Graphitic Carbon Powders for Polymer Applications

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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).

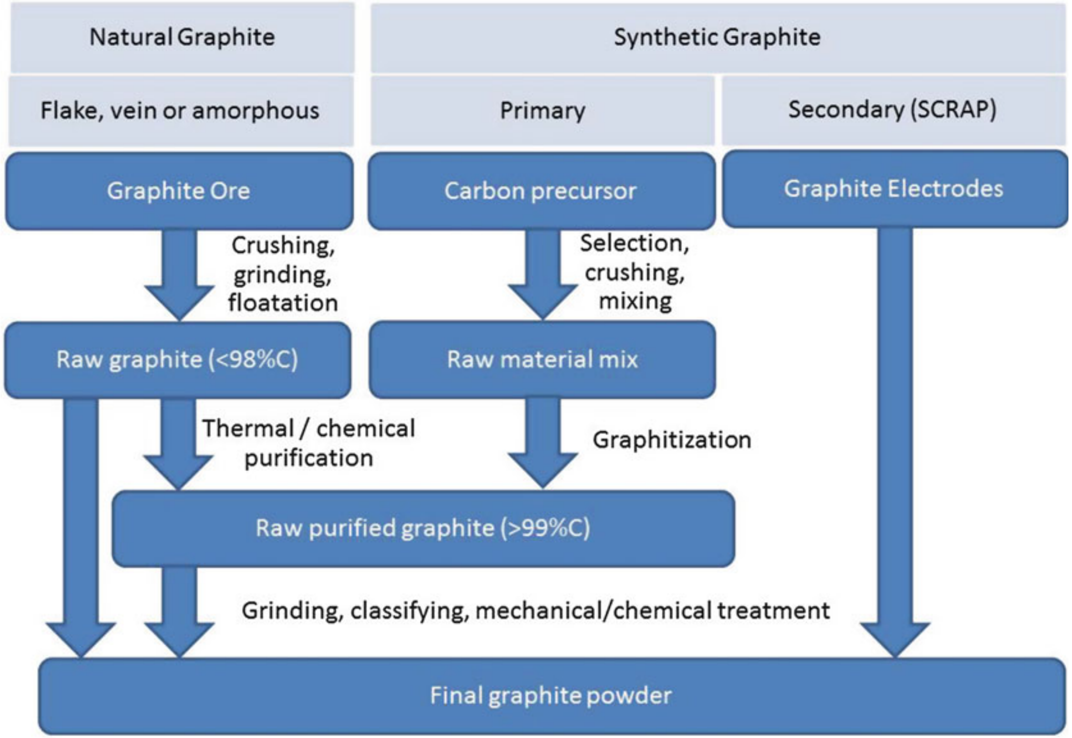

Fig. 1 Main steps of the synthetic and natural graphite manufacturing process

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,

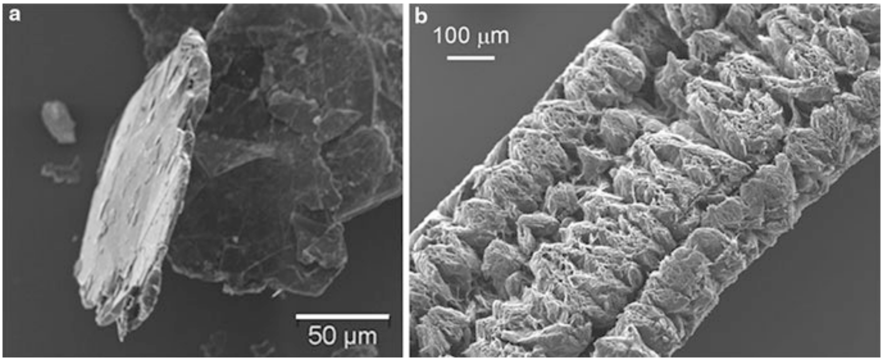

Fig. 2 SEM picture of (**a**) natural flake graphite and (**b**) expanded graphite

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

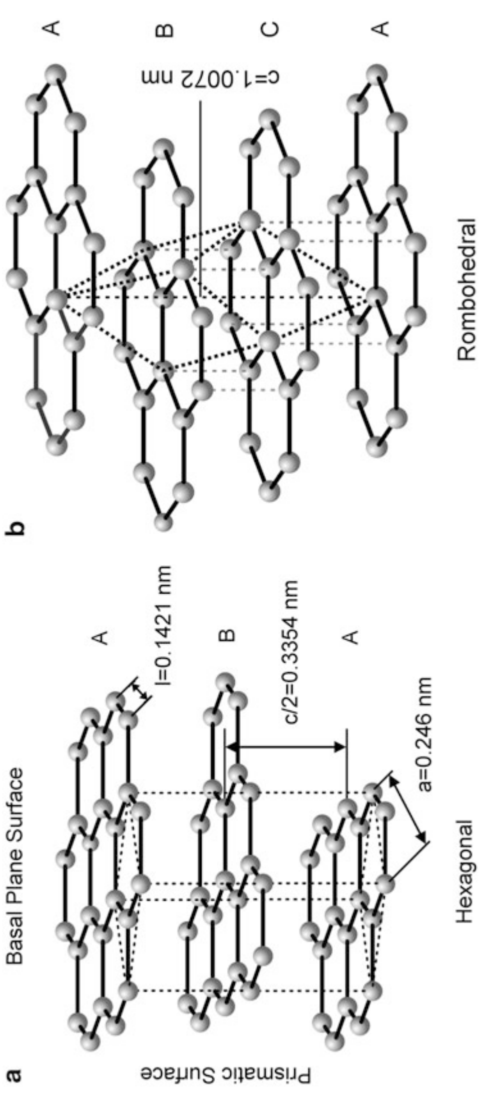

Fig. 3 The hexagonal and rhombohedral graphite crystal structure (from Spahr 2010)

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

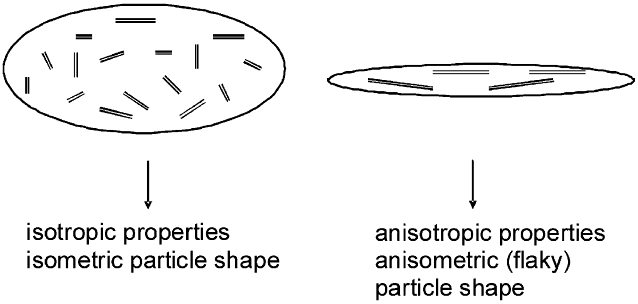

Fig. 4 Schematic of two graphite particle models with an extremely isotropic and an anisotropic graphite texture (from Spahr 2010)

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).

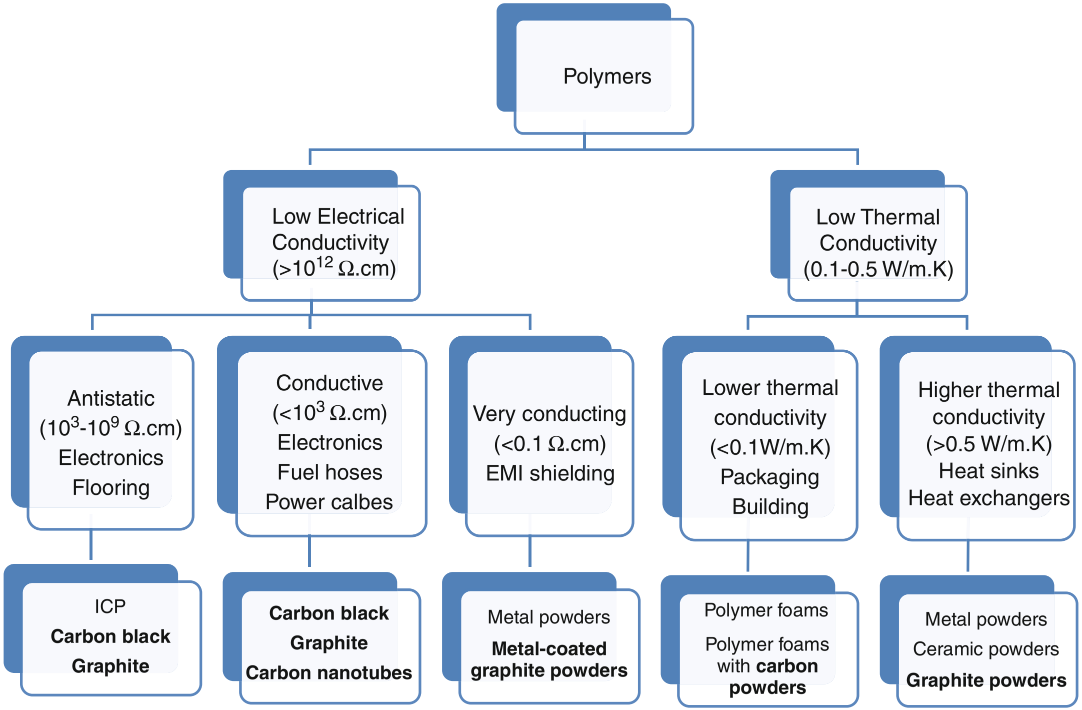

Fig. 5 Polymers are intrinsically, electrically, and thermally insulating. Depending on the application, higher conductivity values are required that can be obtained by polymer compounds with appropriate conductive fillers

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

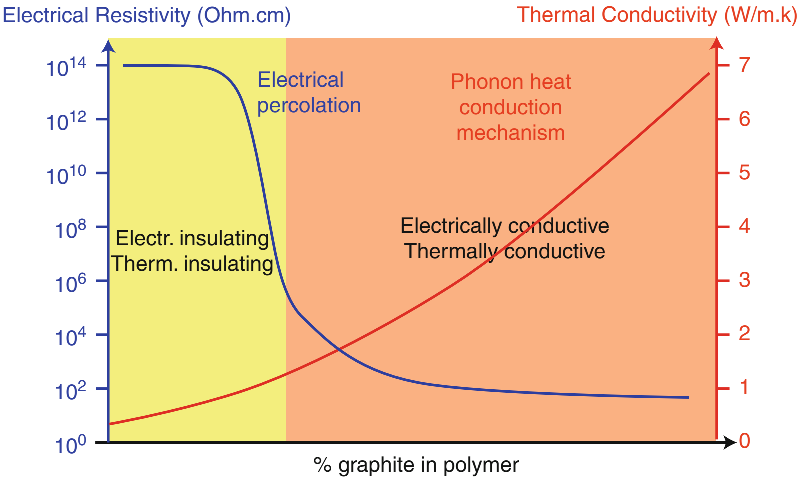

Fig. 6 Schematic view of electrical and thermal conductivity as a function of graphite loading in polymer composite. The electrical resistivity decreases sharply at the percolation threshold, whereas the thermal conductivity increases smoothly

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

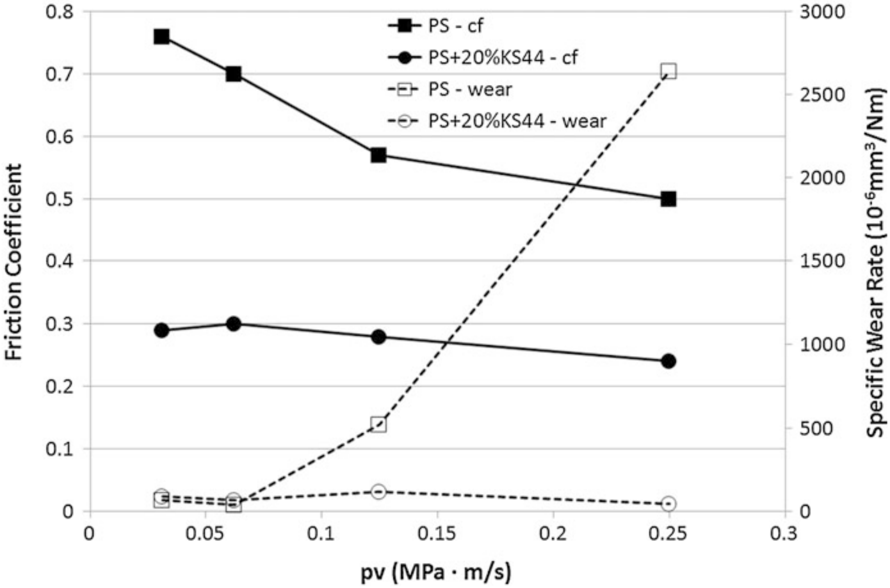

Fig. 7 Friction coefficient and wear rate as a function of tribological stress for virgin PS and graphite-filled PS compound

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

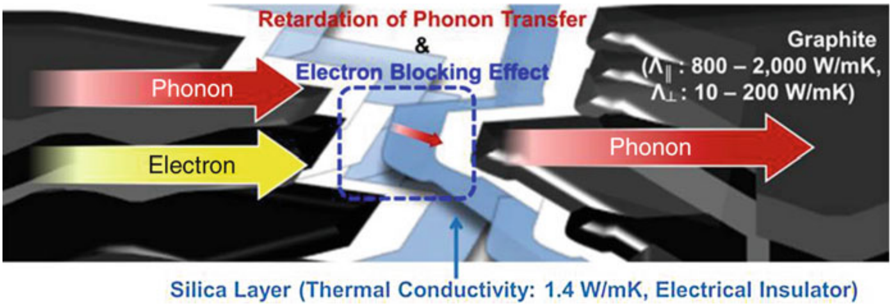

Fig. 8 Illustration of the retardation of phonon transfer and electron blocking effect of silica-coated graphite. The size of the *red arrow* indicates the heat flux (reprinted from Choi et al. (2013) with permission from Elsevier)

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

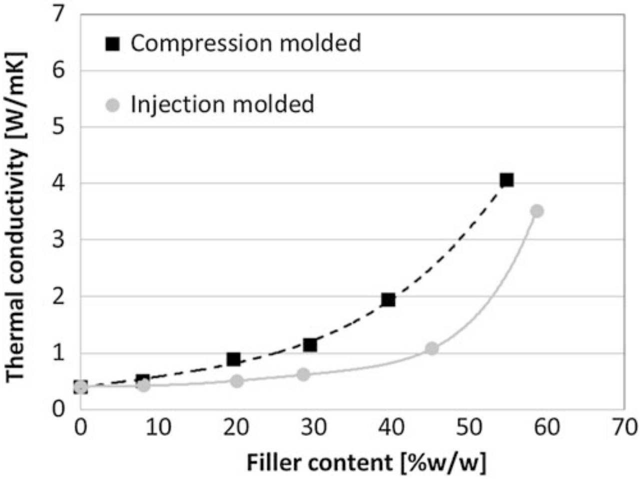

Fig. 9 Through-plane thermal conductivity of compression (*squares*) and injection-molded (*circles*) HDPE samples loaded with TIMREX KS44 synthetic graphite

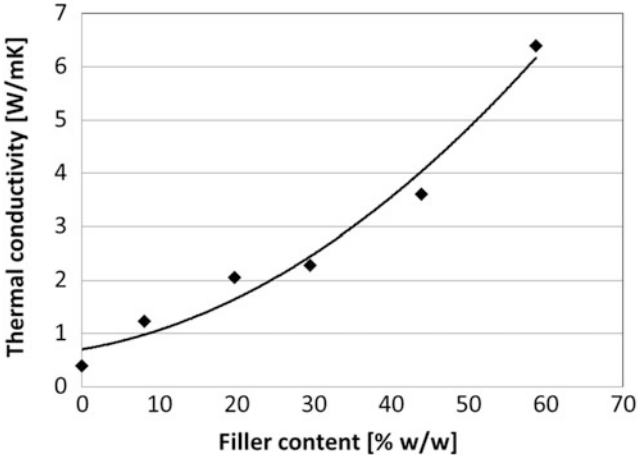

Fig. 10 In-plane thermal conductivity of injection-molded HDPE loaded with TIMREX KS44 synthetic graphite

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.

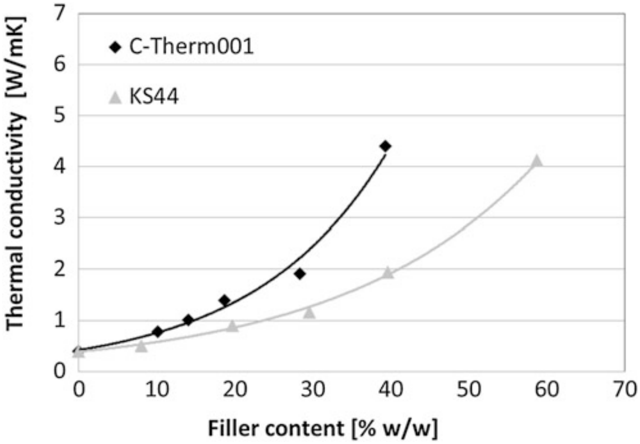

Fig. 11 Through-plane thermal conductivity of compression-molded TIMREX C-THERM 001 (*squares*) and TIMREX KS44 (*triangles*) synthetic graphite-loaded HDPE

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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