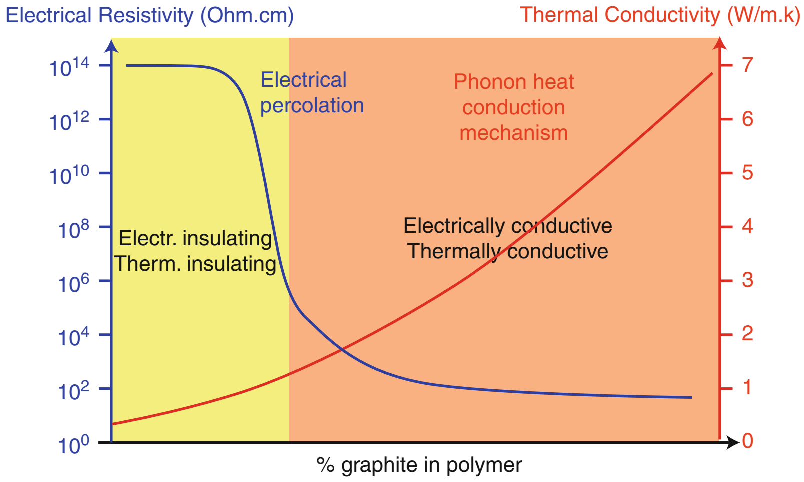

**Fig. 6** Schematic view of electrical and thermal conductivity as a function of graphite loading in polymer composite. The electrical resistivity decreases sharply at the percolation threshold, whereas the thermal conductivity increases smoothly

model, each phase contributes proportionally to its volume fraction to the overall thermal conductivity. This model assumes perfect contact between each particle and generally overestimates the measured thermal conductivity values (upper limit). The series model, on the contrary, assumes no contact between the particles and usually underestimates the real thermal conductivity (lower limit). Most of the experimental results obtained for graphite fillers are between these two models, more likely near the lower limit. More complex models for both isotropic spherical particles and for anisotropic particles (fibers, platelets) have been developed. For example, particle shape and orientation are considered in the Lewis–Nielsen model (Nielsen 1974). In some models, the thermal resistance between particles and matrix is considered (also called Kapitza resistance). The high Kapitza resistance is one of the reasons of the lower thermal conductivity in carbon nanotube polymer composites compared with expectations from the intrinsic thermal conductivity of carbon nanotubes (Hana and Fina 2011). Surface modifications of the filler and addition of compatibilizers during compounding have been suggested in order to improve the interaction to the polymer and to decrease the Kapitza resistance and therefore increase the thermal conductivity of the compound.

## Properties and Applications of Graphite-Filled Polymer Composites

### Lubrication

Most of the polymers have typically high friction coefficients that produce high wear at high loading and/or high sliding velocity. The total tribological stress (PV) is defined by multiplying the pressure (P) by the sliding speed (V). Above the so-called PV limit, the wear and/or friction coefficient drastically increases and the polymer cannot be used under these conditions. The PV limit can be increased by improving the mechanical strength (resistance to deformation) and thermal conductivity (reduction of surface temperature) but most often by decreasing the friction coefficient (reduction of frictional heating). Graphite powders are very well-known fillers used since many decades as solid lubricant for self-lubricating polymers, either alone or in combination with other fillers like PTFE, silicon, or molybdenum disulfide powders (Xian and Zhang 2005). For applications where the plastic piece is subject to severe dynamic conditions (e.g., water meter valves, bearings, gears, bushings, and rollers), graphite is used up to 30% loading in order to reduce the coefficient of friction and wear of polymer composites. Besides graphite crystallinity and granulometry, the most important property is purity, since contamination with hard material such as silicon carbide or silicates can be very detrimental for the final application. The tribological properties of polymer compounds can be evaluated by different methods like thrust washer test (ASTM D3702) and block-on-ring test (ASTM G137). The block-on-ring test determines sliding friction and wear by pressing a plastic block against the outer circumference of a rotating ring. By varying the pressure (P) and/or velocity (V), it is possible to determine the PV limit. In order to evaluate the effect of

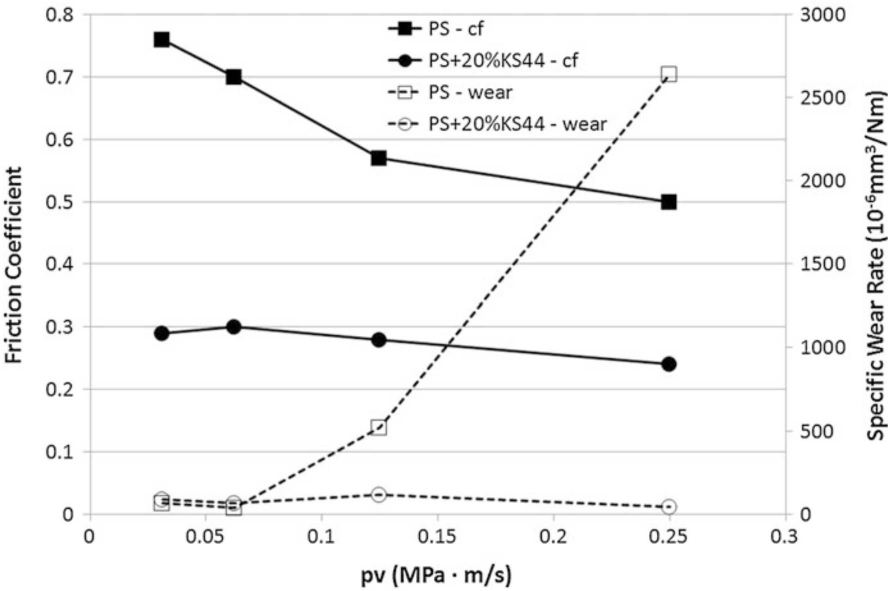

**Fig. 7** Friction coefficient and wear rate as a function of tribological stress for virgin PS and graphite-filled PS compound

graphite on the tribological properties of polystyrene, PS compounds with 20% of primary synthetic graphite (TIMREX KS44) have been produced by twin-screw extruder. Test specimen of both virgin PS and PS-KS44 compounds has been prepared by injection molding. The sample has been then positioned on the counter-body ring made from ground (Ra = 0.1–0.2 μm) and hardened (60 HRc) bearing steel (100Cr6, 1.3505). The graphite particles are aligned during injection molding and are oriented normally to the ring. Tests have been performed on Atlas TriboTester (Tribologic GmbH, Germany) at fixed pressure (0.5 MPa) and varying velocity (0.0625–0.5 m/s). As shown in Fig. 7, the friction coefficient of virgin PS is very high at low tribological stress (0.75 at 0.03 MPa.m/s) and decreases to lower values at higher stress (0.5 at 0.25 MPa.m/s). On the other hand, the wear rate strongly increases above ca. 0.1 MPa.m/s (PV limit). With the addition of graphite, the tribological performance is drastically changed. The friction coefficient is much lower and quite stable (0.25–0.30). The wear rate is maintained low and stable (40–120 10E–6 mm$^3$/Nm) over the tested tribological stress range. These data clearly indicate that graphite works well as a solid lubricant and can significantly increase the PV limit of thermoplastic polymers like PS. Besides polystyrene compounds, graphites are used in polyester fiberglass resin systems (SMC/BMC) that are known to be extremely abrasive for the counter-body (Wypych 2009). The ratio of graphite to glass fibers must be optimized to achieve the desired reduction in wear and friction coefficient. Graphitic carbons are also commonly used to improve wear resistance and deformation strength (creep) of polytetrafluoroethylene (PTFE)

(Kandanur et al. 2012), allowing the use of this polymer for applications like seals, O-rings, and valve housing. Filled PTFE is often not as strong as virgin PTFE, whereas the low friction coefficient is usually maintained due to the formation of a thin PTFE film at the interface between body and counter-body. Because of its low coefficient of friction, graphite can be used without drastically modifying the coefficient of friction of PTFE.

## Thermal Conductivity

Polymers are inherently thermally insulating, with thermal conductivity values always lower than 0.5 W/mK. The main mechanism of heat conduction in polymers is thermal vibrations of the atoms (phonons), since free movement of electrons is not possible. Therefore, the crystallinity of the polymer strongly affects its thermal conductivity, which ranges from 0.1 to 0.2 W/mK for amorphous polymers (e.g., PS) to 0.4–0.5 W/mK for highly crystalline polymers (e.g., HDPE). For some applications, thermally conductive fillers have to be added in order to provide higher values of thermal conductivity. Traditional thermally conductive fillers include metal powders (e.g., silver, copper, aluminum, nickel) or ceramic powders (e.g., boron nitrides, aluminum nitride). However, due to the high density of metals and high cost of ceramic fillers, carbon-based fillers seem to be the most promising thermally conductive additives (Ebadi-Dehaghani and Nazempour 2012). Diamond is electrically insulating but has a very high thermal conductivity (>2000 W/mK); however, diamond powders are very expensive and highly abrasive and rarely used as additives in polymers. Graphite is well known as a good thermally conductive additive. The thermal properties of graphite are highly anisotropic, since phonons propagate very quickly along the graphene planes but are slower to travel from one plane to another (>2000 W/mK in plane, ~10 W/mK through plane). In particular, expanded graphite, due to the particular morphology, high aspect ratio of the particles, and fair dispersion in the polymer matrix, is outperforming in terms of thermal conductivity compared to other carbon-based fillers like tubular and fibrous carbon (Debelak and Lafdi 2007). Compared to metallic powders, graphite has a much lower density, therefore allowing a much higher thermal conductivity at the same weight percent in the polymer. Moreover, metallic powders are quite abrasive and can lead to a higher wear of the equipment, whereas graphite has low hardness and is a chemically inert solid lubricant. For applications where high electrical resistivity is required, ceramic powders (e.g., boron nitride, aluminum oxide, and nitride) can be employed, but the thermal conductivity is lower compared to graphite at the same loading. For loading levels below the electrical percolation threshold or in combination with ceramic powders, the use of graphite allows to manufacture thermally conductive and electrically insulating polymer compounds. For loading levels above the electrical percolation threshold, graphite remains the best solution for making polymers thermally conductive when electrical conductivity is also wished or tolerated. Recently, silica-coated graphite has been suggested as a possible alternative to ceramic fillers (Choi et al. 2013). The silica coating on the graphite

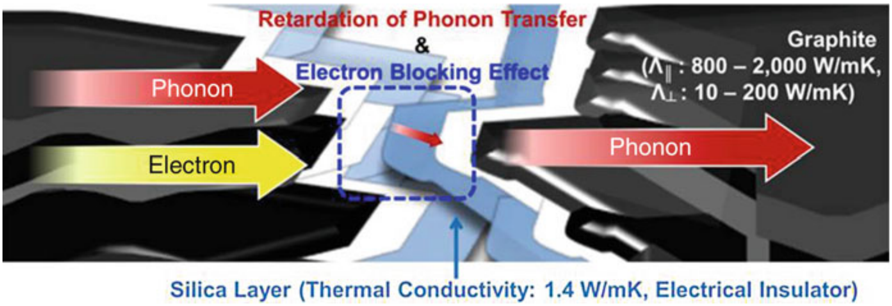

**Fig. 8** Illustration of the retardation of phonon transfer and electron blocking effect of silica-coated graphite. The size of the *red arrow* indicates the heat flux (reprinted from Choi et al. (2013) with permission from Elsevier)

particles acts has an electron blocking effect, whereas the phonon transfer is only slightly retarded, as illustrated in Fig. 8. As a consequence, silica-coated graphite polymer composite remains electrically insulating up to very high loadings, while maintaining good thermal conductivity.

Clearly, high thermal conductivity values can be obtained at high filler loadings (see Fig. 6). However, highly loaded compounds bring problems in terms of processability and strongly modify other properties of the compound like density, viscosity, and mechanical properties. The effect of particle shape on thermal conductivity has been investigated for copper (Tekce et al. 2007). Copper fibers are better performing compared to copper platelets and spherical Cu particles. Similar effect is observed also for graphite, where high thermal conductivities can be achieved at much lower loadings with high aspect-ratio expanded graphite compared to standard graphite (Fukushima et al. 2006). It has been reported that large graphite flakes have lower percolation threshold compared to small graphite flakes (Debelak and Lafdi 2007). Synergistic effects between different carbon fillers (graphite, carbon black, carbon fibers) have been also studied (Hauser et al. 2008). The use of synthetic graphite as main filler and carbon black and carbon fibers as minor fillers has been suggested in order to create thermally conductive pathways between graphite particles.

The effect of processing method and conditions has been investigated for carbon–polymer composites (Haddadi-Asl and Mohammadi 1996). The degree of anisotropy of the thermal conductivity depends on the compounding and finishing process. For graphite-loaded polymer parts, the through-plane thermal conductivity at graphite loadings below 30% is rather low when the graphite compound is injection molded (high degree of orientation of graphite particles), while samples processed via compression molding are much more conductive (low degree of orientation). As illustrated in Fig. 9, the difference between compression and injection-molded samples is less important at very high graphite loadings (>50%), where high through-plane thermal conductivity can be achieved also via injection molding. On the other hand, in-plane thermal conductivity of injection-molded pieces is much higher, and graphite compounds show good thermal conductivity

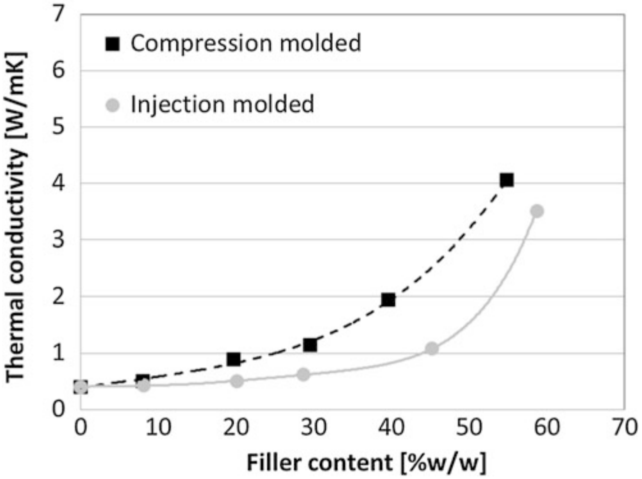

**Fig. 9** Through-plane thermal conductivity of compression (*squares*) and injection-molded (*circles*) HDPE samples loaded with TIMREX KS44 synthetic graphite

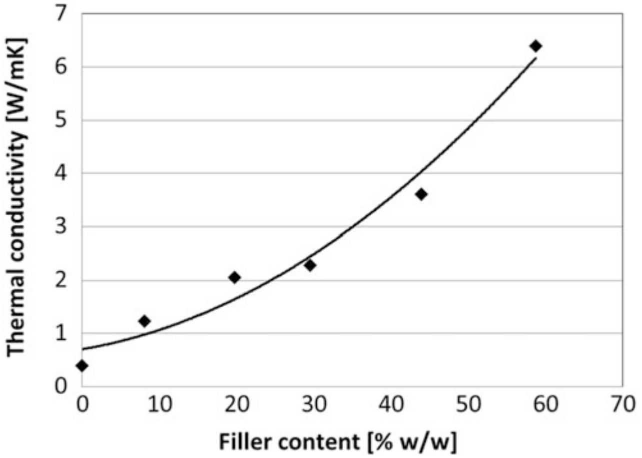

**Fig. 10** In-plane thermal conductivity of injection-molded HDPE loaded with TIMREX KS44 synthetic graphite

already at low loadings and really excellent thermal conductivity at high loadings (>5 W/mK); see Fig. 10. The same conclusions are valid also for expanded graphite-loaded compounds but at much lower loadings; see Fig. 11. In this case, high thermal conductivities can be reached at low C-THERM loadings with weight-saving benefits.

In recent years, there is an increasing demand of thermally conductive polymers for applications that require heat dissipation (heat sinks) or heat exchange.

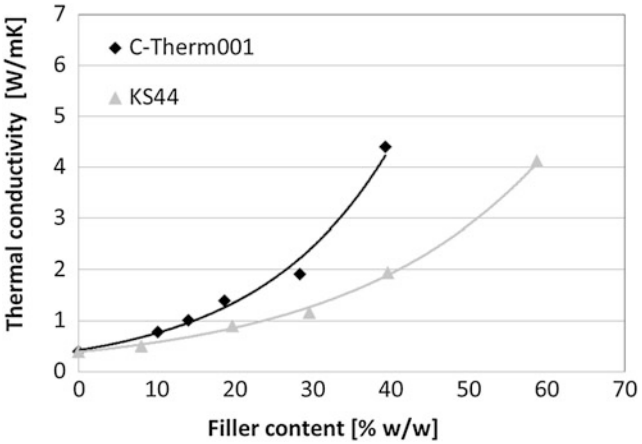

**Fig. 11** Through-plane thermal conductivity of compression-molded TIMREX C-THERM 001 (*squares*) and TIMREX KS44 (*triangles*) synthetic graphite-loaded HDPE

Thermally conductive polymers are considered as a good alternative to metals, offering substantial advantages compared to standard metal-based technologies (Cevallos et al. 2012). Filled polymers will never reach the thermal conductivity values of pure metals (>200 W/mK). However, considering the advantages of plastics in terms of weight reduction, design flexibility, corrosion resistance, durability, and manufacturing cost reduction, the achieved thermal conductivity levels (1–30 W/mK) are often sufficient to fulfill the requirements for certain applications. There are several applications that can benefit from thermally conductive polymers, and the targets in terms of thermal conductivity can vary a lot, from 0.8 W/mK for geothermal pipes to 20 W/mK and more for LED heat sinks. Until now, thermally conductive polymers have been used in mass production only in few applications, mainly as heat sink for LED. In the near future, it is expected to use them also for other industrial and automotive sectors (including air-cooled and liquid-cooled systems for batteries, electric vehicle thermal management, and lightning modules). Thermally conductive pipes can be used for geothermal, solar, and floor heating systems. Typical examples are plastic pipes for geothermal applications, where polyethylene (HDPE)-based pipes have almost completely replaced metallic pipes (copper, stainless steel), thanks to their better properties in terms of flexibility, resistance to corrosion, ease of installation, and costs. However, standard PE pipes used in heat exchangers were originally intended for hot and cold water distribution and have low thermal conductivity (0.4 W/(mK)) which represents a limit to their potentialities. In order to build more efficient geothermal systems, pipe materials with better thermal conductivity are required, while keeping good flexibility and mechanical properties. Such pipes with increased thermal conductivity will reduce the thermal resistance of the borehole and decrease the length needed for geothermal heat exchangers, therefore lowering system costs. Calculations indicate that doubling the thermal conductivity of the pipes to 0.8 W/mK by the addition of graphite is sufficient to significantly reduce the borehole thermal resistivity and consequently of the borehole heat exchanger length (Gilardi and Bonacchi 2012).

## Electrical Conductivity

In traditional polymers, the electrons have low mobility and the resulting electrical resistivity is very high (>1E12 Ω.cm). There are some polymers that exhibit higher electrically conductivity values, the so-called intrinsically conducting polymers (ICP), but ICP are currently used only in few large-scale applications because of poor processability and stability, limited performance (>1E5 Ω.cm), and high costs (Aldissi 1993). There are many traditional applications that require electrically conductive polymers, such as electronic packaging, conductive fuel hoses, and power cables. The electrical conductivity of polymers can be increased by the addition of electrically conductive fillers (see Fig. 5). Graphitic carbons are electrically conductive, but conductive carbon black is usually the preferred choice for applications like ESD electronic packaging, conductive fuel hoses, and power cables due to the lower carbon black concentration required to make the polymer compound electrically conductive as well as the lower impact on the mechanical properties of the resulting polymer composite (▶ Chap. 19, "Carbon Black for Electrically Conductive Polymer Applications"). However, due to the different morphology, the percolation threshold of graphite is less steep than for carbon black, thus enabling compounders to control the final conductivity much better, especially in the antistatic range. Another application where graphite fillers are used is if extremely high conductivity values are needed, as the ultimate electrical conductivity of graphite-loaded compounds (far above the percolation threshold) is higher compared to carbon black ones (graphite is inherently more conductive than carbon black due to the higher crystallinity). In general, graphite is used as electrically conductive filler in special applications when other specific properties are required. An example is polymer bipolar plates for fuel cells, where very low electrical resistivity combined with high thermal conductivity is required (Lee et al. 2009). The fuel cell market is expected to grow in the next years, both for stationary applications (industrial and residential primary and backup power generation) and mobile applications (automotive, buses, forklifts). As a consequence, there will be an increasing demand for graphite and other carbon fillers for bipolar plates for PEM fuel cells.

## Infrared Shielding

Polymers are often used because of their thermal insulating properties and lightweight. Thermal insulation is enhanced by foaming. The addition of carbon powders being typically carbon black or graphite at extremely low loadings (ca. 3%) can further improve the insulation properties by ca. 20% due to the their capability to absorb and reflect infrared radiation (Glenz 2010). Rigid polystyrene foams (EPS, XPS) are widely used for the construction industry and for lightweight and thermally insulating packaging. Especially trend toward energy efficiency improvements to buildings leads to the increasing demand for “gray” EPS with, thanks to the carbon fillers, improved thermal insulation that allows to reduce the thickness of the insulating EPS layer at a given insulation efficiency.

## Mechanical Properties

As for other fillers, the mechanical properties of graphite-filled polymers are strongly modified with regard to the original polymer properties. Due to their flaky morphology, the effect of the graphite loading on the mechanical properties is mainly related to the particle aspect ratio that is in turn dependent on the graphite production process. The mechanical behavior of graphite-filled polymer compounds is similar to talc-filled compounds due to a similar particle shape but with some differences in polymer compatibility due to different surface properties. The incorporation of graphitic fillers in polymers causes a strong increase of stiffness and shows little influence on the tensile strength. Small increases in tensile strength have been reported for PP, PS, and HDPE (Wypych 2009). Decrease in elongation at break is often found together with a decrease of the impact properties (Wang et al. 2001).

## EMI Shielding

Shielding of electromagnetic interferences (EMI) is often linked to good electrical conductivity, with resistivity values typically lower than 0.1 Ω.cm. However, the relation between DC volume resistivity and shielding effectiveness is not direct and can be misleading. In particular, the shielding effectiveness depends on the frequency of the electromagnetic wave. Typical fillers are pure metallic powders or fibers like steel, nickel, copper, or silver, but composite powders like metal-coated graphite are also commonly used. For example, nickel-coated graphite offers synergistic effects of nickel cladding (reflection of EM waves) and the graphite core (absorption of EM waves). Moreover, metal-coated graphite materials are lightweight and cheaper than pure metal powders (Callen 2005). Typically, high loading of metal-coated graphite (>60%) is needed for high shielding effectiveness. EMI shielding properties are crucial for replacement of automotive systems where metals have been used both as heat sinks and EMI shields. Good EMI shielding is important also for many electronic applications like mobile phones, computers, airplane electronics, and medical equipment.

## Gas Barrier

Anisotropic graphitic powders can be used to improve the gas barrier properties (Al-Jabareen et al. 2013). Diffusion of small molecules of gases or liquids through polymers is a three-step process: firstly, the molecule has to dissolve in the polymer, then it has to diffuse through it, and finally it has to desorb back to the gas or liquid phase. High aspect-ratio platy fillers are known to reduce permeability and therefore increase barrier properties of polymers (Thompson et al. 2013). If the filler particles are impermeable to the diffusing molecule and oriented perpendicular to the diffusion direction, they act as impenetrable barrier that force the molecules to go around them. As a consequence, the diffusion path length of the molecule through the composite film significantly increases. Polymer composites with improved barrier properties are required for applications like food packaging in which they improve the food shelf life by retarding or preventing oxygen and moisture to get in contact with the packaged food or by reducing or stopping the carbon dioxide loss from carbonated drinks. Other applications are pipes like water and fuel pipes and tires for an improved pressure retention and reduced rolling resistance. Of course there are also other high aspect-ratio fillers like mica, kaolin, talc, and clay that can be used to reduce the permeability of gas and liquid through a polymer film. Graphitic powders are usually used as multifunctional filler when electrical/thermal conductivity or lubricity, in addition to gas barrier properties, is required.

## Flame Retardant

Graphite salt (also called expandable graphite) is a halogen-free material consisting of graphite and acid. The acid (typically sulfuric acid) is intercalated between the graphene layers. Expandable graphite can be used not only for the production of expanded graphite but also as flame retardant in polymer compounds (▶ Chap. 17, “Mineral Filler Fire Retardants”). When expandable graphite is exposed to heat, it can expand to several hundred times its original volume and covers the entire burning surface of the substrate with a wormlike structure of expanded graphite. The char, formed by the expanded graphite, acts as an insulating agent and dramatically reduces the heat release, mass loss, smoke generation, and toxic gas emission of the substrate. The expansion volume of the graphite salt is a function of the temperature. The temperature, at which expansion begins, the so-called onset temperature, mainly depends on the type of acid. Particle size, carbon, and acid content also affect the expansion.

## Future Directions

Graphitic carbon powders are already used for many different polymer applications, but their potential is not yet completely exploited. Thermally and electrically conductive compounds and self-lubricating polymers containing graphite fillers are already commercially available since several years. In particular, graphitic carbon powders represent a valid solution for thermally conductive polymers in the case that electrical insulation is not a requisite. Current and future development will try to optimize the cost-performance ratio and apply these materials to new applications.

Recent efforts to develop new graphite materials with higher aspect ratio up to nano-graphite, few-layer, or single-layer graphene should further increase the thermal conductivity but lower the impact on the mechanical properties (Li and Zhong 2011). Functionalization of graphitic carbon fillers is evaluated in order to improve the graphite dispersion in the polymer matrix and to reduce thermal resistance between particles. This potentially provides an alternative way to the particle nano-sizing to increase the thermal conductivity of polymer compounds and at the same time to lower the influence of graphite fillers on the mechanical properties of the polymer compound.

## Cross-References

- ▶ Carbon Black for Electrically Conductive Polymer Applications
- ▶ Mineral Filler Fire Retardants

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# Antiblock Additives

# 21

Joerg Ulrich Zilles

## Contents

**Abstract**

Anti-blocking is a term used to describe measures to prevent film sheets to stick together. Polyolefin films tend to adhere to each other due to strong van der Waals interaction or electrostatic charges when being in close contact (adjacent layers). The higher the temperature, pressure, and contact/processing time, the higher the tendency to stick to each other.

To avoid the adherence of layers due to a close contact, particulate matter is introduced into the film in a highly diluted concentration. By that measure a micro-rough surface is created, and contact area of film layers is minimized; the distance between the layers is maximized and adherence suppressed. Minerals used for that application should have little to no impact on the mechanical properties of the film; must not deteriorate transparency, haze, color, gloss of the film; and should be compatible with the film-processing process. Several minerals are used for this purpose: talc, calcined kaolin, cristobalite, precipitated silica, diatomaceous earth, mica, calcium carbonates, calcium sulfate (anhydrite), magnesium carbonate, magnesium sulfate, and feldspars.

Organic alternatives used for anti-blocking or anti-stick are amides, fatty acid amides, fatty acids, salts of fatty acids, silicones, or others. They work with

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different mechanisms compared to the inorganic anti-blocking additives, migrating to the film surface upon cooling and forming a release layer. Sometimes combinations of inorganic and organic anti-blocking additives are used. Organic additives typically have lower anti-blocking ability in comparison to the inorganic ones but better slip effect.

This entry summarizes the mechanisms of anti-blocking and subsumes results from literature on that subject with an emphasis on the mineral anti-blocking additives.

**Keywords**
Feldspar • Cristobalite • Nepheline syenite • Film • Anti-blocking • Greenhouse

## Definition

Anti-blocking describes measures to minimize adhesion of adjacent polymer film layers to each other.

## Introduction

Anti-blocking is a term used to describe measures to prevent film sheets from sticking together. Different strategies are used to achieve anti-blocking, i.e., increasing roughness to decrease contact area between layers by adding mineral particles into the polymer or using slip additives allowing the sheets to slide easily against each other by organic molecules diffusing to the surface. This entry summarizes the mechanisms of anti-blocking and subsumes results from literature on that subject with an emphasis on the mineral anti-blocking additives.

## Key Information

Polyolefin films (mostly blown or cast polyethylene (LLDPE) and polypropylene (PP) – but also PVC and to some extent PET) tend to adhere to each other due to strong van der Waals interaction or electrostatic charges when being in close contact (adjacent layers). The closer the distance between two layers, the stronger the adherence which occurs typically when material is wound up after film production. Once in close contact, it is nearly impossible to move the layers relatively to each other due to resulting high coefficient of friction. The higher the temperature, pressure, and contact/processing time, the higher the tendency to stick to each other. Additionally low-molecular-weight polymers (oligomers) might migrate from bulk to the surface and add as “tackifier.”

To avoid the adherence of layers due to a close contact, particulate matter is introduced into the film in a highly diluted concentration. By that measure a micro-rough surface is created, and contact area of film layers is minimized; the distance between the layers is maximized and adherence suppressed.

Typically this is done by using masterbatches with concentrations up to 50wt% of particulate matter which are added during processing of the film. Final concentration of the anti-blocking or anti-stick agent in the film material is typically in the range of 0.1% up to 1.0%, depending on the application. Minerals used for this application should have little to no impact on the mechanical properties of the film; must not deteriorate transparency, haze, color, and gloss of the film; and must be compatible with the film production process. Several minerals are used for this purpose: talc, calcined kaolin, cristobalite, precipitated silica, diatomaceous earth, mica, calcium carbonates, calcium sulfate (anhydrite), magnesium carbonate, magnesium sulfate, and feldspars. The big advantage of using inorganic anti-blocking additives is that they do not migrate and are not released from the polymer matrix. Especially when films are subjected to food contact or weathering, most inorganic anti-blocking additives (except carbonates) are more persistent in comparison to the migrating organic ones. On the other hand – since they cannot be dissolved in the polymer – it is more difficult to obtain optimum optical properties. In this respect the match of refractive index between polymer and inorganic additive – besides the particle-size distribution (which causes the wanted roughness but on the other hand unwanted light scattering of the surface) – governs transparency as well as haze. Even if the average refractive index of the mineral matches the one of the polymer, the mineral will intensively scatter the light if it has pronounced birefringence. Birefringence is the dependence of refractive index on the direction of a light beam relative to the axis of the crystal lattice. The refractive index of polyethylene (dependent whether it is LD or HD) ranges between 1.51 and 1.54, the one of polypropylene typically around 1.49. Both materials are isotropic (without birefringence) when clarified properly. Table 1 shows data of refractive indices and birefringence of feldspathoids, Table 2 the data of other minerals used for anti-blocking. Looking at those tables, the use of the carbonates calcite and magnesite in films is prohibitive when aiming at optimum transparency due to their high birefringence.

For inorganic additives, average particle sizes chosen are in the range of a fraction of the film thickness, and special care is taken to ensure an absence of oversize particles to avoid blocking of nozzles or partial film rupture during processing (especially when films are blown). Top cuts are chosen typically to exceed the film

**Table 1** Typical data of the pure feldspathoid mineral species (modified from (Robinson 2003)

| Mineral | Stoichiometric formula | Density [kg/L] | Mohs hardness | Refractive indices | Birefringence |
|---|---|---|---|---|---|
| **Albite** | $NaAlSi_3O_8$ | 2.62 | 7 | 1.52–1.54 | 0.010 |
| **Anorthite** | $CaAl_2Si_2O_8$ | 2.73 | 6 | 1.57–1.59 | 0.011 |
| **Microcline** | $KAlSi_3O_8$ | 2.56 | 6 | 1.51–1.53 | 0.007 |
| **Nepheline** | $(Na_{0.75}K_{0.25})AlSiO_4$ | 2.59 | 6 | 1.53–1.55 | 0.004 |
| **Orthoclase** | $KAlSi_3O_8$ | 2.56 | 6 | 1.52 | 0.005 |

**Table 2** Typical data of the pure mineral species

| Mineral | Stoichiometric formula | Density [kg/L] | Mohs hardness | Refractive indices | Birefringence |
|---|---|---|---|---|---|
| **Talc** | $Mg_3Si_4O_{10}(OH)_2$ | 2.75 | 1 | 1.50 | 0.044 |
| **Cristobalite** | $SiO_2$ | 2.30 | 6.5 | 1.48 | 0.003 |
| **Muscovite mica** | $KAl_3Si_3O_{10}(OH)_{18}F_{0.2}$ | 2.83 | 2.5 | 1.56 | 0.040 |
| **Calcite** | $CaCO_3$ | 2.17 | 3 | 1.57 | 0.160 |
| **Anhydrite** | $CaSO_4$ | 2.97 | 3 | 1.57 | 0.043 |
| **Magnesite** | $MgCO_3$ | 3.0 | 4 | 1.51 | 0.190 |

thickness a bit so these particles extend surfaces on both sides of the film. Special care must be taken since some minerals (like talc) act as nucleating agents, changing completely mechanical and optical properties of the film even in small quantities by inducing its crystallization. Also absence of impurities (like iron oxides), promoting the oxidization of the polymer, has to be taken into account. Finally hardness in combination with particle size of the mineral governs wear at least on extruders used to produce the masterbatch and later on equipment used to produce the films.

Organic alternatives used for anti-blocking or anti-stick are amides, fatty acid amides, fatty acids, salts of fatty acids, silicones, or others. They work with different mechanisms compared to the inorganic anti-blocking additives, migrating to the film surface upon cooling and forming a release layer. Sometimes combinations of inorganic and organic anti-blocking additives are used. Organic additives typically have lower anti-blocking ability in comparison to the inorganic ones but better slip effect.

The extent of blocking between films can be measured according to ASTM 3354–89. The force (actually expressed by a weight) to disjoin two adjacent films with a contact area of 100 $cm^2$ is measured. The efficiency of anti-blocking is described by the coefficient of friction (COF) by ASTM 1894. Here the force between the two polymer sheets or of one sheet against a standardized surface (steel) necessary to make the sheet slide over the second surface is measured.

Particle forms of anti-blocking additives are used.

Figures 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, and 11 show the typical particle forms of inorganic anti-blocking agents used in polyolefin films.

Special care has to be taken for the choice of additive combinations in polyolefins since all additives can show specific interaction with each other. Worst case interaction occurs if one additive deactivates to effect of another additive. Those adverse effects or how to circumvent them by proper choice of anti-blocking additive has been described by Imerys (2014). They compared hydrous with calcined clay in anti-blocking applications concerning their surface interaction with organic substances. Starting with inverse gas chromatography, they calculated the free energies of adsorption on those two minerals for various organic substances (e.g., amines as model substance for HALs). Strong interaction of alkenes or polar materials with hydrous clay was attributed to the Lewis acidic site (hydroxyl groups), whereas the calcined material (by calcination metal hydroxyl groups are converted into metal

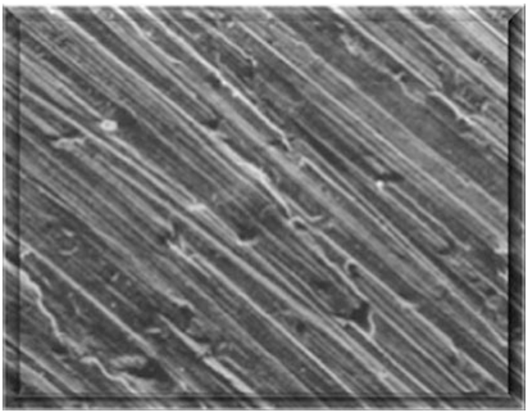


**Figure 1** SEM of feldspar flour 44% orthoclase, 45% albite, 4% anorthite, 7% quartz

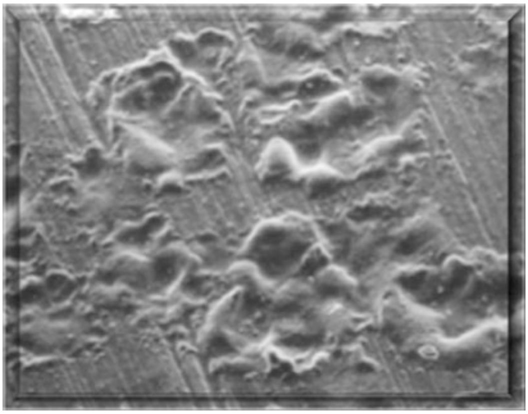


**Figure 2** SEM of feldspar flour 85% albite, 3% orthoclase, 4% anorthite, 8% quartz

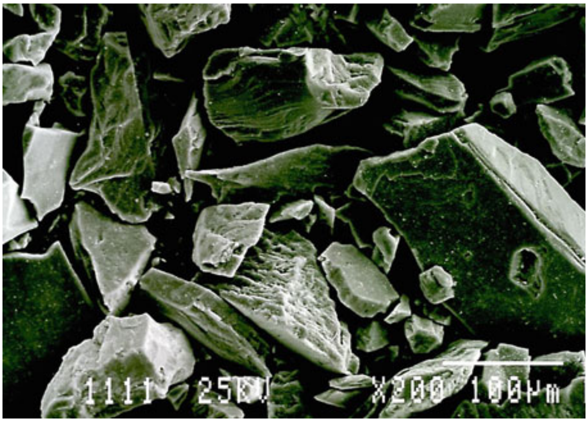


**Figure 3** SEM of feldspar flour 87% orthoclase, 7% albite, 4% kaolinite, 2% quartz

**Figure 4** SEM of nepheline syenite flour 25% nepheline, 73% feldspars, 2% analcime, natrolite

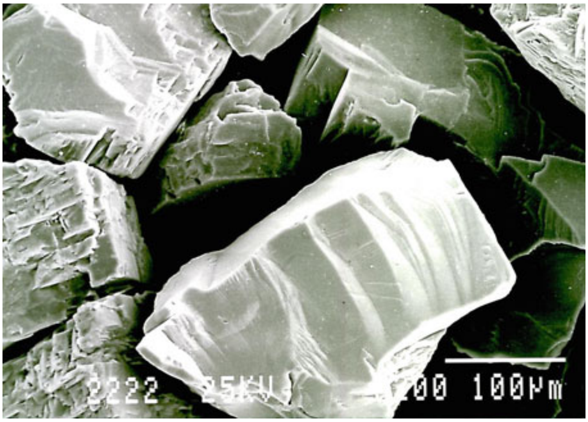
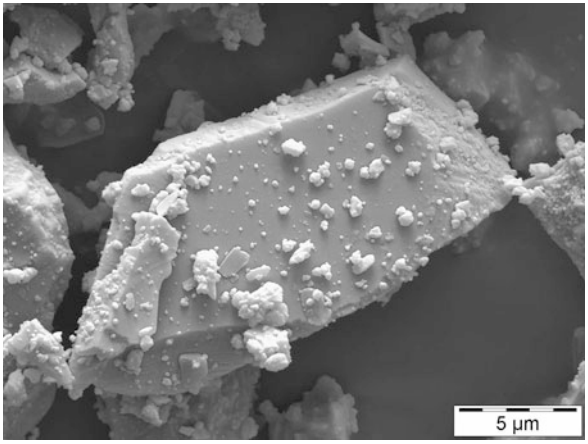


**Figure 5** SEM of anhydrite

**Figure 6** SEM of calcined clay (kaolin)



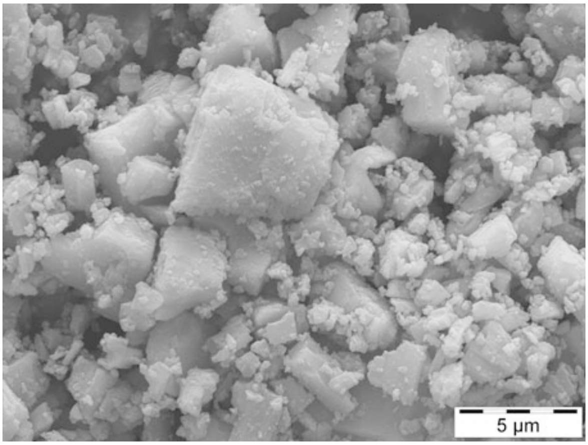


**Figure 7** SEM of precipitated silica

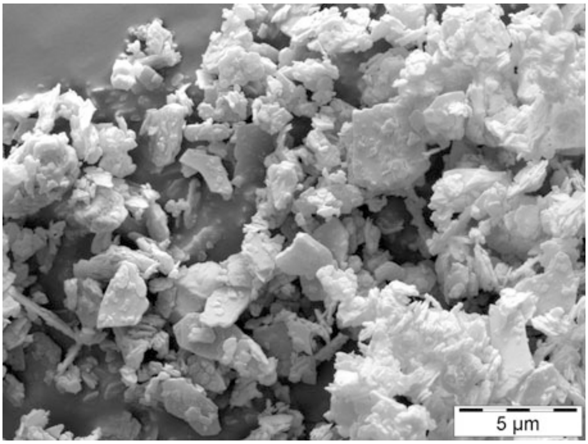


**Figure 8** SEM of cristobalite flour

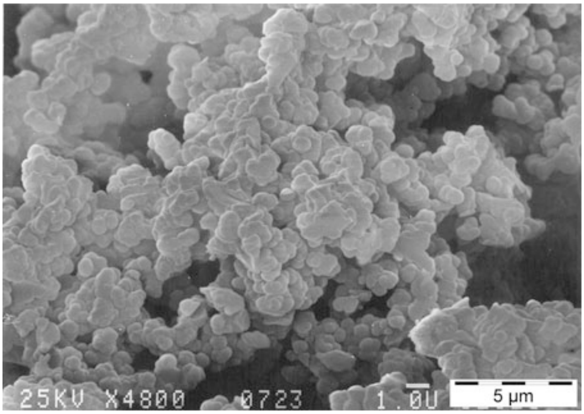


**Figure 9** SEM of diatomaceous earth

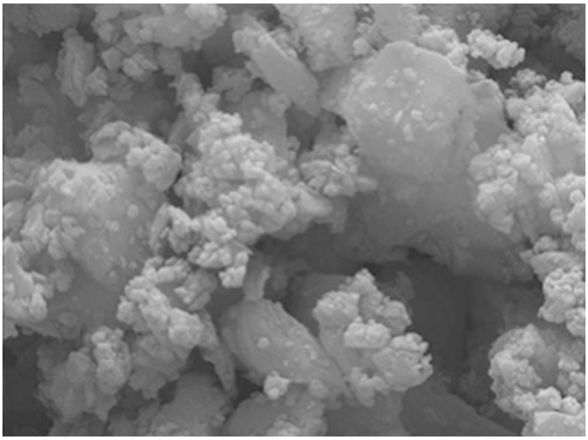


**Figure 10** SEM of muscovite mica

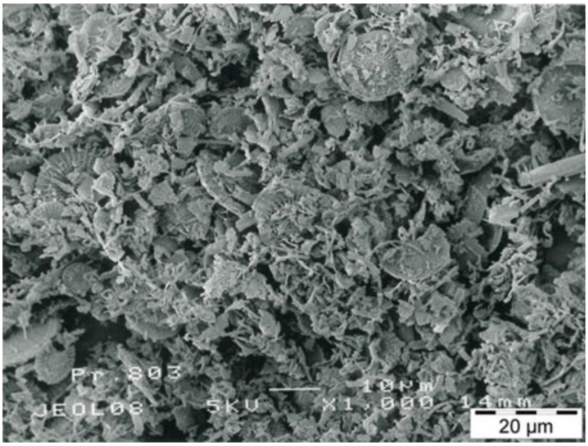


**Figure 11** SEM of calcite

oxide sites) showed much less interaction. They conclude that the reduction of surface polarity by calcination reduced the interaction/adsorption and thus the deactivation of other additives by the anti-blocking material. Subsequently they compared hydrous clay, calcined clay, talc, natural silicas, diatomaceous earth, and synthetic silica in haze and blocking force at 1,500 and 3,000 ppm loading level. Calcined clay imparted lower haze in comparison to the other additives (hydrous clay, talc, diatomaceous earth, as well as natural and synthetic silica). Lowest blocking force (best anti-blocking ability) was observed conversely to haze, with synthetic silica showing the best behavior in that respect.

Smith (2006) published the interaction and its effect on film fracture on LLDPE films of several combinations of polymer-processing aids (PPAs) and different anti-blocking additives. The three PPAs chosen, necessary to prevent film fracture, were all FKMs (fluoroelastomers) based on copolymers of vinylidene fluoride and hexafluoropropylene pure or mixed with other processing aids. The five anti-blocking additives

**Table 3** Physical properties of mineral flours used for anti-blocking in polyethylene

| Mineral | Anhydrite | Anhydrite | Cristobalite | Feldspar | Nepheline syenite |
|---|---|---|---|---|---|
| **d 50** [μm] | 6 | 3 | 5 | 3 | 7.6 |
| **Hardness** (Mohs) | 3.5 | 3.5 | 6.5 | 6 | 6 |
| **Density** [g/cm$^3$] | 3.0 | 3.0 | 2.35 | 2.6 | 2.6 |
| **Refractive index** | 1.57 | 1.57 | 1.48 | 1.52 | 1.53 |
| **Brightness (Y/D65)** | $Y = 85$ | $Y = 89$ | $Y = 97$ | $Y < 90$ | $Y < 90$ |

chosen were diatomaceous earth, surface-treated talc, talc, a mineral mixture of sodium and potassium aluminosilicates, and a synthetic, amorphous silica. He concludes that PPAs based on FKM are effective if they contain additional processing aids, enhancing incompatibility between FKM and the LLDPE. By using this technology, the interaction with most anti-blocking additives in this study could be overcome. However synthetic silica proved to be highly interactive with the PPAs requiring a much higher dosage level of the PPAs to perform properly. Interestingly he found that there was no difference between pure and surface-treated talc in view of the interaction to PPAs.

A comparison of different, common mineral products for anti-blocking has been published by HPF (HPF The Mineral Engineers 2013). Table 3 shows the properties of mineral flours used in comparison.

Films were produced by blow-film extrusion using a 3% polyethylene mineral masterbatch (MFI 2.0 g/10 min) – feldspar additionally in a 60% masterbatch. The concentration of the mineral in the final film was 3,000 ppm; film thickness was 50 μm, MFI (190 °C/2.16 kg) of 0.75 g/10 min.

By dynamic friction coefficient measurement according to DIN EN ISO 8295/ASTM D1894, differences in anti-blocking behavior were recorded. The lower the friction coefficient, the less blocking occurs and the better the anti-blocking performance. Table 4 summarizes the data.

Optical properties were determined by means of haze and transparency measurement according to ASTM D1003 and gloss according to DIN 67530/ASTM D2457. Table 5 shows the results.

- Anhydrite showed excellent anti-blocking, but optical properties (esp. haze) are comparably poor.
- Cristobalite and nepheline syenite showed comparable good results.
- Feldspar (which was orthoclase in this case) showed best anti-blocking and optical properties.

## Light and Thermal Management in Agricultural Films

Blocking of films is a general problem and also highly connected to the production of greenhouse films. But here the anti-blocking additive has to have additional functionality besides a good anti-blocking performance: optical properties. Selective

**Table 4** Coefficients of frictions of polyethylene films with different anti-blocking additives

| Film | Inside-inside | Outside-outside | Inside-stainless steel | Outside-stainless steel |
|---|---|---|---|---|
| Neat PE film | 0.48 | 0.42 | 0.45 | 0.40 |
| Anhydrite d50 = 6 μm | 0.46 | 0.45 | 0.32 | 0.34 |
| Anhydrite d50 = 3 μm | 0.43 | 0.37 | 0.22 | 0.24 |
| Nepheline syenite | 0.45 | 0.39 | 0.29 | 0.30 |
| Cristobalite | 0.46 | 0.43 | 0.27 | 0.31 |
| Feldspar | 0.38 | 0.38 | 0.28 | 0.30 |
| Feldspar from 60% masterbatch | 0.41 | 0.37 | 0.30 | 0.32 |

**Table 5** Optical properties of polyethylene films with different anti-blocking additives

| Film | Gloss 60° | Haze | Transparency |
|---|---|---|---|
| Neat PE film | 69 | 12.7 | 92.1 |
| Anhydrite d50 = 6 μm | 71 | 16.2 | 91.7 |
| Anhydrite d50 = 3 μm | 72 | 16.6 | 92.2 |
| Nepheline syenite | 71 | 15.9 | 92.1 |
| Cristobalite | 73 | 14.8 | 92.8 |
| Feldspar | 71 | 13.3 | 91.8 |
| Feldspar from 60% masterbatch | 67 | 13.5 | 91.9 |

transmittance and reflectance/scattering of specific wavelengths of sunlight are crucial for plant growth. Greenhouses made from polyolefin films (LDPE) offer cost-effective solutions for intensified agriculture. Transmission and reflection of the solar spectrum are important key parameters for the growth of plants and the heat management in greenhouses. The biologically active UV/VIS radiation for plant growth (400–700 nm) should pass through the film as completely as possible (good transparency, little haze), but heat (IR irradiation MID IR 7–14 μm) should be reflected to avoid overheating during the day and too much cooling during the night. Weathering resistance is another key parameter of these films. Minerals are used to make those LDPE films suitable for thermal management. Advantages are early and high-quality crops, protection against cold/frost, and higher yields.

Schwartz (2006) published a comprehensive comparison of different MID IR absorbers in polyethylene films for heat management in greenhouses. LDPE (density, 0.92 g/cm$^3$) MFI: 2 g/10 min was used and compounded with different additives based on silicates in concentrations of 5% and 10% by weight. Hundred micrometer films were produced in an extrusion-blow process. The minerals were cristobalite (CR), talc (TL), organically modified clay (OC), nepheline syenite (NS), calcined kaolin (CC), and synthetic aluminosilicate (SA).

All films showed good optical transparency because refractive indices of the minerals were in the range of 1.48–1.58 close to PE (1.50–1.51). Nevertheless light scattering was dependent on PSD (particle-size distribution). Small particles tend to show less light dispersion (28–33%) and larger particles higher light dispersion (44%).

The thermal loss was dependent on film thickness; the higher the film thickness at a given load of a given mineral, the better the heat retention/the smaller the heat loss.

During QUV weathering tests, time to total degradation and amount of carbonyl groups have been measured. With organically modified clay, calcined kaolin, and talc, the speed of concentration increase of carbonyl groups was the fastest and the exposure time to degradation the shortest. This was attributed to the amount of iron oxide impurities being the highest in those minerals. Cristobalite and nepheline syenite showed the slowest degradation having the lowest iron oxide concentration. An exception of the rule was synthetic aluminosilicate which showed the lowest amount of iron oxides but a high degradation rate. This was attributed to the extremely high surface area of those synthetic aluminosilicates.

Also the effect of deactivation of light stabilizers has been studied. The higher the surface area of the mineral, the more they were absorbed which leads to insufficient performance.

The study concludes that talc and calcined kaolin are good choices for thermal management in sunny countries due to the fact that they strongly scatter light and avoid shadow zones in greenhouses, promoting uniform photosynthesis. In less sunny countries, higher transparency is necessary to achieve maximum transmittance of indirect light. Here nepheline syenite would be the best choice. Organically modified clay could not be recommended due to high degradation and low thermal management capabilities.

Another study performed by Van Aken (2012) gives an overview over optical properties and thermal management potential of several minerals and experimental inorganic compounds: ATH (alumina trihydrate), barite, calcite, cristobalite, metal oxide compound, nepheline syenite, talc, calcined kaolin, and wollastonite. Those minerals were compounded at a concentration of 5% by weight in polyethylene.

Comparing the MID IR/heat retention (during the night), the ranking in efficiency was metal oxide compound < calcined kaolin < cristobalite = nepheline syenite < ATH < wollastonite < calcite < barite < talc. Transparency of all films was in the region of 89% (calcined kaolin) to 92% (metal oxide compound). Haze was lowest on nepheline syenite and highest on wollastonite.

Another study was published by HPF (HPF The Mineral Engineers 2013). Here feldspar and nepheline syenite were compared directly in a polyethylene with an MFI of (190 °C/2.16 kg) 0.75 g/10 min by using a 60% masterbatch of polyethylene with an MFI of 2.0 g/10 min. Films with 10% mineral were extrude blown to form films with 50 μm thickness.

Figure 12 shows the UV/VIS spectra of the samples.

Feldspar showed a slightly higher transmission in the biologically active range of UV/VIS radiation for plant growth (400–700 nm) (Table 6).

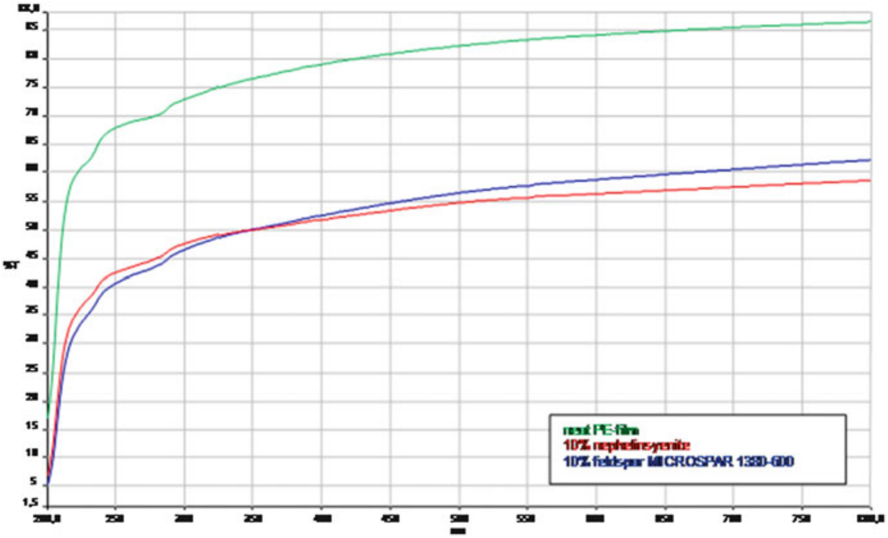


**Figure 12** UV/VIS spectra of polyethylene films for thermal management in greenhouses

**Table 6** Transmissions for different wavelengths of the UV/VIS spectrum of light for greenhouse films

| | UV/VIS transmission at wavelength | | | | |
|---|---|---|---|---|---|
| | 250 | 400 | 600 | 700 | 800 |
| Film | Nm | nm | nm | nm | nm |
| Neat PE film | 68.0 | 79.1 | 84.2 | 85.5 | 86.6 |
| PE film with 10% nepheline syenite | 42.4 | 51.6 | 56.2 | 57.4 | 58.5 |
| PE film with 10% feldspar | 40.7 | 52.6 | 58.9 | 60.6 | 62.3 |

IR spectra were recorded for the films and displayed in Figure 13.

Both minerals for thermal management show characteristic spectra in the region of 700–1400 cm$^{-1}$ (IR, heat radiation). Both are capable of retaining the warmth in the greenhouse, preventing too much cooling in comparison to a neat PE during the night.

Optical properties of greenhouse films have been assessed by transparency and haze measurement according to ASTM D1003 and gloss according to DIN 67530/ ASTM D2457. Table 7 shows the data.

In comparison with nepheline syenite, feldspar showed better optical performance by means of higher transparency, less haze, and more gloss of the films.

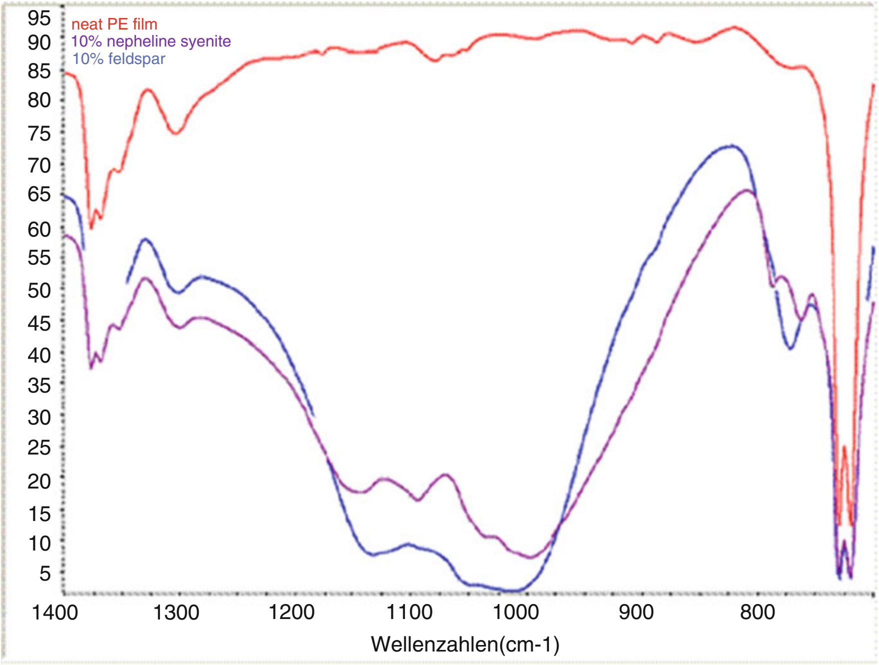


**Figure 13** IR spectra of polyethylene films for thermal management in greenhouses

**Table 7** Optical properties of greenhouse films

| Film | Gloss 60° | Haze | Transparency |
|---|---|---|---|
| Neat PE | 69 | 12.7 | 92.1 |
| PE film with 10% nepheline syenite | 26 | 51.2 | 90.7 |
| PE film with 10% feldspar | 27 | 45.3 | 91.0 |

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# Sustainable and Recycled Particulate Fillers 22

Roger Rothon

## Contents

**Abstract**

Environmental issues, such as life cycle impact and sustainability, are becoming important concerns for most industrial activities. Because of their scale of operation, composite materials are particularly affected, and this is filtering down to their major components, such as fillers.

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In defense of using fillers at all, it has been shown that at least in some cases, replacing part of a synthetic polymer by fillers can reduce the environmental impact of a composite. While this is true, more could be done, and the main thrusts are for recycling and the use of renewables. The industry recognizes this; but, despite significant commercial activity, there are difficult obstacles to overcome and only limited success has been achieved so far. Recovery and recycling of fillers themselves is hampered by the low cost of many virgin products and has made little headway. Recycling of waste products from other industries has also made little progress, often due to competition from more valuable alternative applications for the wastes.

More progress has been made where the composite itself is recycled, examples being talc/polyolefin composites in automotive applications. This is much harder to accomplish in cross-linked polymers (thermosets and elastomers), which are inherently more difficult to recycle. The majority of fillers are currently from nonrenewable (although often vast) mineral resources. The exceptions are natural fibers, such as wood, cotton, and flax, and these are considered to be more sustainable.

Despite much effort from the tire companies on products such as starch, renewable particulate fillers have so far made little progress. It has, however, been demonstrated that carbon black can be made from biomass rather than petroleum oil, and this may develop as a significant commercial option in the future.

Despite the difficulties, pressure on the major volume products is only going to increase and we can expect more recycling and use of renewables in the future. This will mainly be in large volume products used in applications such as vehicles.

**Keywords**

Fillers • Recycling • Sustainability • Glass • Calcium carbonate • Carbon black • Talc • Wood flour • Starch • Lignin • Surface modifiers • Granulation • Pyrolysis • Devulcanization

## Introduction

Filler and especially composite manufacturers increasingly have to take environmental matters, such as recycling, sustainability, and life cycle impact into consideration, and these pressures are expected to increase in future. In recent years, the advanced economies have become very much based on linear economics of “extract-make-consume-discard.” But increasing industrialization, affluence, and population are making this model untenable in the medium to long term. Estimates for when we start to run out of resources vary, but all agree that it is fast becoming imperative to find alternative economic models and to use materials more efficiently. We are thus seeing more emphasis on sustainability and especially recycling. This is increasingly being backed up by regulations, such as restrictions on landfill and on the recycling of the components of some major products, such as automobiles (e.g., in the EU, the End of Life Vehicle Directive requires that a minimum of 95% of a vehicles weight must be reused or recycled). Some major customers and retailers such as Wal-Mart Stores Inc. also aggressively apply sustainability scorecards to their sourcing and purchasing processes.

The composite industries are very significant consumers of raw materials (much of it currently nonrenewable) and also large waste generators and so are under considerable scrutiny. This has a knock-on effect on widely used additives such as particulate fillers. It is estimated that over 25 million tons of particulate fillers are currently consumed in polymer applications worldwide. Accurate figures do not exist, but well under 10% of this is currently reused in polymer applications.

Present approaches to this are currently fragmented and still developing, but the main trends in both sustainable resourcing and recycling are discussed here. It should be noted that much of the published information is from trade journals and conferences but not from peer-reviewed publications.

## Definitions

Sustainability and recycling are becoming of increasing importance in all areas of human activity which involve materials use. They are also areas where definitions are very important, especially when regulations and commercial claims are involved. This is still a developing area; but the following terms are used in this article.

### Linear and Circular Economies

The economic model prevailing since the industrial revolution has been one that is described as a linear model, based on “extract-make-consume-discard.” The alternative circular model aims to decouple economic growth from the use of natural resources and ecosystems by using them more efficiently.

### Sustainability

Sustainable development is defined (by the United Nations initially and now adopted by most nations) as “development which meets the needs of current generations, without compromising the ability of future generations to meet their own needs.” It is linked with renewability which is defined later.

### Renewability

Renewability is defined as “any material or energy that can be replenished in full without loss or degradation in quality.” Biological as opposed to mineral and fossil raw material sources are preferred in the circular model, as they are seen as renewable

**Table 1** The main levels of recycling that are generally recognized

| ASTM D7209-06 | Equivalent ISO 15270 | Other terms |
|---|---|---|
| Primary recycling | Mechanical recycling | Closed loop recycling |
| Secondary recycling | Mechanical recycling | Downgrading, open loop recycling |
| Tertiary recycling | Chemical recycling | Feedstock recycling |
| Quaternary recycling | Energy recovery | Valorization |

and thus not finite. This simple definition is, however, coming under criticism. Plant sources are themselves finite and have many alternative uses, particularly for food production. Even where they do not directly compete, plants used for materials production occupy land which could often have been used for food crops. Finally there is a loss of biodiversity and habitat when land is cleared for their growth.

## Recycling

Recycling is a broad term for the process of reclaiming materials from used products or from materials used in their manufacture and using them in the manufacturing of new products. Many products are now marked with a variety of recycling symbols, which are meant to help consumers and waste managers in separating recycled products and materials. Not all materials and products can be recycled, however. Those designed for disassembly or made from one material are the easiest. Even when used materials and products are recycled, often there is no economically viable market for these materials, and they are either disposed of with other waste or stored in warehouses for future uses. In an extreme example, we are now witnessing mining of old waste tips.

The following definition of recycling is from the European Union Waste Framework Directive (Directive 2008/98/EC on waste). “Any waste recovery operation by which waste materials are reprocessed into products, materials or substances whether for the original or other purposes. It does not include energy recovery or reprocessing into materials that are to be used as fuels or for backfilling operations.”

Various levels of recycling are recognized as set out in Table 1. It should be noted that quaternary recycling is outside of the EU definition (Table 1).

Closed loop recycling is the process of utilizing a recycled product in the manufacturing of a similar product or the remanufacturing of the same product. Ideally, this process can be repeated indefinitely.

Open loop recycling is the conversion of material from one or more products into a new product, involving a change in the inherent properties of the material itself (often with degradation in quality), for example, recycling plastic bottles into plastic drainage pipes. This is often called down-cycling or reprocessing.

For the purpose of this report, we regard the end application to be as a particulate filler, which may be recycled from the same use, or up or down-cycled from other uses. We do not include up or down-cycling of fillers to nonfiller uses.

## Sustainability (Renewability) Issues

There are three aspects to this: does the use of fillers generally improve the sustainability of composites? Can fillers be made from renewable raw materials? and Can recycling improve sustainability?

## Effect of Particulate Fillers on Composite Sustainability

It can be argued that while not renewable, common minerals are available in abundance and thus depletion is not an immediate concern. Sustainability to date has therefore focussed mainly on limiting the environmental impact of their extraction. This includes reducing the water and power used, responsibly treating any waste, and most importantly remediation of sites once extraction is over. The main filler companies are, by and large, very responsible about this today.

In addition, it is also argued that replacing part of the oil-based polymers in a composite by minerals significantly reduces the environmental impact of the product. There are several studies to support this contention. As an example, thermoplastics compounder Heritage Plastics Inc. has published a detailed study into the processing and environmental benefits of using calcium carbonate as a filler in high-density polyethylene film (http://www.heritage-plastics.com/en/sustainability.htm).

Heritage claims that independent research confirms that use of the filler in HDPE film reduces petrochemical and energy usage during the manufacturing process and minimizes the carbon footprint and greenhouse gas impact of finished plastic products. The life cycle analysis study was carried out by Boustead Consulting & Associates LLC. The study compared the energy consumption and environmental impacts of using 100% pure polyethylene resin compared to displacing 20% of the PE resin with its Heritage's HM10 additive, in both prefilm plastic pellet production and in film production scenarios. Boustead based its calculations on a database built over 25 years, and the LCA considered both the manufacturing process of Heritage's additive and its use in HDPE film production.

Some of the test findings, assuming the displacement of about 20% of the petrochemical-based components in film with the HM10 additive, are given below:

- 15–20% overall energy savings
- 16–20% reductions in the use of crude oil
- 15–19% reductions in the use of natural gas
- 12–17% reductions in the use of coal
- 12–16% reductions in the use of electricity
- 13–17% reductions of greenhouse gasses
- 15–20% reductions of oxides of sulfur
- 13–17% reductions of oxides of nitrogen
- 11–15% reductions of particulates

Heritage said that producing one ton of its HM10 concentrate uses 72% less energy than producing one ton of HDPE. (Note that because of the difference in specific gravity, more than one ton of concentrate is needed to replace one ton of HDPE, but there is still a significant saving.) It further claims that replacing 20% of the HDPE in film with the additive reduces the amount of electrical energy needed to convert the film by 23%.

## Sustainable Sourcing

To be more sustainable, fillers need to be derived from natural, growing products. But while there is already considerable use of natural fibers such as wood, cellulose, hemp, silk, and rayon, there is virtually no commercial use of natural product-derived particulates at present, apart from wood flour. The main activities to date are summarized below, and more information can be found in ► Chaps. 16, “Fillers from Organic Sources” and ► 23, “Nanofillers”.

### Polysaccharides

Polysaccharides can be sustainably sourced and are potentially available in large quantities. The main polysaccharides of interest have been and remain starch and cellulose. These are briefly discussed here and more information can be found in ► Chaps. 16, “Fillers from Organic Sources” and ► 23, “Nanofillers”.

#### Starch

In the past, there was considerable interest in starch-derived products for use in tire applications, with Goodyear leading the way starting as long ago as 1997, when they had a patent (US 5,672,639) to a starch reinforced rubber composition and tire. In this work, the filler was a plasticized form of starch, with the plasticizer being necessary to soften the starch granules and allow dispersion into the rubber. Shortly later, it was reported that Novamont, working in conjunction with Goodyear, had developed a nanoparticle-sized, corn-derived starch product that significantly reduced the rolling resistance of tires compared to the use of precipitated silica, and this was reported to be used in Goodyear’s GT3 tire. This tire is still marketed and is described as an ecological tire for city cars which uses some materials derived from corn-starch to replace petroleum oil derivatives; it does not now specifically mention that these corn-starch products are fillers. The development work for this tire application was the subject of a European Union research grant, and the details can be found in “Bio Tyre Project, Layman’s Report, LIFE06ENV/L/000118, http://ec.europe.com). More details on nano-starch fillers can be found in ► Chap. 23, “Nanofillers” and in Lin et al. (2011).

#### Cellulose

More recently, other polysaccharides in abundant supply have become of interest, notably cellulose. Micro- and more recently nano-crystalline cellulose has been rumored as being studied for tire applications, but few details are available. Micro-crystalline cellulose consists of bundles of very small fibers (fibrils). The best properties are from nano-crystalline cellulose where the fibrils have been separated from the bundles, but considerable energy is required to carry out the delamination. (See ▶ Chap. 23, "Nanofillers" for more on nano-cellulose, also Mariano et al. (2014).)

One of the problems with plant-based cellulose technologies is the need to disrupt cell walls to access the cellulose and then to separate this from the rest of the plant matter. In what may prove to be a breakout development, the University of Austin, in Texas, USA, has recently announced the development of a route that starts from a blue-green algae (a genetically engineered cyano-bacteria). This offers the prospect of a much more efficient and environmentally sound process than those starting from cellulose-containing plants such as wood.

### Lignin

A very recent patent to Goodyear Tire and Rubber (US 8664305) indicates that they may be following a new path in what might eventually lead to a new tire filler technology. This patent describes the functionalization of the surface of lignin, especially using esterification or silylation and proceeding through lignin sulfonate. It is claimed that the so modified lignin can be used as a reinforcing filler for rubber, where it can replace precipitated silica. Lignin is also being studied as filler for use in thermoplastics (Mainka et al. 2015).

### Wood Flour

This is the most widely used particulate filler of plant origin used today. It is discussed in detail in ▶ Chap. 16, "Fillers from Organic Sources" and only treated in outline here (Clemons 2010).

### General

Wood flour is a fairly fine particulate powder and was one of the first fillers to be used commercially in polymer applications, being an important component of Bakelite, a phenol-formaldehyde composite, first produced over 100 years ago and still in use today. While made from a fibrous material, the fibers in wood flour are relatively short (aspect ratio below 5).

Wood flour is usually made from scrap wood sources and can thus be regarded as recycled as well as being sustainable. Its properties dictate that it cannot be regarded as a substitute for common mineral particulate fillers and must find applications of its own.

Wood flour is a very variable material, with a variety of wood sources and types being used to make it. The main steps in production are purification, size reduction, and classification. Size reduction can be accomplished in a variety of ways including hammer mills, chippers, rollers, or attritors. The methods used will depend on the source material, especially its initial size. Classification can be achieved by standard methods such as screens or by using air classification. Some drying is also often necessary, although, for practical reasons, wood flour is usually shipped with some moisture.

The chemical composition of wood flour is complex. The main components are cellulose, hemi-cellulose, and lignin. There will also be some extractables such as oils and inorganic ash. The exact ratio of these major components and the nature of the minor ones will vary with the wood type. Typical values are:

| | |
|---|---|
| Cellulose | 37–45% w/w |
| Hemicellulose | 19–30% w/w |
| Lignin | 21–34% w/w |
| Extractables | 2–5% w/w |
| Ash | <0.7% w/w |

### Applications

The applications for wood flour are dictated by a number of important properties. On the positive side, as well as being regarded as sustainable, it is lower in density and gives some reinforcement, although not as much as wood fibers.

There are significant limitations though.

- Color: It can only be used for dark colored products and can show color fade on outdoor exposure.
- Thermal stability: This limits processing temperatures to about 200 °C, unless special precautions are taken.
- Moisture content: It will rapidly pick up moisture from the atmosphere when dry and so must be processed immediately after drying in applications where moisture would affect processing.
- Flammability: It is flammable which creates some hazards in transportation, storage, and processing, and it can also decrease the fire rating of the host polymer.
- Weathering: Water absorption, swelling, and discoloration can be issues.
- Durability: Biological attack including mold and fungal effects can occur unless additives are used to prevent it.

These problems are least important in thermoset applications, explaining the early use of this material in such polymers. The processing temperatures are low and the moisture present can be tolerated in many instances. They are far more important in thermoplastic applications.

Despite this, the main application today, and one that has seen rapid growth, is in what are known as wood polymer composites. These are combinations of wood flour in thermoplastic matrices, predominately polyethylene, but also using polypropylene and rigid PVC. About 80% of this market is in outdoor products particularly decking. This market is most developed in North America, but is gaining acceptance elsewhere. Most applications use reclaimed polymer as well, further increasing their green image. Some manufacturers also include finely ground tire rubber, which helps with sound absorption properties. Estimates for the size of the market vary, but most agree that several hundred thousand tons of composite are used, with wood flour contents from 40% to 65% w/w.

In theory, wood polymer composites are themselves recyclable, although there are significant problems to doing this on an industrial scale. Some are those related to collection and variability common to nearly all recycling operations. The others are due to deterioration of both the polymer and wood flour during processing and also use in an outdoor environment. These include molecular weight degradation of the polymer and oxidative, light and weather degradation of the wood. Despite this, it appears that these issues can be overcome sufficiently by careful processing and addition of stabilizers, to allow some incorporation into new product.

### Rice Hull Ash

Rice hulls or husks are the outer coating on rice grains and provide protection to the seeds during the growing period. They contain large amounts of amorphous silica and lignin and are not very digestible for humans. As a result, the hulls are usually removed when rice is harvested. The hulls are usually burnt as a source of energy and leave behind an ash known as RHA (rice hull ash), which is largely silica.

This is a very significant waste stream, estimated at over three million tons of silica worldwide. Moreover, it can be regarded as sustainable due to the plant origin. As such, it has been much studied as a raw material for many applications, including as polymer filler.

Recovering the silica in a suitable form for direct polymer applications is not easy and requires careful pyrolysis, which results in the retention of some carbon (see ▶ Chap. 16, “Fillers from Organic Sources” for more details). This led to attempts in the USA to commercialize it as a substitute for some carbon blacks in the 1970s (Haxo and Mehta 1975), but these did not succeed. Research has continued however, and the use of rice hull ash in polymers was reviewed by D.S. Chaudhary et al. (2004), while R. Srilathakutty et al. described the successful use in microcellular shoe soles (2002). More recently E.P. Aysawarya et al. (2012) have described its potential for use in HDPE. One of the difficulties is that an alternative, relatively high value, use in cement products has emerged as a competitor and the ash cannot now always be regarded as a waste resource.

Some of the tire majors are also seeing it as a useful raw material for use in the manufacture of precipitated silica for tire use. This involves dissolution as sodium silicate and reprecipitating. The substitution of rice hull ash for sand or other crystalline silica normally used is claimed to reduce energy consumption, as lower temperatures can be employed. Ghosh and Bhattacherjee (2013) and Bhuiyan et al. (2011) also describe advantages of making precipitated silicas in this way.

### Carbon Blacks

Carbon blacks are widely used as fillers and pigments and are almost exclusively derived from nonsustainable sources, mainly fuel oils, today. Technically there is no reason that they could not be produced from more sustainable raw materials, such as vegetable oils, and there has already been some work along these lines for the tire industry; this may develop as a commercial option in the future. Another option for improving sustainability would be to produce carbon blacks from the oils obtained by end of life tire pyrolysis. It is also perfectly possible to produce carbon blacks from natural gas, and this process can coproduce hydrogen for use as a clean fuel. This approach is starting to be exploited commercially by companies such as Monolith Technologies (http://monolithmaterials.com).

### Use of Particulate Fillers to Improve Sustainability

In a breakout development, Imerys has shown that mineral fillers can be used as compatibalizing agents for mixed polymer recyclate. Based on this, they recently commercialized ImerPlast™, a compatibalized, mixed polymer compound consisting of recycled polyethylene and polypropylene resin and a mineral-based compatibalizing agent. (http://www.imerplast.com/)

According to the company, ImerPlast™ extends the number of useful applications for recycled plastic feedstock, allowing a higher recycling rate and increasing the number of uses for recycled polymers. They say that just 6 out of the 25 million tons of plastic waste generated in Europe are currently recycled. Material recycling facilities collect plastic waste and resell the easily sorted major fractions, such as bottles, to recyclers. The remainder, usually only sorted by density, is mixed polymer and often mixed color, which until now has had little value and few applications. While mixed polyolefins have been used for some time in certain injection molding applications, phase separation, especially in slow cooling applications, has been a barrier for their use in extrusion. This is because polypropylene and polyethylene are not miscible. If fed together into an extruder manufacturing products such as pipes, phase separation happens and breaks or holes can occur. ImerPlast™-engineered mineral overcomes phase separation and ensures stable production.

## Filler Recycling

Recycling is the ultimate way of improving sustainability but is proving to be hard to achieve.

### Types of Filler Recycling

Particulate fillers can be considered as being recycled in several ways.

- Conversion of end of life, or off-specification, products from other applications into particulate fillers. Glass powders from end of life containers or glass fiber are good examples.
- As a powder recovered from, and returned to, a polymer application. Pyrolysis carbon blacks are a good example of this.

**Table 2** The main particulate fillers in use and their estimated global consumption: (all polymer types)

| Filler | Approximate world consumption (tons) | Issues to be considered with finding substitutes |
|---|---|---|
| Ground natural carbonates | 11,000,000 | Low cost and relatively low hardness |
| Carbon black | 10,000,000 | Very small size and controlled shape |
| Kaolin | 1,400,000 | Low cost and platy in shape |
| Talc | 800,000 | Very soft and platy in shape |
| Precipitated silica | 800,000 | Very small size and controlled shape |
| Aluminum hydroxide | 725,000 | Flame retardant properties required |

- As part of a filled system that is being recycled. Carbon black in crumb rubber recyclate and carbonates in PVC are good examples of this.

## Advantages and Limitations

While recycling of fillers sounds to be sensible and straightforward, there are many hurdles to be overcome if it is to be a commercial success and this is why it is still in its infancy today.

First we must consider availability, security, and consistency of supply. These can all be serious problems for waste and by-product materials. The principal fillers used in volume applications (greater than 500,000 tons worldwide) are presented in Table 2. They all have specific characteristics which make them difficult to substitute by other powders and the main sources of recycled powders that might be used as fillers do not fit these requirements very well. As an example, most by-product powders (glass, fly ash, rice husks) have high hardness, while polymer-processing equipment for most of the bulk fillers (carbonates, talc ) is designed around their relatively low hardness and would not be suitable. As a result, we currently see little up or down-cycling of other products into filler applications, with the main emphasis being on recycling of existing fillers.

Next is cost. Many of the bulk particulate fillers are relatively low in cost. The raw materials are essentially free, and the production costs are those involved in extraction, beneficiation (purification), and size modification. These costs are not dissimilar to that for an equivalent recyclate which must bear collection, separation, purification, and possibly size reduction costs. As a result, they can be similar to or even higher in price than the virgin product.

Finally, one must consider competition from alternative uses for the powder. This is particularly felt with many silica waste powders, which often find more lucrative applications in areas such as cement, for instance.

## Main Sources for Recycled Powders from Other Areas Potentially Useful for Filler Applications

### Glass

Glass of various types is widely available in recycled form and can be theoretically converted into powders for polymer filler use. The main limitations to its widespread adoption as a filler are due to water sensitivity of the commonest glass compositions and their relatively high hardness, which can cause unacceptable wear rates on conventional equipment designed for use with other fillers.

Glass is a mixture of various oxides, of which the principle one is silicon dioxide. There are a number of different compositions in bulk use; the main ones being:

- Commercial glass (soda-lime glass)
- Borosilicate glass
- Glass fiber
- Lead glass

#### Commercial Glass (Soda-Lime Glass)

This is the most common glass form and is used in bottles and jars and flat glass for windows. The main constituent of commercial glass is sand. While sand by itself can be fused to produce glass, this requires high temperatures (about 1,700 °C) and other ingredients are added to lower this.

The principal additive is sodium carbonate ($Na_2CO_3$), known as soda ash, but this would on its own make the glass too soluble and so other oxides such as calcium and magnesium are also added (usually in the form of limestone).

Most commercial soda-lime glasses have roughly similar chemical compositions of:

70–74% $SiO_2$ (silica) 12–16% $Na_2O$ (sodium oxide) 5–11% CaO (calcium oxide) 1–3% MgO (magnesium oxide) 1–3% $Al_2O_3$ (aluminum oxide)

#### Borosilicate Glass (Also Known as Pyrex)

Borosilicate glass (or sodium borosilicate glass) is made mainly of silica (70–80%) and boric oxide (7–13%) with smaller amounts of the alkalis (sodium and potassium oxides) and aluminum oxide. This type of glass has excellent chemical durability and thermal shock resistance – meaning it does not break when changing temperature quickly. As a result of its special properties, sodium borosilicate glass is widely used for laboratory apparatus, pharmaceutical containers, high intensity lighting applications, and as glass fibers for textile and plastic reinforcement – as well as for common household oven and cookware. It is significantly more expensive than soda-lime glass.

### Glass Fiber

The composition of glass fiber varies with the application. Commercial (soda-lime) glass is used for building insulation and glass wool, while alumino-borosilicate glass with very low sodium oxide content is preferred for textiles and in reinforced plastics, because of its good chemical durability and high softening point.

### Lead Glass

Lead glass is made by using lead oxide instead of calcium oxide, and potassium oxide instead of all, or most of, the sodium oxide. The lead is not readily extractable from the silicate matrix. Lead glass has a high refractive index, making it sparkle brightly, and a relatively soft surface so that it is easy to decorate by grinding, cutting, and engraving, which makes it popular for drinking glasses, decanters, and other decorative objects. Lead glass is also used for radiation shielding and can be found in cathode ray tubes which are used, for example, in TV and monitors.

The type of glass is very important when making fine powders for polymer applications, as these often require particle sizes below 10 μm. Commercial (soda-lime) glass is difficult to prepare and use at such small size, largely due to the water sensitivity of the composition. This leads to caking under humid conditions and problems with wet grinding. Borosilicate and alumina borosilicate are much less soluble and so can be produced at such low sizes more readily.

The main potential sources of glass powder are.

1. Dust fractions of soda-lime glass collected during crushing operations: These are usually too fine to be used in the glass furnaces.
2. Borosilicate glass: This has too high a melting point for recycling through conventional furnaces.
3. Glass fibers: These can be ground down to be used as particulate fillers. These can be soda-lime or alumina borosilicate. Because of the solubility issues, the main interest is in alumina borosilicate powders.

Despite being widely available and relatively low cost, recycling of glass into polymer fillers is fairly limited. This is mainly due to its high abrasiveness, which makes use in many polymer-processing lines using softer fillers such as carbonates and talcs, impractical. The water sensitivity of soda-lime glass also makes it difficult to make and store at very small particle size.

## Power Station Ash

The burning of coal for electricity generation produces a residual ash consisting predominantly of the inorganic component of the coal. The ash is recovered in two ways: furnace bottom ash (FBA) and fly ash or pulverized fuel ash (PFA). As the name implies, FBA is recovered from the bottom of the furnace. Fly ash is much finer and is recovered from the furnace off-gasses, by, for example, electrostatic precipitation or bag filters. The composition and other properties of the ash vary with the type of coal used, the coal grind size, and the combustion conditions. The fly ash is the form of most interest for polymer applications. Two main types of particle can be recognized in fly ash. The largest amount is solid and known as precipitator ash. The second type is hollow and known as cenospheres. Due to their hollow structure, cenospheres have a much lower density.

Much attention has been focussed on finding polymer applications for the finer fly ash in the past. The particles are usually spherical in shape and typically range in size from 0.3 to 300 μm. Although the rapid cooling they experience means that they are predominately amorphous (a mixed silicate glass), they can still contain measurable amounts of crystalline material. Their mineralogy is very diverse, but common phases found include quartz, mullite, and iron oxides such as hematite and magnetite. A variety of toxic metals plus organics such as dioxins and polyaromatic hydrocarbons (PAHs) can also be present, although these are usually at low concentrations (e.g., less than 25 pg/g for dioxins and <0.9 μg/g for total PAHs). These concentrations are similar to those of sediments and soils found in the general environment. Toxic metal concentrations are comparable to those found in other mineral fillers (range 0 to 1,000 μg/g), and leaching tests have demonstrated that the mobility of these minor elements is generally low, because they are encapsulated in the glassy matrix.

The spherical nature, fine size, and chemical composition of fly ash make it attractive for use in cementitious applications, for example, type II additions in concrete. Historically, this has been the primary outlet but has become increasingly difficult to sustain, because new emission abatement technologies at the power stations have been introduced, which have led to an increase in the residual carbon content and a lower quality of fly ash. The spherical shape, particle size, and inertness also make the fly ash suitable for use in polymer applications, but this has been slow to develop for various reasons. There is reported to be some use of fly ash in carpet backing formulations (Universal Textile Technologies, universal-textile.com); however more recently, at least one industrial concern (RockTron Mineral Services) has revived interest in the area. Their approach is to treat the fly ash to physically separate some of the deleterious components, thereby improving the color and quality, as well as to clean the particle surfaces and finally to separate the alumina-silicate component into various size fractions. Part of the cost of the operation is met by realizing the added value of some of the separated materials. The purified products are then used for a range of Eco-Mineral Fillers (MinTron™).

The following is based on the company literature;

Substituting RockTron Eco-Mineral Fillers in product formulations offers many benefits depending on the application, such as:

- Increased output and lower energy consumption resulting in lower costs (evidence of 30–50% increase in throughput in HDPE extrusion application, where it is common to see extruder screw motor power reduced on addition of MinTron™ in PP and PVC)

- Density reduction (MinTron™ density is 2.2–2.3 compared to 2.4–2.8 for most other mineral fillers)
- Improved flow characteristics (low aspect ratio, tendency of spheres to roll, and not interlock)
- Low shrinkage (no flow induced orientation and uniform shrinkage, evidence of benefit in reducing differential shrinkage in a complex PP injection molded part)
- Improved stress distribution (spheres have good dimensional stability, thereby uniformly distribute stress)
- Low oil (resin) absorption (typically 20–30 ml oil 100 g MinTron™)
- Increased impact strength (less effect on impact properties compared to equivalent loadings of other mineral fillers)
- Good chemical resistance (glassy matrix is inert and resistant to most solvents)
- Higher abrasion resistance (evidence from applications testing in industrial floor coatings)
- Improved thermal properties (lower heat capacity than other mineral fillers, improved heat deflection temperatures)
- Improved mechanical properties (tensile and flexural properties have been seen to improve in PP and PA6 composites)

Since 2011 RockTron Mineral Services has been selling their MinTron™7 product as a substitute for man-made glass spheres for use in fiber reinforced polyamide (PA) composites and has been developing highly filled (50–80%) master batches for use in PP, PVC, HDPE, and PA composites. They have also had some success in other application areas such as elastomers, coatings, and thermosets.

Other companies actively promoting fly ash in polymer filler applications include Revolutionary Plastics LLC in North America, Boral in Australia (see http://www.boral.com.au), and Ash Resources in South Africa (see Plasfill™, http://ashresources.co.za). There has also been extensive academic research carried out around the world investigating the use of fly ash in various polymer systems.

The low density of the hollow cenospheres makes them attractive for a number of polymer applications. They are usually “harvested” or scooped up from ash ponds when wet disposal methods are used. The wet cenospheres are then dried, processed to specifications, and packaged.

Cenospheres are available from a number of companies globally and generally have particle sizes in the range 5–500 μm, and specific gravities are typically 0.6–0.9. Most of the particles are complete hollow spheres, but some can have openings in the wall. The gas in the whole ones is a mixture of carbon dioxide and nitrogen, resulting from trapping of the furnace gasses. They are much sought after for a variety of applications, including, but not restricted to, polymers. Production is limited and thus they are in tight supply and relatively highly priced.

The main polymer uses of cenospheres are for lightweighting, shrinkage control, and thermal and acoustic insulating properties. While fairly robust, they are most suited to polymer processing where shear and compressive forces are relatively modest.

### Rice Hull Ash

This has already been discussed in the sustainable fillers section “Wood Flour.”

### Spent Oil Refinery Catalysts

Zeolite-based fluid bed cracking catalysts used in petroleum refining are a significant waste product (estimated at over 300,000 tons per annum worldwide). They have been reported as having potential for use as a synergistic component of intumescent flame retardant formulations for use in polymer systems (L.R. Demoura Estevao et al. 2005).

### Precipitated Silica from Geothermal Power Plants

Geothermal energy generation is a well-established global technology, which is expected to increase significantly over the next decade. The water from the wells can contain significant amounts of dissolved silica, which causes operational problems. There are various ways of controlling this, but one way, which is starting to attract interest, is to remove the silica, either as a concentrated dispersion or as a precipitate. The quantities involved are large; for instance, it is estimated that the amount of silica that precipitates out of geothermal waste water in Iceland amounts to over 40,000 tons annually. One potential use for the precipitate is as an alternative to conventional precipitated silica used in polymer and coating applications. At least two companies are already working on commercial scale recovery and use of this silica (see www.geosilica.com and www.environmetals.co.nz).

### Silica Fume (Microsilica) (CAS Number 69012-64-2, EINECS Number 273-761-1)

This is yet another source of by-product silica and is an amorphous, submicron, powder arising from silicon and ferrosilicon alloy production. Silica Fume consists of spherical particles with an average particle diameter of 150 nm. Despite the name, it should not be confused with fumed silica, which is a totally different type of silica of much smaller size.

There has been some interesting industrial work on the use of silica fume as a polymer filler. However, this has not really progressed commercially, due to limited availability and the emergence of relatively high value uses as a specialty cement additive. Indeed, this highlights one of the problems faced in the search for recycled fillers. The value in use often cannot compete with alternative nonfiller applications.

## Recovery and Recycling of Particulate Fillers from Polymer Composites

There are two aspects to this: recovery and recycling of the filler itself, or recovery and recycling of the filled composite.

Where the filled polymer itself can be recycled, then this is preferable to separating it from the polymer first. This applies mainly to thermoplastic composites, where nearly all filler recycling is carried out in this way. This type of recycling is discussed in section “Recycling in the Form of a Filled Polymer.”

The situation is different for cross-linked polymers (thermosets and elastomers) which are not so readily reprocessable, and this is where efforts on recovery and recycling of fillers themselves are concentrated today. These efforts are largely focussed on carbon black and, to a much lesser extent, on calcium carbonate.

### Recovery of Carbon Black

Carbon blacks are one of the main particulate fillers in use and also relatively expensive. This leads to both pressures to recycle and an economic incentive to do so. Elastomer applications consume about 90% of all carbon black production with tires making up over 70% of this sector. Most of the attention has thus been on recycling of carbon black used in elastomer applications, especially tires. This has been assisted in some regions (notably the European Union) by the banning of tires from going to landfill. There is also an advantage here from the fact that tires and some other elastomer wastes are already collected and segregated. Because of the large quantities used, recovery and recycling of carbon blacks is receiving much attention, with end of life tires (ELTs) providing a large and readily available source, with high levels of carbon black. The cross-linked nature of rubber makes direct recycling difficult due to cross-linking (but not impossible, see section "Carbon Black Recycling in Elastomer Compounds") and so recovery and recycling of the filler itself is receiving a great deal of attention.

Removal of the rubber from ELTs using pyrolysis is the most investigated process, and a number of commercial pyrolysis processes have been developed. These processes involve heating in the absence of air and can be used to break down organic matter into volatile products, allowing the fillers to be recovered for reuse. They are seen by some as the best way of closed loop recycling for tires. The following description is based on tire pyrolysis, but can be applied with slight modification to other sources of filled elastomers.

Pyrolysis is usually applied to tires after the steel and textiles have been removed by shredding. The steel can be recycled. Carefully controlled heating is then used to convert the rubber into gaseous and liquid fractions which are swept out of the reactor, leaving behind an ash. Some processes use added catalysts to help the breakdown processes (usually some form of active clay). The ash is mainly reinforcing filler (carbon black and/or precipitated silica) together with carbonaceous residues from the breakdown of the rubber and other organic content and various minor inorganics such as zinc oxide from the cure system together with catalyst residues where these have been used.

The energy for the pyrolysis process can be obtained by burning some of the gaseous fraction. The rest of the pyrolysis oil can be used for a variety of purposes, including energy generation.

Currently the ash, which is referred to as pyrolysis carbon black (pCB), is the most valuable product; and the economics of the operation depend on maximizing income from this source

**Table 3** Typical properties of commercial pyrolysis carbon blacks (From Norris and Bennett 2014)

| Property | Range | Comments |
|---|---|---|
| Surface area $m^2/g$ | 59–93 | Reinforcing carbon blacks 60–110. Semireinforcing 60–90 |
| Oil absorption (crushed) ml/100 g | 76–84 | Reinforcing carbon blacks 70–140. Semireinforcing 30–45 |
| Ash% | 12–36 | Main component silica, others included zinc oxide, sulfur, iron, and aluminum. Traditional carbon blacks below 1% |

### Properties of Typical Pyrolysis Blacks

Carbon blacks are complex materials with a larger number of important characteristics than most other fillers. These include particle size, specific surface area, “structure” as measured by oil absorption, surface chemistry, and presence of impurities, especially larger sized grit.

There are also a large number of different grades, each optimized for a particular application. Various nomenclatures are used to describe carbon black fillers, of which ASTM D1765-14 is the most important today. Tires use a variety of carbon black types, depending on the tire part involved. The main types are the higher specific area, highly reinforcing types with ASTM numbers 399 and below. Often referred to as high or super abrasion furnace blacks, they are found especially in tire treads, where the highest reinforcement is required. Carbon blacks with ASTM numbers above 500 (Fast extrusion furnace, general purpose furnace, and semireinforcing furnace) are the other main type, mainly used in carcass and inner liner applications. The properties of the pyrolysis blacks vary with the rubber source and pyrolysis conditions, but do not currently equal those of the virgin carbon blacks present, even when tread rubber containing the most reinforcing types is used in their production.

Most manufacturers’ literature is fairly vague but usually gives specific surface area and oil absorption values which suggest that they are similar to the less reinforcing ASTM 500 and above blacks. An independent laboratory, ARTIS www.artis.uk.com, have published more informative data (Norris and Bennett 2014). According to their independent analysis, these claims may be optimistic. They analyzed five commercially available pCBs from different producers, with the results shown in Table 3.

They also tested them against a range of carbon blacks in an SBR elastomer compound. They found that the dispersion was invariably poorer for the pCBs and that the property levels obtained were closer to the weakly reinforcing N700 blacks than to the N500 series usually claimed. Given the more promising surface area and oil absorption numbers reported above, this is probably due to the high ash content and poor dispersion.

## Current and Future Applications for Pyrolysis Blacks

The large quantities involved and the present use of nonrenewables in their generation mean that there is a great incentive to recycle carbon blacks and this pressure is expected to intensify.

Unfortunately, the present discrepancy in properties between the pyrolysis blacks and the tire grades means that they can presently only be recycled at fairly low levels and into the least demanding tire parts, such as carcass and inner liner. This is unlikely to change much in the immediate future, although it is fairly new technology and improvements are steadily being made. Currently they are more suited to some general rubber goods applications, where they do not require such levels of reinforcement, and this is already happening to a limited extent. They can also be used to replace pigment blacks in some applications.

Significant property improvements are needed to make these products serious contenders for the larger volume tire and general rubber goods applications, however. In addition to improving the surface area and oil absorption properties, the questions of the ash content and dispersion difficulties also need resolving.

The present ash levels are much higher (more than an order of magnitude) than those of conventional blacks. In fairness, a significant amount of the ash is silica filler and zinc oxide which are common rubber ingredients anyway, but they dilute the effect of the black. Others may actually be detrimental. In theory, it should not be too difficult to reduce the ash content very significantly, but this will have cost implications. Most studies show poorer dispersion of pyrolysis blacks, and this may be part of the reason for the relatively low reinforcement observed. The dispersion issues are probably mainly due to carbonaceous material from the polymer degradation and may possibly be improved by developments in pyrolysis conditions. Better milling of the product is also said to be showing promise.

Probably the biggest threat to the pyrolysis black industry will come from the efforts on recycling filled rubber discussed in section “Carbon Black Recycling in Elastomer Compounds.”

## Calcium Carbonate Recovery and Recycling

While the main route for recycling calcium carbonate is in the form of filled thermoplastics, such as PVC; large quantities are used in applications where the polymer matrix is not easily recycled. Latex carpet backing is one such application. This is usually an SBR latex polymer with high filler levels (mainly calcium carbonate but often with other fillers, especially aluminum hydroxide). Being cross-linked, the polymer is not readily recycled. There is a significant incentive to use recycled materials in products such as carpets in order to meet various legislative and certification levels around the world. In response to this, some work has gone into filler recovery and reuse from carpet backing. One of the leaders in this is Polar Minerals in the USA. (http://polarmat.com/). They offer powders made from latex-based recycled carpet backing, blended with new filler, and claim that they make an excellent filler for new carpet backing, while allowing high levels of recycling certification to be achieved (e.g., NSF 140 Platinum Level). The fillers are recovered from the polymer backing by mechanical methods. An alternative approach using recyclable polymer in place of the SBR is described in the next section.

## Recycling in the Form of a Filled Polymer

This is the main form of filler recycling in operation today and is likely to remain the preferred option where the polymer itself is readily recycled. Why go to the trouble and expense of separating the filler, only to have to reintroduce it later?

The main fillers recycled in this way are carbon black (in elastomer compounds), talcs (in polyolefins), and carbonates (in PVC compounds).

### Carbon Black Recycling in Elastomer Compounds

The recycling of the fillers themselves has been discussed earlier. This section deals with the case where the rubber compound containing the carbon black is recycled.

The global tire industry currently produces over 1.5 billion tires each year, containing over seven million tons of carbon black fillers, and the global demand is expected to grow at a rate of 4.1–4.5% (CAGR) over the period 2012–2019, largely driven by growth of demand in the BRIC economies plus Eastern Europe. There is thus great incentive to recycle end of life tires, especially closed loop recycling.

The main problem for tires and also rubber in general is its cross-linked nature; unlike thermoplastics, most rubbers cannot be reprocessed in the same way as the virgin material unless the cross-links are broken, and this is a difficult process. Despite this, rubber recycling by devulcanization is being actively pursued as well as by the simpler method of size reduction. The various approaches being pursued for tires are briefly described below. The same processes can be easily adapted to other carbon black-containing elastomeric products.

### Granulation

Three grinding methods can be used for turning the waste rubber into a fine powder: ambient grinding, cryo-genic grinding, and water grinding. In most instances, it is necessary to first remove steel and fabric by shredding. The recovered steel has a ready market and is seen as fully recyclable. The fabric usually goes to lower grade uses.

For returning to tire applications, it is necessary to select the rubber source to meet the final use, with tread rubber, especially truck tread rubber (which contains more natural rubber than that used in automotive tires) being the premium product. Some form of sieving is usually also required to produce different particle size grades.

Currently these powders can only be added to tire compounds at a few percentage if the properties are to be maintained. Better results can be achieved if the rubber powder is surface activated and this can be accomplished by chemical treatment (e.g., chlorine of fluorine) or physical methods (e.g., plasma). This activation improves interaction with the virgin polymer and improves properties, allowing higher loadings. Most of the rubber powder recovered by granulation goes into lower level rubber applications or nonrubber ones.

### Devulcanization

This process is aimed at reconverting rubber compounds to their precure state, ready for reuse. This means breaking the sulfur cross-links introduced during curing, without significantly breaking the carbon to carbon bonds in the polymer chains. Although there are a number of cross-link systems used in rubber, most rubber (virtually all that used by the tire industry) is sulfur cross-linked and contains monosulfidic, di-sulfidic, and polysulfidic links. All of these have to be treated, while maintaining as many of the carbon to carbon bonds as possible (to minimize chain length reduction and loss of properties).

Four approaches can be used to preferentially break the bonds: chemical, mechanical, thermal, and biochemical. These are sometimes used in combination. The mechanical and thermal methods rely on the cross-links being weaker than the carbon to carbon ones. The chemical method uses selective reagents to target the sulfur containing bonds. These chemicals are usually amine/thiol mixtures or diaryl disulfides. There are also biological processes which use specific microbiological agents. Two levels of devulcanization can also be recognized, completely throughout the solid mass or just at the surface. The latter is much easier and less costly to achieve and approaches the bulk method if submicron powder is used.

Michelin, one of the tire majors, recently announced that they were participating in a project to be known as TREC Regeneration. This will test the technical and economic feasibility of using granulation, micronization, and selective biochemical devulcanization for recycling tire rubber. The project will include the company Proteus (a member of the PCAS group) and SDTech. Proteus is a biotechnology company who specialized in the design, development, and implementation of industrial processes using enzymes and microbial strains. SDTech is an industrial company specializing in micronization and treatment of ultrafine powders. The TREC project has an 8-year timetable, indicating how long it may be before commercial results can be expected from this type of process.

## Carbonate Filler Recycling in PVC

There are two main forms of PVC in use; unplasticized or rigid (uPVC) and plasticized. Both forms of PVC are used in large quantities and usually contain significant filler levels. PVC is a problem waste as, unlike other bulk plastic, it is not suitable for incineration. Indeed, under UK legislation if any waste being incinerated contains 1% or more PVC, then the waste gasses have to be treated to prevent release of highly toxic dioxins. Hence, recycling is very popular for PVC.

Both forms of PVC make extensive use of fillers, mainly carbonates and aluminum hydroxide flame retardant (the latter mainly for the plasticized form of PVC).

Most progress has been made in closed loop recycling of rigid PVC, mainly from buildings (e.g., window frames and cladding). This is achieved by removal of contaminants (metals, rubber, etc.) and reduction to a powder that can be processed like the original. This procedure automatically recycles the filler.

While recycling of plasticized PVC is also widespread, this is usually downcycled from applications such as cable insulation and flooring into lower value ones, such as traffic calming products (e.g., road cones).

There are also very efficient, but costly, processes for recovery of the PVC content, using solvents (e.g., www.vinyloop.com). This may also allow recovery and reuse of the fillers. There are currently only two commercial plants operating in Europe (France and Italy).

### Carbonate Recycling in Polyvinyl butyral (PVB) Carpet Backing

At least one company (www.tandus-centiva.com) has developed a fully recyclable, filled backing, based on the thermoplastic polymer PVB. This polymer is sourced from the recovered interlayer in safety glass such as postconsumer vehicle windscreens, further adding to the eco-credentials. The high filler loading (a mix of calcium carbonates and aluminum hydroxide) is automatically recycled in this product.

### Talc Recycling in Polyolefins

The main polymer use for talc fillers is in thermoplastic compounds for the automotive industry, and it is believed that these compounds have a high recycling rate. Many of the major automotive markets have stringent environment targets which encourage recycling. Thus, in the EU, the End of Life Vehicle Directive requires that a minimum of 95% of a vehicles weight must be reused or recycled. Talc-filled thermoplastics are recovered and reused for a variety of automotive applications, mainly in under bonnet parts, body arch liners, and cable harness parts. There is also down-cycling into nonautomotive parts such as water and sewage pipes, furniture feet, etc. According to the Industrial Minerals Association (Ima-europe.eu), about 95% of the talc used in automotive applications in Europe is recycled in some way.

### Surface Modification and Coupling Agents

Filler surface modification is widely used for improving the processing and properties of composites and will be equally important for recycled and sustainable fillers. In most cases, these additives will be the same as used with the virgin filler of the same composition. In a few cases, such as natural products like wood, new types of treatment are being developed, such as maleated polyolefins. The most extreme case is for particulate organic fillers, such as lignin, intended for use in tire applications. These products are still in their infancy, with little published detail.

## Future Prospects

There is no doubt that pressures to improve sustainability of the volume fillers, especially those used in automotive applications such as tires, will increase. As such, despite the difficulties involved, we can expect more recycling and use of renewables in the future.

## Cross-References

- ▶ Carbon Black as a Polymer Filler
- ▶ Calcium Carbonate Fillers
- ▶ Fillers from Organic Sources
- ▶ Nanofillers
- ▶ Surface Modifiers for Use with Particulate Fillers
- ▶ Talcs

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# Nanofillers

# 23

Roger Rothon

## Contents

## Abstract

Nanofillers, especially those based on clays and carbon nanotubes, have received a great deal of attention recently. The accepted definition of nanoparticles is that they should have at least one dimension in the range 1–100 nm and that the others should be greater than 100 nm. This can be further divided; when three dimensions are in the nano range we have nanoparticles, when it is two then nanofibers, and when one then nanoplates.

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The first thing to notice is that, despite all the recent publicity, nanofillers are nothing new, and nanoparticle fillers already have a very significant market presence. These include the carbon blacks, precipitated and fumed silicas, and precipitated calcium carbonates. More recently interest in using synthetic polymer nanoparticles has been revived.

Where the principal novelty lies today is with the nanoplates and nanofibers, which are more recent arrivals on the scene. Mineral derived nanoplate fillers are the more promising for volume applications, due to a relatively low cost compared to the fibers. Color is also a limiting factor for the nanocarbon fillers.

While a large number of layer minerals exist with the potential for delamination and dispersion as nanoplates, clays and especially those of the montmorillonite family have shown most promise and have been focused on commercially. Nanoclays offer the potential for high stiffness at low loadings, excellent barrier properties, and some useful flame retardant properties. However, after more than two decades of effort and some limited successes, their market penetration is well short of initial hopes and commercial interest is declining. This is due to the practical difficulties in fully delaminating and dispersing them, and thus realizing their potential benefits, in all but a few cases.

Among other nanoplates, graphite and ultimately graphene have promise for some advanced composite applications. Cost (and color) are likely to be limiting factors. The same factors will affect graphene fiber analogues, such as carbon nanofibers and tubes.

Extraction of nanocrystals such as starch and cellulose from abundant plant materials is also of interest, especially from the sustainability angle. Despite some promise, the current production processes are costly and far from truly “green.” They also face similar difficulties in redispersion into polymer matrices as the nanoclays.

**Keywords**

Nanofillers • Nanocomposites • Nanoparticles • Nanofibers • Nanoplates • Nanoclays • Graphite • Graphene • Carbon nanotubes • Nanostarch • Nanocellulose • Asbestos • Halloysite

## Definitions

The definition of what is meant by a nanoparticle is critical, as there has been a lot of confusion and also misuse of the term. Various bodies have brought out standards to regularize this situation, notably ISO in ISO/TS 80004-2:2015 (en) Nano-Technologies –Vocabularly-Part2, Nano-objects (available at http://www.iso.org/iso/iso_catalogue.htm) and ASTM in ASTM 2456-06 Standard Terminology Relating to Nanotechnology (available at: http://www.astm.org/Standard/index.shtml).

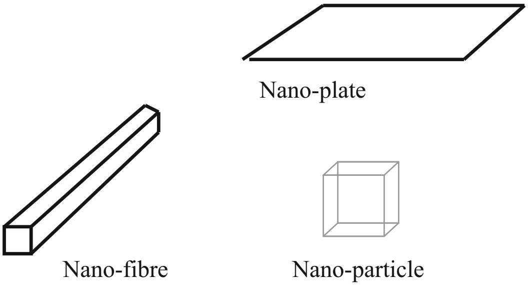

**Fig. 1** Various nanofiller shapes (reproduced, with permission, from Particulate-Filled Polymer Composites (Ed Rothon R.N.), 2nd Edition, Rapra Technology, Shawbury UK, 2003)

There are some differences in detail between them, but both agree that nanoparticles should have at least one dimension in the range 1–100 nm and that the others may be greater than 100 nm. The lower limit of 1 nm is to eliminate molecules and molecular clusters. This definition is adopted here (with the exception of some plate materials, such as graphene, where the theoretical thickness is below 1 nm). Specific surface areas (in the absence of porosity effects) can also be used as a guide and will be in the range 25 – over 750 $m^2/g$. This property does vary with specific gravity however, and can be surprisingly low for a given size, if the density is high.

Here the term nanoparticles is restricted to those with three nano dimensions, those with two are described as nanofibers, and those with one as nanoplates. This is shown in Fig. 1.

In addition, there are some terms used with layer minerals which need defining:

Gallery. The space between the layers that make up the crystalline structure.

Intercalation. The insertion of (mainly organic) molecules (intercalants) into the gallery, in order to help in the separation of the individual layers.

Exfoliation. The stripping of layers from the bulk, also called delamination. It is frequently assumed that these are individual layers, but this is not necessarily the case.

Tactoid. In this context it refers to a stack of a small number of plates which have been separated from the original particle.

## Introduction

The world-wide interest in nanotechnology in general over the last two decades has been accompanied by a similar interest in nanocomposites and nanofillers, both from the scientific and commercial communities.

In the present context, nanofiller refers to particles in which at least one dimension is in the nanometer range (1–100 nm, see definition above).

Despite the recent excitement, a reality check is needed and it has to be stressed that nanofillers are far from a new concept. Nanoparticulate fillers have been with us for a very long time, and are already successfully established with a very significant market presence. These materials are the carbon blacks, fumed silicas, precipitated silicas and silicates, and precipitated calcium carbonates. Thus, a lot of the potential nanoparticle market has already been satisfied and any novelty is more likely to come in the areas of plates and fibers. Also, in the rush to find something novel and exploitable, some producers have added the term nano to some well-established products, implying some novelty which did not really exist.

## General

The main attraction of nanosized particles is because it has been found that many desirable composite properties improve significantly as filler particle size decreases. This offers two opportunities: better absolute properties, or the same properties at much lower filler levels, and so a lighter product (as fillers generally have a higher specific gravity than polymers). Many proposed applications are in the 5–10% of additive range, which means that the market size for such fillers is going to be much smaller in weight terms than for conventional ones; as a result it is not completely fair to judge their success on this basis.

A number of issues are limiting the commercial success of the recently introduced nanofillers. The first is that reducing size nearly always costs money, especially for nano sizes. Secondly, dispersing particles into polymers and processing the mix becomes more difficult as size reduces and can further add significantly to the cost. Thirdly, surface properties of the filler become more and more significant as size reduces, and this can have unexpected effects on issues such as stabilizer deactivation, as well as adversely affecting the polymer structure (discussed later). The high amount of surface can also significantly increase the amount of expensive coupling agent where this is needed. Next, the maximum addition level attainable decreases with particle size and this can prevent properties above that of conventional composites from being achieved. Finally, very small size can lead to handling issues, and most importantly of all to potential health issues. A discussion of the health issue can be found in NIOSH (2009).

Of all the above, cost is probably the most important factor limiting nanofiller penetration. Thus, nanoclays, one of the least expensive of the new generation of nanofillers, are 10–20 times the cost of good talcs and carbonates and 5–10 times that of other precipitated fillers, such as silica and calcium carbonate. The addition of just 5% of a nanoclay to a commodity polyolefin can thus be expected to increase raw material costs by at least 40%.

Handling and health issues must also not be overlooked and are responsible for much of the difficulty in commercializing some of the technologies. If nanoparticles are generated in the free state, they are extremely light and dusty. Fumed silicas are an excellent example; the bulk density of typical products is in the range 0.05–0.1 which creates very real handling problems. Much of the work on developing nanofillers suitable for general use is thus aimed at producing forms which only release the nanoparticles during composite production, but this is far from easy to do.

Another important consideration that is frequently overlooked is the effect of the filler surface itself on polymer structure and properties. Polymer in the vicinity of a solid surface becomes altered, due to a decrease in the degrees of freedom (see for example, Napper 1983). This modified polymer is usually denser, stiffer, and with a higher Tg than the bulk, but also with less elongation. In thermoplastics, it is also usually more brittle. The thickness of such layers varies with the polymer but is usually regarded as being between 1 and 10 nm. This effect is most noticeable in thermoplastics and elastomers and more detail on the former can be found in ▶ Chap. 3, "Particulate Fillers in Thermoplastics". As shown in Tables 1 and 2, the amount of such modified polymer starts to become significant below 1 μm particle size and is dominant once the nanometer range is reached. This modified polymer can be expected to contribute to the effects produced by nanosized fillers. It is probably the cause of many of the effects produced by nanoparticles, but should not be ignored as a contributing factor for nanoplates and fibers as well.

**Table 1** The effect of particle size on the amount of immobilized polymer as percentage by weight of the filler (cubic particles)

| Particle size (micron) | Specific surface area $m^2/g$ IF Filler SG = 1 (IF Filler SG = 2) | Immobilized polymer (as % w/w on filler particle, assuming filler and layer have an SG of 1 and 5 nm layer) | Immobilized polymer (as % w/w on filler particle, assuming filler and layer have an SG of 2 and 5 nm layer) |
|---|---|---|---|
| 0.01 | 600 (300) | 300 | 150 |
| 0.1 | 60 (30) | 30 | 15 |
| 0.5 | 12 (6) | 6 | 3 |
| 1.0 | 6 (3) | 3 | 1.5 |
| 5.0 | 1.2 (0.6) | 0.6 | 0.3 |
| 10.0 | 0.6 (0.3) | 0.3 | 0.15 |

**Table 2** Immobilized polymer produced by a filler as a function of size and addition level (assumes filler specific gravity = 2)

| Filler addition level % w/w | Amount of altered polymer phase % w/w (100 nm particle) | Amount of altered polymer phase % w/w (50 nm particle) | Amount of altered polymer phase % w/w (10 nm particle) |
|---|---|---|---|
| 0 | 0 | 0 | 0 |
| 10 | 3.3 | 6.6 | 33 |
| 20 | 7.5 | 15 | 75 |
| 30 | 12.8 | 26 | 100 |
| 40 | 20 | 40 | 100 |
| 50 | 30 | 60 | 100 |

**Table 3** Established particulate nanofillers

| Material | Particle size range (primary nm) | Specific surface area range ($m^2/g$) | Comments |
|---|---|---|---|
| Precipitated calcium carbonates | 20–80 | 20–75 | Mainly used in PVC, elastomers and sealants |
| Precipitated silicas | 7–40 | 40–400 | Used in large quantities, mainly in elastomers, especially tires |
| Fumed silicas | 5–20 | 100–400 | Main use is in silicone rubber, but has many other polymer applications |
| Carbon blacks | 10–80 | 20–200 | Very widely used in polymers, both as a filler and pigment. Largest use is in elastomers |

## Particles with Three Nano Dimensions

The long established commercial nanofillers with fairly isotropic particle shapes (carbon blacks, precipitated and fumed silicas, and precipitated calcium carbonate) are briefly described in Table 3. They are all treated elsewhere in this publication and are not discussed further here, except to say that precipitated calcium carbonate is an example of how nanoparticle handling issues may be tackled. Precipitated calcium carbonates can have crystals well into the nano range (as low as 20 nm) and which disperse as such in polymers, but have bulk densities typical of conventional micron sized fillers. This is achieved by the manufacturing process; this first forms an intermediate particle of micron size, which recrystallizes into a collection of nanocrystals. This recrystallization is controlled so that the collection only breaks down and releases the nanocrystals during composite production.

In addition, there are a number of emerging and niche nanoparticulate fillers. Some of these taken from manufacturers' literature are listed in Table 4. Many of them are relatively expensive to produce and principally made for other applications, with some spin off into the higher value polymer ones.

Cross-linked organic polymers are an interesting emerging class of fillers. Emulsion polymerization can be used to produce nanosized particles of various organic polymers. This was exploited as long ago as the 1950s to produce model particles for studying rubber reinforcement (Burke 1965). The resins were produced by emulsion polymerization of divinyl benzene and styrene. The divinyl benzene was used to cross-link the particle (thus increasing rigidity and stabilizing it against deformation during processing), it also resulted in some residual unsaturation. Particles in the range 20–750 nm were made and tested in an emulsion SBR elastomer. Those in the range 25–50 nm were found to be strongly reinforcing (in terms of tensile strength) but this rapidly fell away as the size increased.

For a long time this approach appears to have been dormant, but seems to have recently been revived by a major supplier to the rubber industry (Lanxess,

**Table 4** Emerging and niche nanoparticulate fillers (Based on Manufacturers Literature. e.g., Nanoparticles and Microspheres Co. Ltd. www.nanoparticles-microspheres.com web site accessed March 2016)

| Material | Size available nm | Comments |
|---|---|---|
| Antimony tin oxide $SnO_2:Sb_2O_3$ | 50 | Semiconductive and main use is as an antistatic additive |
| Alumina $Al_2O_3$ | 20–100 | Main use in ceramics. Said to have some use in synthetic fibers for enhanced wear resistance |
| Synthetic boehmite AlO (OH) | 5–60 | Also said to be available as needles or plates and with surface modifications. Claimed to be usable in most polymers and to be particularly useful for transparency and flame retardancy (Torno 2006) |
| Magnesia MgO | 30–50 | Again main use is in ceramics. Said to be some use as a fire retardant additive for fibers |
| Titania $TiO_2$ | 5–100 | Many uses outside of polymers (including in sunscreens). Good UV absorber. Has a pro-degradant effect, which can be utilized in polymers |
| Zinc oxide ZnO | 5–100 | Many applications outside of polymers. Vulcanizing agent for elastomers, antibacterial agent, UV absorber |
| Aluminum nitride AlN | | Used where good thermal conductivity is required |
| Silicon carbide SiC | | Used to improve the wear resistance, especially for engineering plastics. Also used for its high thermal conductivity and low thermal expansion coefficient |
| Barium titanate $BaTiO_3$ | | Used in capacitors for dielectric effect |
| Polyhedral oligomeric silsesquioxanes, or POSS™ | 1–2 | Extremely small silica cages, carrying reactive and/or nonreactive organic groups. They have a number of niche polymer applications. (See DeArmitt 2011) |
| Cross-linked polymer resins | 20–100 | Being developed as performance enhancers for elastomers, especially for tire applications |

http://lanxess.com/en/corporate/home/) who has developed a range of products under the Nanoprene trade name. While the manufacturer states that the products are intended for a range of polymers, current interest is mainly in elastomers, especially for tire applications. The following is from the manufacturer’s literature.

> “In principle, Nanoprene consists of pre-crosslinked rubber particles that are manufactured by LANXESS in an innovative patented emulsion process. Different conditions can be achieved during the synthesis process, e.g. in terms of the degree of crosslinking (glass transition temperature) or polarity of the particles, depending on the required application. With particle sizes ranging between 40 and 200 nanometers, after the manufacturing process, the rubber additive is available in the usual delivery forms such as bales, granules, powders,

> pastes and master batches. These additives are very similar to many other elastomers in terms of appearance and consistency, and they can be processed in the usual way. Special processes ensure that the particles disperse easily when used by customers.
>
> In practice, comprehensive tests conducted by LANXESS have shown that using Nanoprene in summer tires, for example, improves dry road grip by between 10 and 15 percent. What's more, adding Nanoprene also improves the stiffness of the tread blocks, which has a positive impact on the cornering properties under aquaplaning conditions. The abrasion resistance of tire treads containing Nanoprene is also much higher than those based on standard silica mixtures. The test results show that Nanoprene increases the service life of tires significantly."

## Nanoplates

Plate fillers offer some advantages over regular shapes because of their aspect ratio. This includes increased modulus and higher gas barrier properties. To some extent this can already be met by fillers such as talc and mica, but there is a limit to the aspect ratio attainable if the plates are to be kept to a size that is processable and does not detract too much from properties such as appearance, surface roughness, and impact strength.

The way around this is to have plates with a thickness of just a few nanometers, in which case the plate size is still small enough to be useful, even at high aspect ratios (See Table 5). This is why nanoplate fillers have become of such interest, especially when based on materials with a high intrinsic stiffness. While such nanoplates can be synthesized, this is an expensive process and starting from naturally occurring materials is generally favored. There are a large number of layer minerals, which consist of stacks of strong and stiff plates, of the order of 1 nm in thickness, and where the plates are relatively weakly bonded to the next layer. In principle these layer minerals offer a much lower cost route to the production of high aspect ratio nanoplate fillers, than using direct synthesis. As such, they have received considerable attention, but as often happens, while the concept is great, the practicalities provide significant problems, especially for commercial, as opposed to laboratory, realization.

In this case, the problem lies not in being able to separate the plates but in being able to achieve this in a polymer environment. The ideal is to have an easily handled powder form, which can be processed on conventional composite equipment and

**Table 5** Plate length as a function of thickness and aspect ratio (assumes a square plate)

| Plate thickness (nm) | Plate length for aspect ratio of 100 (micron) |
|---|---|
| 1 | 0.1 |
| 5 | 0.5 |
| 10 | 1 |
| 50 | 5 |
| 100 | 10 |
| 500 | 50 |
| 1000 | 100 |

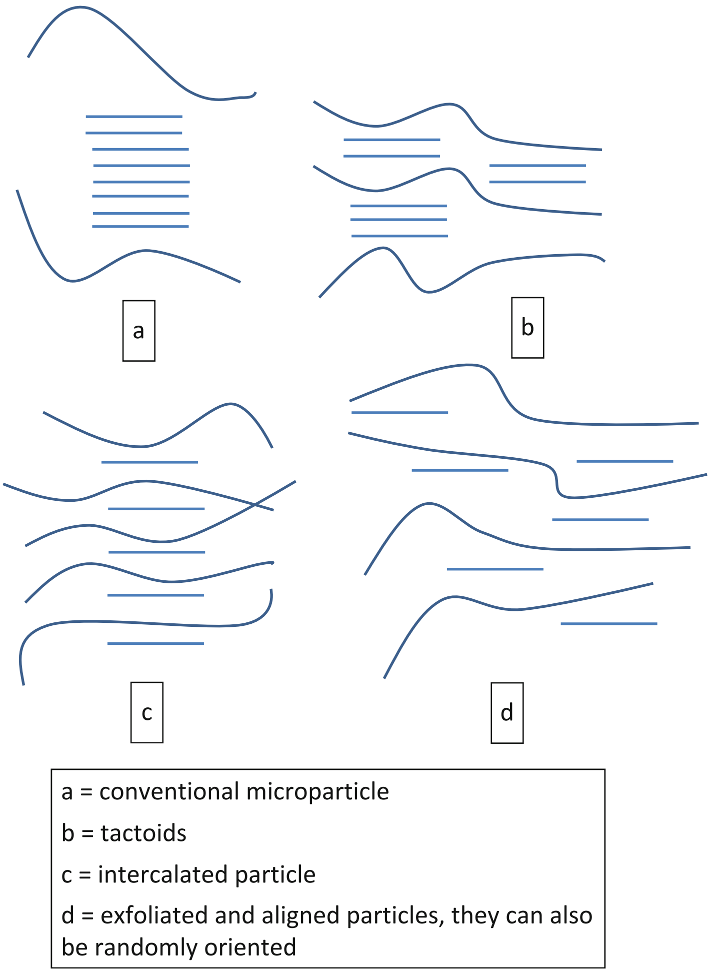

**Fig. 2** Different structures for a layered mineral composite

fully disperses to nanoplates in the polymer, but this is very hard to achieve in practice. Indeed it is probably rarely, if ever, fully achieved outside of the laboratory, (Hari and Pukanszky 2011).

Various levels of dispersion of a layer mineral in a polymer can be recognized as illustrated in Fig. 2. These are:

Conventional or micromineral dispersion. In this, small blocks of the mineral are present, each containing many layers.

Partial delamination. Here some plate separation has occurred, resulting in thinner blocks with just a few layers. These are referred to as tactoids.

Intercalation. Here the stacks still exist, but polymer matrix has penetrated into the galleries between them.

Exfoliation or complete separation and dispersion. This is the desired state for best properties in most cases.

In practice these different stages often coexist, but while the scientific community often aims for complete exfoliation, this is not necessary for useful effects to be obtained.

There are two extreme approaches to achieving an exfoliated structure in a polymer composite. The first approach is to completely exfoliate the mineral prior to use in composites. This method is frequently used in laboratory work, but is hard to utilize in practice, especially in most common polymers. It is usually carried out by producing the exfoliation in a liquid medium, using dispersion methods such as ultrasonics together with suitable dispersants and then transferring the dispersion directly into the polymer or its precursor, without intermediate isolation. This is only feasible when the exfoliation can be achieved in a liquid monomer or possibly in a latex polymer, but these are exceptional cases. Attempts to dry the exfoliated product, and then redisperse it (during melt compounding), nearly always lead to strong agglomeration and poor results.

The second approach is to only produce the exfoliation during composite formation. This is more practical, but still difficult to achieve. Some layer minerals, such as talcs and clays, can be partially delaminated mechanically and may undergo some delamination during compounding, especially in high shear systems such as with elastomers, but this still leaves quite thick stacks of modest aspect ratio. Most other layer minerals require some weakening of the structure in order to achieve dispersion during composite production. This is usually achieved by introducing relatively small molecules as intercalants between the plates, thus pushing them apart and reducing the interplate attraction. Relatively high levels of such intercalants (10–30% or more relative to the mineral) are required for this and will remain in the filler and composite; so they have to be chosen with care.

## Nanoclays

The most intense academic and commercial activity in recent years has been on nanoplates, especially those derived from naturally occurring clay minerals, notably montmorillonites. This has been seen as a potential route to competitively priced nanofillers.

Clays are very complex minerals and can only be briefly discussed here, and standard works, such as Jepson (1984), should be consulted for more detail, while a separate chapter in this work discusses kaolin-type clays. The field of polymer clay nanocomposites was also reviewed in the book by Pinnavaia and Beall (2000) and more recently by Kamena (2010).

All clays are layer silicates made up of stacks of metal silicate layers which are relatively loosely held together. These stacks can often be penetrated by low molecular weight species, such as water, resulting in some swelling. The degree to which this occurs varies from clay to clay, but offers a route to producing high aspect ratio thin plates. One group of clays, known as montmorillonites (also known as bentonites), are widely available and with layers which are fairly easy to separate, and these have been the basis for developing nanoplate fillers for polymer applications.

The montmorillonites have plates with three layers, a central dioctahedral gibbsite (alumina) layer with trioctahedral silicate layers ($Si_2O_5$) strongly bonded on each side. As a result they are described as 2:1 silicates. The plates have charge deficiencies mainly due to isomorphous substitution of $Al^{3+}$ and $Si^{4+}$ in each layer, and these are balanced by cations (principally sodium and calcium). Water, other hydroxyl-containing groups, and amines readily penetrate between the plates and disrupt the ionic bonds. Once this has happened, more layers, or larger species, can be introduced, producing a marked expansion of the structure. This process, called intercalation, is best carried out by ion exchange of the interlayer cations, using water soluble species, such as quaternary ammonium salts. Montmorillonites treated with up to 40 wt% long chain fatty amines (such as octadecylamine) are often called organoclays and have been used for a long time to give structure or thixotropy to organic liquids and as such are widely used in solvent based paints.

Under certain conditions, the swollen structures can be further processed to cause complete separation of the platelets into very high aspect ratio products. The plate thickness is approximately 1 nm, so these platelets can have extremely high specific surface areas (over 750 $m^2/g$). The size of the starting clay particles means that they can also have high aspect ratios, up to and even over 1,000:1.

As the plates have a high stiffness as well as a high aspect ratio, they offer significant potential for polymer applications. Although this effect was known for a long time, delaminating the plates and then dispersing them effectively into polymers is no simple exercise. In most cases, the plates need to finally separate during composite preparation, not beforehand, or they will be too difficult to handle. It is thus necessary for the intercalant that has pushed the plates apart, to remain in the particle, and this is often at levels of 15% w/w or more. This intercalant will then also be present in the final composite. It was only in the 1970s that ways of exploiting this approach for practical polymer applications were discovered (Fujiwara and Usuki 1976). This was further developed in the 1980s by Toyota's research laboratories (Okada 1988; Kato and Usuki 2000). Toyota's initial work was concentrated on a particular polymer, nylon 6, and led to great initial excitement, with predictions of large volume applications. Despite massive development programs, these have so far not been realized, for two main reasons. The first is that nylon 6 is a very special case, as far as use of nanoclays is concerned, and is one where it is possible to approach complete exfoliation of the clay. This is because an intercalant (amino acid) can be used that actually becomes part of nylon structure and equally important, the organically modified clay can be dispersed into the prepolymerization mix where the nylon 6 monomer (gamma caprolactone) is able to enter into the galleries and react with the amino acid. This approach is known as polymerization filling and allows excellent exfoliation and dispersion to be achieved. Unfortunately, nylon 6 is a relatively expensive polymer and the polymerization filling method cannot be used with many others, including the bulk thermoplastics.

For this reason it has proved very difficult to get the same level of effect in volume polymers such as polyolefins or even in other nylons. Another factor limiting uptake of the technology is that there is an upper limit to the amount of nanoclay that can be incorporated before the effects tail off. This is due to physical limitations on the interparticle spacing obtainable as loading increases. This tailing off in performance means that the actual property levels achievable are often no better than can be achieved, albeit at lower cost, by higher loadings of conventional fillers. Due to impurities present in the starting mineral, nanoclays have also been found to cause more severe heat aging problems in polymers such as polypropylenes than most fillers do, and this requires extra stabilizer to be used.

The potentially exploitable properties that reasonably fully exfoliated nanoclays can bring to a polymer composite are shape related, with the main ones being:

Enhanced stiffness
Increased heat distortion temperature
Reduced gas permeability
Reduced flammability

These various aspects are discussed separately below.

## Stiffness and Heat Distortion Temperature

Nanoclays have a big effect on these properties in thermoplastic composites, and this was the first area to arouse interest. Typical results are presented in Table 6 and show how much benefit can be achieved at very low loadings. It also shows how the effect soon starts to tail off, as loading increases. Conventional fillers such as glass fiber and mica give similar improvements, albeit at higher addition levels. Because of the loading restrictions on the nanoclays, conventional fillers are often also able to give higher absolute property levels, and glass fiber still appears to be more cost competitive for general thermoplastics use.

Despite these limitations, the nanoclays combine these effects with others such as transparency, low density, good surface finish, and better scratch and mar resistance and are beginning to be used where these are important.

## Gas Barrier Properties

Properly aligned and dispersed, low levels of clay are able to give good barrier properties, accompanied by good clarity and low density. This application has

**Table 6** Typical effects of a well dispersed nanoclay in a Pa 6 matrix (optimal situation)

| Amount of nanoclay % w/w | Flex modulus MPa | Heat distortion temperature °C |
|---|---|---|
| 0 | 2,840 | 56 |
| 2 | 4,325 | 125 |
| 4 | 4,578 | 131 |
| 6 | 5,388 | 136 |

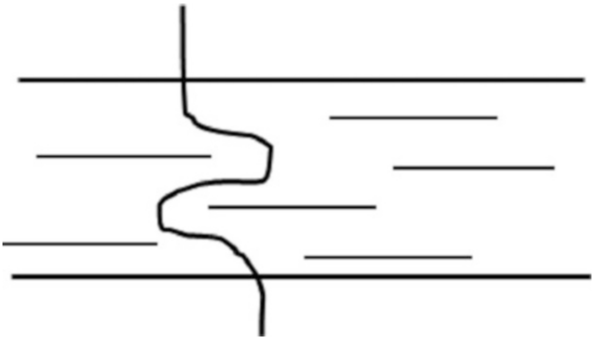

**Fig. 3** Tortuous diffusion path created by aligned plate-like particles in a polymer film (reproduced, with permission, from Particulate-Filled Polymer Composites (Ed Rothon R.N.), 2nd Edition, Rapra Technology, Shawbury UK, 2003)

recently been reviewed by Cui et al. (2015). Their effect on diffusivity is believed to be due to the creation of a tortuous diffusion path, as shown in Fig. 3. Because of their extreme thinness and ability to align, they are able to be used in thin films, such as found in packaging. This was one of the first areas to be commercialized but has not grown as fast as expected, due to the difficulties in extending the excellent performance found in nylon 6 to more common packaging materials.

### Flame Retardancy

The use of nanoclays as flame retardant additives has received a great deal of attention. It has been reviewed by Porter et al. (2000).

This interest was based on early observations showing unexpectedly good results in certain laboratory tests, especially in cone calorimetry, which is regarded as a fairly reliable guide to full scale performance. Such effects do not seem to require complete exfoliation and are achievable in widely used polymers, such as polyolefins.

Some typical data is shown in Fig. 4. This shows that very small amounts of a nanoclay can significantly decrease the peak heat release rate and slow down the overall rate of combustion. Much higher levels of a conventional flame retardant filler, such as aluminum hydroxide, would be needed for the same effect. These improvements are believed to be due to a combination of char promotion and gas barrier effects. While these are very useful effects, it has also been found that there is little benefit to ignition time, total heat release, and on smoke generation. Indeed, ignition time can often be shortened, as shown in Fig. 4, and this is not desirable.

Despite the good cone calorimeter results, the use of nanoclays alone does not give similar enhancements in other laboratory tests, such as Oxygen Index and UL94 Vertical burn and, more crucially, in full scale product tests. As a result, interest has moved to using nanoclays in conjunction with other flame retardant additives.

## Other Layer Silicates

While the montmorillonites have received most attention for making nanoplate fillers, other layer silicate minerals can be used. This includes kaolin itself,

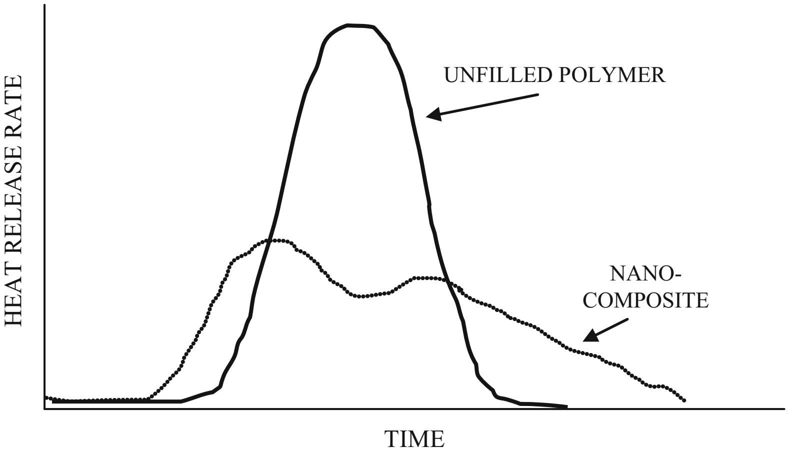

**Fig. 4** Schematic of the sort of cone calorimeter results obtainable from low levels of nanoclays (reproduced, with permission, from Particulate-Filled Polymer Composites (Ed Rothon R.N.), 2nd Edition, Rapra Technology, Shawbury UK, 2003)

vermiculites, and talcs. Intercalation and separation is more difficult, however, requiring more aggressive reagents and conditions and little commercial progress has occurred. It is also possible to synthesize clays that are suitable for manufacture of nanoplates. This has the advantage of higher purity, resulting in benefits such as better color and heat aging resistance in polymers, but at higher cost. One such product, a synthetic mica, has been commercially available for some time (Somasif from CO-OP Chemical Company, Japan, www.co-op.jp).

## Other Nanoplate Materials

In addition to many clays and micas, there are a number of other layer minerals, both natural and synthetic, which could, in theory at least, be exfoliated to produce nanoplates. These include layer hydroxides and hydroxycarbonates (e.g., hydrotalcites).

Probably the most interesting is graphite, and the related materials graphene and carbon nanotubes and fibers.

## Graphite

Graphite is a layer mineral made up of stacked graphene layers and is the stiffest known natural product, with a Young's modulus of over 1,000 MPa. The graphene layers have exceptional strength and stiffness, making them ideal nanoplates.

The general practical problems described earlier affect these materials as much as any other layer mineral. Graphite can be intercalated by a number of chemicals, and

**Table 7** Effect of various treatments on the properties of graphite intercalated compounds

| GIC graphite treatment | Specific surface area (BET $m^2/g$) | Average diameter (micron, by SEM) | Thickness (nm) (Calculated) | Aspect ratio |
|---|---|---|---|---|
| *None* | 0.2 | 300 | 5,170 | 58 |
| *Heat exfoliated* only | 10.5 | 15 | 95 | 155 |
| *Heat exfoliated* and *milled* | 24 | 1.1 | 45 | 24 |
| xGnP (Drzal process) | 105 | 15 | 9.5 | 1,575 |
| xGnP (Drazl process, different conditions) | 94 | 0.9 | 11 | 80 |

this is used in the production of a commercially available range known as expandable graphites or graphite intercalated compounds (GIC). In these, an acid is intercalated between the layers and, on heating, vaporizes pushing the plates apart. The main use of expandable graphite in polymers today is as an intumescent fire retardant additive. These GICs are designed to be stable during polymer processing and only exfoliate if combustion occurs, so are not a direct route to nanoplate filled polymers. So far, no more suitable intercalants have emerged.

A compromise approach is to use preheating and mechanical processing of commercial GICs to make delaminated forms which can be used in conventional thermoplastics and thermoset processing to make filled composites. This approach has been pioneered by Drzal and coworkers at Michigan State University (Drzal and Fukushima 2006) who have developed special processing techniques, incorporating ultrasonics, to maximize plate separation and to produce plates of suitable properties for use in polymers. Typical properties of such plates (christened xGnP, exfoliated graphite nanoplates) are shown in Table 7 and compared with standard methods for GIC delamination.

These workers have also developed surface treatments to improve the dispersion and performance in polymers, with acrylamide grafting being particularly useful. Acrylamide grafted xGnP has been shown to be an effective reinforcement in thermoset (epoxy) and thermoplastic (polyamide) polymers.

Drzal's group have since extended this work to produce even higher surface areas and this has started to merge with graphene (a single graphite plate) developments, discussed next. The work is now the basis of a spin-out company from Michigan State University (XGSsciences.com).

## Graphene

Graphene itself is generating great deal of excitement. It is actually a single layer of graphitic carbon, and being only one atom thick is a true two-dimensional material.

(It is worth noting that, as such, it is under the minimum size of 1 nm in the nano definition.) Graphene is also the fundamental unit of nano carbon fibers and carbon nanotubes.

The interest in this material stems from its strength and stiffness, which are put at 130 GPa and 1 TPa (terra Pascal), respectively. It is said to be the strongest material currently known. From a composites point of view, it has the potential for very strong and stiff but light composite materials (its effective specific gravity is 2.25). While graphene was known theoretically for many years, it was only recently that an effective method of producing these single layers was discovered (Novoselov et al. 2004). This involved the mechanical removal of single atomic layers from graphite. This work resulted in the award of the Nobel Prize for Physics in 2010. Better methods were required for scale up and commercial exploitation, and over time a number of alternatives have been developed. These have been reviewed by Soldano et al. (2010). The approaches being investigated include chemical vapor deposition, graphitization of silicon carbide, a large variety of graphite exfoliation methods (including the ultrasonic method of the Drzal group described above), unzipping of carbon nanotubes, and chemical synthesis.

Enormous effort is going on worldwide to develop commercially affordable methods of production and to find applications for graphene and its composites. These efforts are expected to start to come to fruition in the next few years. Even so, there are significant issues in being able to produce graphene in a form suitable for use as a plate in composites manufacture though. Not least is its desire to roll up into a tube or to form buckled or crumpled plates. It may be that the use of stacks of a few sheets, as described under graphite above, may be more practical for composites.

## Nanostarch Platelets

In nature, starch is found in plants as semicrystalline beads with a size range of 2–100 μm in diameter depending on the plant. The extraction and processing of these for use as conventional polymer fillers is covered in ▶ Chaps. 16, "Fillers from Organic Sources," and ▶ 22, "Sustainable and Recycled Particulate Fillers". Further processing can produce nanosized particles and this is discussed here.

The production of such nanosized particles proceeds through the isolation of the crystalline phase of the beads. This is generally achieved by acid hydrolysis which dissolves the amorphous and poorly crystalline regions and leaves the water-insoluble highly crystalline regions behind. The structure of the extracted crystallites is mainly determined by the botanical origin of the starch, while the extraction conditions mainly affect the size.

Starch nanocrystals derived from various plants have been shown to have a platelet type morphology with lengths from 20 to 200 nm, widths from 10 to 30 nm, and thicknesses from 5 to 10 nm. They are highly hydroxylated, with up to 14% of the hydroxyls being on the surface and they are thus very hydrophilic. If sulfuric acid is used for the hydrolysis, then many of the surface groups are sulfonated. While this sulfonation helps with some properties, it reduces the thermal stability, unless the sulphonate groups are neutralized by reaction with an alkali. The hydrophilic nature of the crystals can be modified by reaction of the hydroxyls and this is widely practiced, especially for improving compatibility with many organic polymers.

The use of starch nanocrystals in polymer composites is currently limited by cost and processing issues. The "green" and sustainable badge is also compromised by the chemical processing needed to extract the crystals, and by the amount of co-product which needs to be utilized. The processing problems are those common to many solution processed fine particles, that is, the need to isolate them in a redispersible form for most polymer uses. Most progress has been made with direct transfer into a polymer dispersion such as an aqueous latex, examples being natural rubber latex or styrene butadiene rubber latex. This has led to some promising developments in the tire industry (see ▶ Chap. 16, "Fillers from Organic Sources"). Solution casting techniques have also been used with some success in the laboratory, but are not suited to industrial applications. Producing a dry powder suitable for melt processing or adding to bulk rubbers on a commercial scale is far more difficult and still has not been achieved.

More details can be found in the reviews by Miller and Hobbie (2013) and Lin et al. (2011). Starch fillers in general are also discussed in ▶ Chap. 22, "Sustainable and Recycled Particulate Fillers".

## Nanofibers

These have two dimensions in the nano range, and those of most interest for polymer applications are nanocellulose and the nanocarbon materials, carbon nanofibers and nanotubes. Asbestos and halloysite are examples of inorganic nanofibers.

### Nanocellulose

Cellulose is a highly crystalline, high molecular weight, linear polymer and is present in many plants in the form of microfibrils. There are a number of different crystal forms and plant (native) cellulose is a mixture of two of the polymorphs, cellulose Iα and cellulose Iβ. Cellulose provides much of the strength and stiffness of the plant. Plant fibers themselves are cellular biocomposites designed by nature and are essentially an amorphous matrix made principally of hemicellulose, lignin, waxes, and trace elements, reinforced by the cellulose microfibrils. These plant fibers are themselves cemented together by an intracellular ligneous material. The cellulose microfibrils typically have a diameter of about 2–20 nm and are made up of 30–100 cellulose molecules in an extended chain conformation.

The reinforcing ability of cellulose fibrils is ascribed to their crystalline nature and the extended chain conformation of the cellulose molecules. This particular conformation results from strong intermolecular hydrogen bonding caused by the high density of hydroxyl groups present in the cellulose molecule. The specific strength is significantly higher than steel.

The extraction of cellulose nanocrystals from cellulosic fibers is similar to that described for starch nanocrystals and usually involves an acid-induced destructuring process, involving hydrolysis of gylcosidic bonds. The hydrolysis step is followed by procedures such as centrifugation, dialysis, and ultrasonication. Various acids can be used for the hydrolysis, including sulfuric, hydrochloric, phosphoric, and nitric acids. Based on papermaking technology, hydrolysis with sulfuric acid has been most investigated and appears to be the most effective method. If hydrochloric acid is used, then the ability of the resulting nanocrystals to disperse in solvents is limited and the suspension is unstable, with a tendency to flocculate. On the other hand, if sulfuric acid is used for the hydrolysis, it reacts with the surface hydroxyl groups via esterification, with the formation of anionic sulfate ester groups ($OSO_3^-$). The presence of these negatively charged groups provides an electrostatic layer around the nanocrystals and promotes their dispersion and stability in water. However, as for starch, the sulfate ester groups also compromise the thermal stability of the nanocrystals. Neutralization of the sulfate ester groups by sodium hydroxide (NaOH) can be used to eliminate this problem.

The nomenclature used to describe acid-hydrolyzed crystalline cellulose nanoparticles has been uncontrolled until recently, with terms such as cellulose whiskers or nanowhiskers and nanocrystalline cellulose being employed. TAPPI (Technical Association of the Pulp and Paper Industry) has now proposed a standardized terminology – cellulose nanocrystal (Standard Terms and Their Definition for Cellulose Nanomaterial WI 3021).

The nanoparticles occur as high aspect ratio rod-like nanocrystals. Their actual dimensions depend on the plant origin and hydrolysis conditions. The length distribution is quite broad, due to the diffusion-controlled hydrolysis process. The aspect ratio varies with the plant from about 10–70.

Like starch, the use of cellulose nanocrystals in polymer composites is currently limited by cost and processing issues and the “green” and sustainable badge is compromised by the chemical processing needed to extract the crystals and by the amount of co-product which needs to be utilized.

The processing problems are those common to many solution processed fine particles; the need to isolate them in a redispersible form for most polymer uses. Most progress has been made with direct transfer into a polymer from an aqueous dispersion of the cellulose nanocrystals. This can be achieved by mixing an aqueous dispersion of the cellulose nanocrystals with either water soluble polymers or polymer aqueous dispersions (lattices). Correctly implemented, this method preserves the original dispersion of the nanoparticles, and has been used extensively in the academic work. For commercial purposes, natural rubber latex or styrene butadiene rubber latex are of most interest. Solution casting techniques have also been used with some success in the laboratory, but are not suited to industrial applications. Producing a dry powder suitable for melt processing or adding to bulk rubbers on a commercial scale is far more difficult and still has not been achieved. Problems include thermal degradation and poor dispersion. The dried particles agglomerate due to hydrogen bonds between nanoparticles. Functionalizing the surface of the cellulose nanocrystals before drying can help with the agglomeration and dispersion issues.

Commercial development of nanocellulose is at a very early stage. A large pilot plant was opened in 2013 at the University of Maine (USA). Another pilot plant came on stream in Mumbai, India, in 2014 (at the Central Institute for Research on Cotton Technology, CIRCOT).

More details can be found in the reviews by Miller and Hobbie (2013) and Mariano et al. (2014). Cellulose fillers in general are also discussed in ▶ Chaps. 16, "Fillers from Organic Sources," and ▶ 22, "Sustainable and Recycled Particulate Fillers."

## Carbon Nanofibers and Tubes

The high cost of the carbon based products (at least 1,000 times that of a conventional filler) means that, even allowing for efficiency improvements and scale reduction as they become more mature, they are only going to be of interest in specialist applications, where cost is not a major factor. As such they will only be briefly discussed here. More details can be found in Iqbal and Goyal (2010).

### Carbon Nanofibers

Conventional carbon fibers are well established as polymer reinforcements. They are produced by heat treatment or controlled pyrolysis of various polymer fiber precursors and have micron sized diameters, outside of the nano range. Vapor growth processes allow much finer fibers with nanosized diameters to be produced.

### Carbon Nanotubes

These are produced by similar vapor growth methods to those used for nanofibers, but the particles are hollow hence the name tubes. The tube walls are composed of rolled up graphene sheets and can exist in two forms, single or multi-walled, and the tubes are closed at the ends.

Two important issues are affecting the development of composite applications. The first is cost and the second is effective dispersion into a polymer matrix. As a result there is little commercialization today, but progress is being continually made and both nanofibers and tubes are expected to play an important role in advanced composites.

## Asbestos

Now largely removed from the market because of severe health issues, asbestos is an example of a naturally occurring nanofiber. Asbestos is the name given to a family of hydrated metal silicates, of which only two, chrysotile and anthophyllite, have been of any major significance in composites. Chrysotile is a highly hydrated magnesium silicate, with the formula $Mg_6[(OH)_4Si_2O_5]_2$ and anthophyllite has the formula $(MgFe)_7[(OH)Si_4O_{11}]_2$. They are both crystalline materials with fibrous particles which can be broken down to very fine fibrils 15–90 nm in diameter.

The health issues associated with asbestos are now well known, but help to account for the great caution exercised over the safety of new nanofibers. There is no useful recent literature on asbestos in composites, but Axelson (1987) is a useful introduction to the topic.

## Halloysite (CAS: 1332-58-7)

Halloysite is one of a number of silicate minerals which exist as hollow tubes (Pasbakhsh and Churchman 2015) and has received some interest as a polymer additive.

Halloysite is an aluminosilicate mineral, the same as kaolinite in composition, but with a more disordered stacking of the plates and the ability to form rolled up, hollow tubes. While relatively rare, significant workable deposits are found in several places including the USA and New Zealand.

The shape and purity vary from deposit to deposit and according to the processing used. The tubular, high aspect ratio, particles of most interest for composites production are ~1–2 μm long, 50 nm across, and with a 15 nm hole or "lumen." The surface area depends on processing and is in the range ~50–150 $m^2g^{-1}$. The outside of the tubes has a siloxane (Si–O–Si) surface chemistry while the inside has an hydroxylated aluminum surface chemistry.

Unlike carbon nanotubes, halloysite tubes are open ended, allowing some molecules to enter. The central lumen accounts for 20% of the particle volume and this has an effect on the effective density when it is encapsulated within a matrix. For example, if the polymer fills the inside of the tube then the effective density of the halloysite is 2.54 $gcm^{-3}$. In the case where it is not filled by the polymer, then the effective density of the halloysite is 20% less, i.e., ~2.00 $gcm^{-3}$.

Appropriately processed halloysite particles can be used to reinforce all types of polymer and also to produce special effects such as polymer crystal nucleation and flame retardancy. More information can be found in the review by Du et al. (2010) and in the *Dragonite Handbook* from Phantom Plastics (http://phantomplastics.com).

## Cross-References

- ▶ Calcium Carbonate Fillers
- ▶ Carbon Black as a Polymer Filler

► Fillers from Organic Sources
► Precipitated and Fumed Silicas and Related Products
► Sustainable and Recycled Particulate Fillers

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# Index

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