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Contents

Definitions	162
Introduction	162
Kaolin Occurrence and Extraction	164
Properties	166
Uses in Polymers	167
Calcined Clays	169
Flash Calcined Clays	171
Uses of Calcined Clays in Polymers	172
Cross-References	175
References	175

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 $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$.

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 $\text{Si}_2\text{O}_5^{-2}$. 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 $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$. 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 ($\text{Al}_2(\text{OH})_4$) 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, degrittied 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)

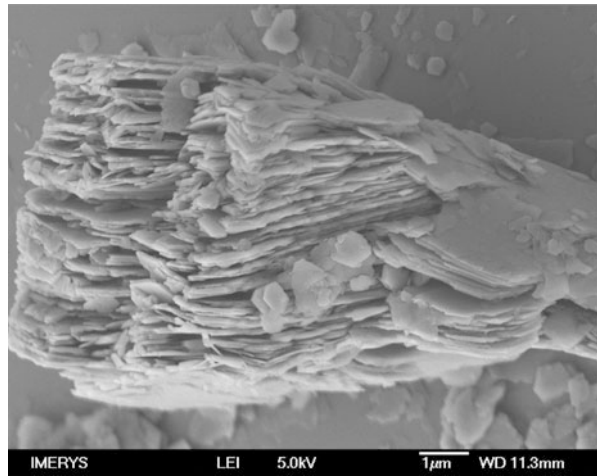
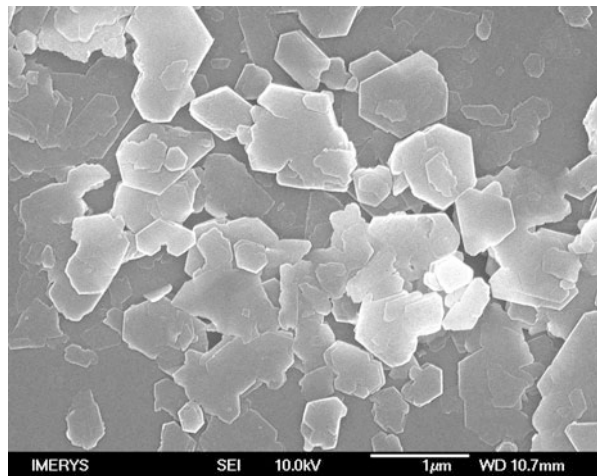


Fig. 2 Typical kaolinite plates (reproduced with kind permission from Imerys)



Properties

Pure kaolinite has the idealized chemical composition $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$. It is a crystalline material with a triclinic form found in microscopic pseudo-hexagonal 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, $\text{Al}(\text{OH})_3$, 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 flatness 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 degrittied 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 degrittied 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 m²/g, while the soft (non-reinforcing) ones are in the range 5–7 m²/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)

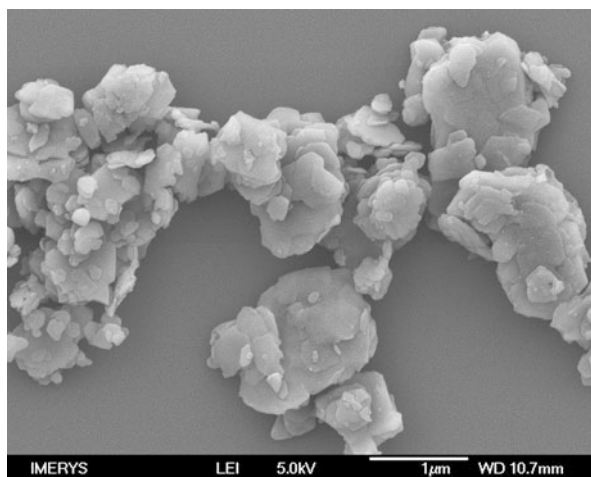


Table 4 Important properties of calcined products compared with uncalcined kaolin

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

^aNote 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

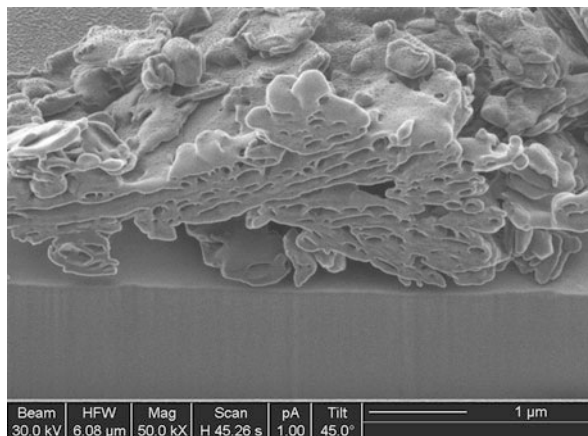
Metakaolin and the amorphous aluminosilicate produced at 980–1100 °C have approximately the same Mohs hardness of 4.0, specific gravity 2.6, and refractive index 1.6. Other important characteristics of typical products compared with kaolinite clay are given in Table 4. One of the principal attractions 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

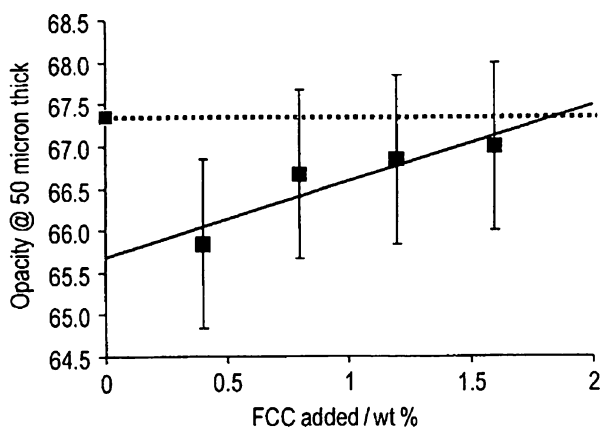
Internal porosity is the main differentiating feature of flash calcined clays. This results in a lower specific gravity and refractive index than standard calcination. The amount of porosity varies according to the flash calcination conditions, but typical results are given in Table 8.

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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