FILLERS

1. Introduction

By definition, fillers are used to extend a material and to reduce its cost. However, despite this fact that few inexpensive fillers, such as walnut shells, fly ash, wood flour, and wood cellulose, are still being used purely for filling purposes, nearly all fillers employed provide more than space filling. Considering their relative higher stiffness to the material matrix, they will always modify the mechanical properties of the final filled products, or composites. Fillers can constitute either a major or a minor part of a composite. The structure of filler particles ranges from precise geometrical forms, such as spheres, hexagonal plates, or short fibers, to irregular masses. Fillers are generally used for nondecorative purposes in contrast to pigments, although they may incidentally impart color or opacity to a material. Additives that supply bulk to drugs, cosmetics, and detergents, often referred to as fillers, are actually applied as diluents because their primary purpose is to adjust the dose or concentration of a product, rather than modify its properties or reduce cost. Fibers and whiskers are not discussed here because they are generally regarded as reinforcements, not fillers, although a majority of the fillers discussed here have reinforcing effects. Also, fillers and additives that primarily modify or impart electromagnetic properties, such as electrical conductivity, are not discussed.

The first manmade composites appeared in ~5000 BC in the Middle East region, where pitch was used as a binder for reeds in building boats. Although glass fiber was known to be used by Phoenicians for bottle making, the use of fillers to modify the properties of a material started in early Roman times, when artisans used ground marble in lime plaster, frescoes, and pozzolanic mortar. It was not until the establishment of the modern polymer industry in the mid-nineteenth century that the rapid development of commercial fillers occurred. The first polyester resin was prepared by the Swedish chemist Berzelius in 1847, although the first commercial plastic was not forthcoming until 1862 when Parkes introduced a cellulose nitrate plastic. With the marketing of Bakelite resin in 1909, a phenol–formaldehyde plastic filled with paper or

Table 1. **Fillers Used in Commercial Polymers**

Particulate		Fibrous	
Organic	Inorganic	Organic	Inorganic
wood flour	glass	cellulose	whiskers
cork	calcium carbonate	wool	asbestos
nutshell	beryllium oxide	carbon/graphite	glass
starch	iron oxide	aramid fiber	mineral wool
polymers	magnesia	nylons	calcium sulphate
carbon	magnesium carbonate	polyesters	potassium titanate
proteins	titanium dioxide		boron
carbon nanotube	zinc oxide		alumina
	zirconia		metals
	hydrated alumina		
	antimony oxide		
	metal powder		
	silica		
	silicates		
	organo-nanoclays		
	clays		
	barium ferrite		
	silicon carbide		
	potassium titanate		

cloth, along with the usage of carbon black fillers by B. F. Goodrich in natural rubbers, the modern age of filled polymers was ushered in.

Fillers can be classified according to their source, function, composition, and/or morphology. No single classification scheme is entirely adequate due to the overlap and ambiguity of these categories. Considering some examples of fillers used in modern polymers listed in Table 1 (1), the emphasis of this article is on particulate fillers. Extensive usage of particulate fillers in many commerical polymers is for the enhancement in stiffness, strength, dimensional stability, toughness, heat distortion temperature, damping, impermeability, and cost reduction, although not all of these desirable features are found in any single filled polymer. The properties of particulate-filled polymers are determined by the properties of the components, by the shape of the filler phase, by the morphology of the system, and by the polymer-filler interfacial interactions.

2. Physical Properties of Fillers

The overall value of a filler is a complex function of intrinsic material characteristics, such as average particle size, particle shape, intrinsic strength, and chemical composition; of process-dependent factors, such as particle-size distribution, surface chemistry, particle agglomeration, and bulk density; and of cost. Abrasion and hardness properties are also important for their impact on the wear and maintenance of processing and molding equipment.

2.1. Particle Morphology, Shape, Size, and Distribution. Filler particles come in a variety of shapes and sizes. In general, for most polymer applications, the filler size required is $<40\ \mu$. Finer particles, $<3\ \mu$, provide stronger enhancements in properties. Nanoparticles, with dimensions ranging up to 100 nm, deliver the strongest enhancements when they all are properly dispersed. Due to increases in both the surface area and the corresponding surface area to volume ratio with a reduction in filler particle size, finer particles are prone to agglomerate for the conservation of internal energy (2) and are more difficult to be dispersed.

The shape of an individual particle has great impact on the flexural modulus (3), permeability (4), and flow behavior (5) of a filled polymer. Although there are many ways to measure the shape (6) of a filler particle, the aspect ratio, or the ratio of the longest length of particle to its thickness, is most commonly used. A sphere, regardless of its size, has the lowest aspect ratio equal to 1.0. As a filler's shape progresses from a sphere to a block, to a plate, to a flake, the aspect ratio increases. The aspect ratio of a filler affects its packing and, hence, its loading level in a polymer. Theoretically, percolation, or filler networking, occurs when the volume fraction of monodispersed spherical particles reaches 0.156 (7). The increase in the filler's aspect ratio lowers the percolation threshold and this reduction, in turn, is of critical importance in loading electrical conductive fillers in a material to achieve electrical conductivity (8).

Almost all fillers do not exist as the discrete individual particles of their primary structure. They form aggregates, ie, secondary structure, which can agglomerate into tertiary structures in the material to be filled. An aggregate is a collection of primary particles that are chemically bonded together. The surface area of an aggregate is less than the sum of surface areas of all primary particles in that aggregate. In general, aggregates are extremely difficult to be broken down into individual primary particles by physical methods such as mechanical mixing. The union of aggregates, although weakly associated through nonbonded physical interactions, leads to an agglomerate. Filler materials often exist as agglomerates in their natural state. The total surface area of an agglomerate is similar to the sum of individual surface areas of aggregates in that agglomerate. The mixing and dispersion of fillers in a material involves primarily the incorporation and distribution of filler pellets or powders, and breakdown into agglomerates, then into aggregate structures.

In any commercial filler grade, there exists a collection of multiple shapes and sizes. The particle size and shape distributions of fillers can be best measured by direct microscopic inspection together with image processing although there are other methods to determine particle sizes and shapes. The size distribution of fillers that are >40 μ and are also moderately spherical in shape could be determined conveniently by sieving in accordance to the ASTM E-11-70 sieve designation. The Coulter technique could be used to measure fillers in sizes ranging form 4–40 μ. Filler particle-size distributions <4 μ could be obtained by sedimentation, permeametry, or light scattering methods (9,10). Laser light scattering method can now analyze particles ranging from 0.05 to 2,000 μ. Most descriptions of particulate fillers are given in terms of equivalent spherical diameter, ie, the diameter of a sphere having the same volume as the particle. Although microscopy can provide direct observation of filler particles, two-dimensional (2D), instead of the true three-dimensional (3D), size and shape distributions are acquired in most cases. Statistical transformation of a 2D size distribution into a 3D size distribution for near spherical, randomly distributed, particles can be performed (11).

2.2. Intrinsic Strength, Hardness, and Abrasivity. The intrinsic strengths and moduli of some crystalline fillers can be calculated along the crystallographic axes using molecular simulation (12,13). For these crystalline fillers, such as talc and mica, the common fracture results from the delamination between the crystalline planes. As for the hardness, the primary measure is based on the Mohs hardness scale, which is an empirical hardness measure according to the ability of one material to scratch another (14). The Mohs hardness goes from 1, such as for talc, to 3, such as for calcite, to 7, such as for quartz, to 10, such as for diamond, on a nonlinear scale. Abrasivity of a filler particle depends on its hardness, but also on its size and shape. Particles with sharp edges or rod shapes are more abrasive than those of smooth and round particles, and large particles are more abrasive that smaller particles of the same shape. Additionally, the coefficient of friction, surface treatment, surface energy, and purity of a filler all affect its abrasivity. Purity is important since one of the most common contaminants in natural fillers is the highly abrasive sand.

2.3. Surface Area, Chemistry, Wetting, and Coupling. Available surface areas of fillers include surfaces of filler aggregates and agglomerates and surfaces in their pores, crevices, and cracks. Measured values of surface area of fillers vary depending on the measurement methods. The direct method of surface area summation from microscopic imaging of filler particle size distribution typically yields a lower surface area value due to the inability to measure surfaces in pores–crevices by microscopy. In practice, surface area is determined from the measured nitrogen adsorption assuming monolayer coverage on the filler particle surface (15) according to the BET theory (16) and is expressed in square meters per gram (m^2/g).

The chemical compatibility between the filler surface and a polymer to be filled is critically important in both the wetting and dispersion of this filler by the polymer and the final physical performance of the resulting filled polymer. Filler surfaces are commonly defined, according to water affinity, as hydrophilic, which has a high affinity for water, to hydrophobic. Many commercial fillers, especially mineral types, are surface coated or chemically treated with hydrophobic wetting agents to modify their surface chemistry, to alter wetting characteristics and to aid their dispersion in organic polymers, particularly in nonpolar polymers. These wetting agents also assist in deagglomerating filler particles which, in turn, allow for higher filler loadings with lower viscosities during filler incorporation. A filler particle's oil or water absorption value provides an indirect measurement of filler relative wetting properties. The wettability can also be estimated by the contact angle (17) measured between a drop of water or oil and the filler surface. Commercial wetting agents typically include polymeric esters, stearates, fatty-acid esters, and organosilanes among which the organosilanes are the most widely used.

Organosilane wetting agents are also called silane coupling agents and, in general, consist of a trialkoxy group and a functional group having a $(RO)_3{-}Si{-}R^*$ structure. The trialkoxy $(RO)_3$ group provides chemical interactions or reactions with functional groups on the filler surface, and the R^* functional group delivers compatibility with the polymer matrix across the silane coupling bridge. This functional group can be selected from various chemical groups, such as isobutyl, mercapto, aminopropyl, methacryl, vinyl, epoxy, or haloalkyl, in accordance to the desirable interactions required with the polymer matrix (3). However, the extent and uniformity of the alkoxide reaction with a filler particle's surfaces vary depending on the treatment method. The pretreatment of fillers generally results in a more uniform reaction with a coupling agent than that obtained by mixing all ingredients in an internal mixer, particularly under low shear conditions.

2.4. Loading and Density. The amount of filler in a filled polymer is termed the loading and is always expressed quantitatively although the quantitative measures vary from industry to industry. In plastics and rubber industries, filler loading is formulated according to parts of filler used per 100 parts of polymer (phr), weight percent (wt%), or volume percent (vol%). In the paint industry, volume percent pigment (filler) in the dry paint film or the volume ratio of filler to binder is commonly used. In the paper industry, filler weight percent of sheet weight or percent ash based on a loss-on-ignition method is applied.

The optimal loading of fillers in a polymer is a balance between physical property enhancement and trade-off, and processing and material cost over the filler loading range. A theoretical maximum filler loading based on packing efficiency of monodispersed particles sets the upper limit of filler loading. The maximum volume fraction of spherical fillers in a hexagonal close packing is 0.74, whereas the maximum volume fractions achievable in a random close packing and in a cubic packing are 0.64 and 0.52, respectively (18). In practice, the maximum packing varies with particle shape, particle size distribution, and state of particle agglomeration. Agglomerates and nonspherical particles generally have smaller maximum packing than that of spheres (19). It is possible to achieve maximum packing with minimum void volumes by having very wide particle-size-distribution (20). Except in a few cases, it is difficult to predict the maximum volume fraction from theory.

The average mass per unit volume of the individual particle is the true density or specific gravity of the filler. It is used to calculate the volume fraction of fillers and is determined by a simple liquid displacement method for large, nonporous, and spherical particles. Densities of finely divided, porous, and irregular fillers are typically measured by a gas pycnometer that ensures all pores and crevices of filler agglomerates are penetrated. Apparent, or bulk, filler density refers to the total amount of volume occupied by a given mass of dry fillers and it includes the void volumes in the filler aggregates and agglomerates. Bulk density is used in weighting fillers during filler purchasing, shipping, and storage.

3. Filled Polymers

It is probably true that all polymers contain some form of additive, ranging from small fractions of catalyst residue to large-scale incorporation of fillers. Fillers commonly used in plastics and rubbers and their primary functions have been extensively discussed (21,22). In paper, fillers, such as clay, kaolin, talc, calcium carbonate, or silica, and pigments, such as titanium dioxide, are typically added in a pulp slurry prior to its deposition onto the wire for paper making. Similarly, these types of fillers along with pigments are incorporated into paint formulations prior to paint application. All fillers are employed for such reasons as processing improvements, mechanical reinforcements, thermal stability, optical properties, permeability reduction, or cost saving.

3.1. Rheology and Processability.

The presence of fillers affects the flow characteristics of the filled polymers. The immediate effect of a filler is to increase viscosity, interfere with the polymer flow pattern in a given process, produce thixotropy, and to give rise to machine wear. The relevant properties of the filler are concentration, size, aspect ratio, stiffness, strength, and specific interaction between filler and the polymer matrix. Within these are the special cases of easily deformable fillers that could easily be broken down or shaped during flow.

In a simplest case with nondeformable, or rigid, spherical fillers in a very diluted concentration, the viscosity of the filled Newtonian polymer melt can be predicted by a simple Einstein equation (23).

$$\eta = \eta_s\ (1 + 2.5\ \phi) \tag{1}$$

Here, the viscosity of the filled polymer, η, is related to the viscosity of the polymer, η_s, and the filler volume fraction, ϕ. At higher filler concentrations where the particles start to physically interact with one another, the Einstein equation is no longer applicable.

When filler spheres are close enough, hydrodynamic interactions between particles need to be considered. By factoring in the effects of two-body interactions, a modified equation was derived that is applicable up to $\phi = 0.1$ (24).

$$\eta/\eta_s = 1 + 2.5\phi + 6.2\phi^2 \tag{2}$$

For filled Newtonian polymer melts of even higher filler volume fractions, a general empirical expression can be used to calculate shear viscosity of the composite (25).

$$\eta/\eta_s = (1 - \phi/\phi_{\mathrm{m}})^{-[\eta]\phi_{\mathrm{m}}} \tag{3}$$

Here, ϕ_{m} is the maximum packing volume fraction and its value and $[\eta]$ have been tabulated (26) for a variety of particles from spheres to glass fibers. It needs to be emphasized that at high filler loading the particle size distribution has a strong effect on viscosity.

With an increase in filler concentration that exceeds the filler percolation threshold, a loose filler network is formed that would show elastic behavior, and in particular, a yield stress or thixotropy (5,27,28). This non-Newtonian behavior is not limited to filled polymers with high filler concentrations. Many polymer melts are viscoelastic and non- Newtonian. In these filled polymer melts, flow behavior is governed by viscoelastic properties of polymer compounded by the diverse properties of densely packed fillers and cannot be modeled and predicted theoretically. However, fine and particulate fillers are known to suppress elasticity of viscoleastic gum rubbers and render them better processability, such as less die swell, less shrinkage, and less melt fracture.

3.2. Mixing and Dispersion. In preparation of filled polymers, the process of uniformly distributing fillers without forming any filler composition gradients is most important. The process of mixing consists of three basic elements: incorporation, distribution, and dispersion. These elements occur simultaneously throughout the mixing cycle. Incorporation, which predominates the early stage of mixing, involves blending of separate ingredients into a coherent, although still inhomogenous, mass. In the distribution step, homogenizing occurs in which the ingredient become randomly distributed throughout the polymer matrix.

Dispersion is specifically concerned with the breakdown of filler agglomeration or physical association. It consists of three stages: initial wetting, breakdown of agglomerates, and intimate wetting of particles to displace air pockets. Dispersion becomes increasingly more difficult as particle size decreases and as processing continues. The actual choice of mixing and dispersion process and equipment depends on cost and polymer-filler system. Typically, it involves the high-viscosity shear mixing, such as internal mixing, blade mixing, and single or twin screw extrusion.

The lower the filler loading, the more physical mixing is required to attain a suitable distribution. It is for this reason that the technique of masterbatching, a concentrated mix of polymer and filler, is commonly used in polymer compounding for adding smaller amounts of filler in a polymer by diluting the masterbatch with the polymer. The acceptable level of mixing depends on the particular filled polymer system and its property requirements. Not all filled polymers require fillers to be completely randomized.

3.3. Mechanical Properties. In addition to the hydrodynamic effects of particulate fillers on polymer flow behavior, an enhanced stiffening effect is observed in filled polymers. For soft polymers, such as elastomers, with diluted filler loading, effects of filler on modulus are proportional to that on viscosity and can be represented by the Einstein equation, equation (1), with viscosity terms replaced by modulus terms. However, this viscosity to modulus relationship only holds when the polymer is incompressible, such as elastomers with Poisson's ratio of 0.5, and when the rigidity of the filler is very much greater than that of the polymer.

The Guth-Gold model (29) is an extension of the Einstein model, whereby interactions of neighboring particles are incorporated. Normalized initial moduli, normalized against the polymer modulus, of filled polymers are related to the filler volume fraction by a polynomial series as:

$$E/E_{\mathrm{s}} = (1 + 2.5\ \phi + 14.1\ \phi^2) \tag{4}$$

Here, E_s is the modulus of the polymer and ϕ is the filler volume fraction. Further modification of the Guth-Gold model leads to the Guth model (30) in which a geometric factor, g, was introduced. The Guth model is shown below.

$$E/E_{\mathrm{s}} = (1 + 0.67\ g\phi + 1.62(g\phi)^2) \tag{5}$$

This geometric factor is applied to account for the fact that the filler aggregate structure could affect the stiffness strongly at high filler loading and represent initially the ratio of the length to the width of the filler aggregate. Typically, g is used as a fitting parameter and has a value between 4 and 10. According to 3D finite element simulations with randomly placed filler particles in polymers, the modulus enhancement of filled polymers can be well modeled by amplification of the first stretch invariant (31,32). The polynomial amplification factor employed for the stretch invariant is similar to the Guth-Gold model but with different prefactor for ϕ^2 term.

Although the modulus increases for polymers upon filler addition, the tensile strength and elongation to break values do not follow the same relationship. Tensile strengths of rigid polymers filled with rigid fillers, in general, decrease with increasing filler loading due to stress concentration effects. However, for some filled soft elastomers, tensile strength increases with an increase in filler concentration, up to an optimal concentration (33). Other factors that could affect the ultimate tensile properties are interfacial adhesion, particle size, and geometric shape. Large particles give rise to higher stress concentration and thus lower tensile strength, than do smaller particles. It is for this reason that fillers used, especially in elastomers, are preferred to be smaller than micron size.

Rigid fillers, in general, cause a decrease in elongation to break since, proportionally, more of the experimental strain is being sustained by intrinsically less polymer. Additionally, the actual strain experienced by the polymer matrix is much higher than the applied strain around rigid fillers (34). For filler particles that have good adhesion with the polymer matrix, it was found that the elongation to break of the filled polymers, ε, follows (34,35)

$$\epsilon = \epsilon_{\mathrm{s}}\ (1 - \phi^{1/3}) \tag{6}$$

where ε_S is the elongation to break of the unfilled polymer. If there is poor adhesion between fillers and the polymer matrix, the decrease in elongation to break with increasing filler loading is more gradual than that calculated from Equation 6. However, there are cases where fillers promote craze formation that give rise to an increase in elongation to break with filler addition (36).

Rigid fillers in a rigid polymer generally decrease the impact strength of a polymer (37). Impact strength in a filled polymer is largely determined by the dewetting and crazing phenomena. Typically, dewetting and cavitation at the poles of spherical particles during tensile loading of polymers occur first, followed by crack–craze formation at the equators of filler particles (38). Although debonding and crack formation lower the strengths in filled polymers, there are cases in which the actual fracture energy of brittle plastics, such as polyesters and epoxies, increase in the presence of fillers. It is believed that, in these cases, fillers can impede crack growth (1). Additionally, rigid polymers filled with elastomeric particles could have high impact strengths if good interfacial adhesion exists between fillers and polymers (39).

3.4. Thermal Properties. Since polymers generally have a much larger thermal expansion coefficient than most rigid fillers, there is a significant mismatch in thermal expansion in a filled polymer. This mismatch could lead to generation of thermal stresses around filler particles during fabrication and, most severely, induce microcracks at the filler interface that could lead to premature failure of the filled polymer. As for the thermal expansion coefficient of a filled polymer, it generally falls below the value calculated from the simple rule of mixtures but follows the Kerner equation (40) for nearly spherical particles.

$$\alpha = \alpha_1\phi_1 + \alpha_2\phi_2 - (\alpha_1 - \alpha_2)\phi_1\phi_2(1/B_1 - 1/B_2)/(\phi_1/B_2 + \phi_2/B_1 + 3/4\ G) \tag{7}$$

The volume coefficients of thermal expansion of the composite, polymer, and filler are α, α_1, and α_2 respectively. The bulk moduli of the components are B_1 and B_2, respectively. The parameter G is the shear modulus of the polymer. The more the filler particles deviate from spherical, the greater the divergence of the thermal expansion coefficient from this equation. In such cases, the Thomas equation (41), or the logarithmic rule of mixtures, provides a better estimate.

$$\log\,\alpha = \phi_1 \log\,\alpha_1 + \phi_2 \log\,\alpha_2 \tag{8}$$

Polymers have lower thermal conductivity compared to metals and many inorganic materials (1). By the incorporation of metal or carbon fillers, a substantial increase in thermal conductivity can be obtained. Considering that thermal conductivities of filled polymers typically lie in between the limits set by rule of mixtures, Ziebland (42) proposed the use of the arbitrary relationship:

$$\log\,k = \phi_1 \log\,k_1 + \phi_2 \log\,k_2 \tag{9}$$

where k and k_1 are the thermal conductivities of the composite and polymer, respectively. The parameter k_2 is the hypothetical thermal conductivity of the particulate filler and it is determined from a one-point solution based on a single reading on the filled polymer of known composition. It is noted that this equation is similar to that of the Thomas equation for thermal expansion coefficient.

The melting temperature of a crystalline polymer is largely unaffected by the presence of fillers whereas the glass transition temperature of a polymer is slightly raised by fillers. But the increase in heat distortion temperature in the presence of fillers could be quite substantial, often by as much as 10–20°C or more. In general, fillers raise the heat distortion temperature of a material by the increase in modulus and the reduction in high temperature creep of a material in the presence of fillers (43–45).

3.5. Optical Properties. The use of fillers has indirect effect, or direct in the case of pigments, on the optical properties of polymers. The light transmissivity in a filled polymer is controlled primarily by light scattering which, in turn, depends on the differences in refractive indexes between the polymer and filler. A filler with a refractive index near to that of the polymer, such as silica in polyester, can provide a translucent filled polymer. If the filler is optically anisotropic, such as calcite and talc, the corresponding filled polymers may appear in color under the polarized light or by optical interference. When the filler particle size is smaller than the wavelength of the light, $<0.4\ \mu$, the filled polymer becomes transparent, which is one reason for the interest in using nanofillers.

3.6. Permeability. High aspect-ratio plate-like fillers can drastically lower the diffusivity or permeability of gases in solid polymers. Experimentally, it has been demonstrated that the barrier properties of a polymer could be significantly improved with just a few percent of exfoliated high aspect-ratio silicate fillers (46–49). Without considering the possible changes in the local permeability values due to molecular-level transformation by the presence of silicates, this permeability reduction simply arises from the increase in diffusion path lengths. Since molecules are now required to make long detours around the platelets, Nielsen (4) developed a simple model to determine the reduction in permeability in a polymer by accounting for the increase in torturosity with impermeable and planarly oriented platy fillers.

$$P/P_\mathrm{s} = (1-\phi)/(1+a\phi/2) \tag{10}$$

Here, P is the permeability, P_s is the permeability of the polymer without fillers, ϕ is the filler volume fraction, and a is the aspect ratio. Cussler and co-workers (50) and Fredrickson and Bicerano (51) provided further refinements of the model by removing the position order but with perfect orientation. Recently, Gusev and Lusti (52) conducted direct 3D finite-element permeability calculations with a multiinclusion computer model comprising of randomly dispersed, perfectly oriented, and nonoverlapping platelets. They found all their numerical simulated permeability values could be well represented with a stretched exponential function as

$$P/P_\mathrm{s} = \exp\left[-(a\phi/3.47)^{0.71}\right] \tag{11}$$

This Gusev and Lusti equation, despite its empirical nature, has been demonstrated to model excellently the literature data for nylon-layered silicate nanocomposites.

4. Filler Types

4.1. Mineral Fillers. Mineral fillers (21,53) are naturally occurring materials that are mined and are ground to a specified particle size. Grinding may be done dry using mechanical mills. For a finer product the ore is ground wet. Wet grinding may be autogenous where the ore grinds by attrition with itself or a grinding media may be employed. Additional processing may include a combination of steps. They include (*1*) separation of fine and coarse particles by use of screens, by air- or water flotation, or by centrifugal filtration; (*2*) removal of impurities by washing, heat treatment, magnetic separation, or chemical treatment; and/or (*3*) surface treatment with a variety of chemicals to improve the compatibility with the polymer matrix.

Calcium carbonate ($CaCO_3$), also known as whiting, limestone, marble, chalk, or calcite, that has been ground, is added to polymer compounds to reduce cost and to impart hardness and opacity to polymer articles. Particle sizes range from 2 to 80 μm for dry-ground product and from 0.5 to 11 μm for wet-ground product. The chemical composition and crystalline nature depend on the limestone deposit that is mined, eg, chalk or marble, and the color of the deposit. The most important applications of calcium carbonate by the polymer industry are uses in electrical wire and cable insulation where the low moisture content and natural insulating properties make it a preferred filler, in the production of articles where low cost and smooth surface appearance are desired, such as footwear, and in extruded hoses and automotive sealing parts. Typical calcium carbonate levels used in polymer compounds range from 20 to 300 phr.

Baryte is predominately barium sulfate ($BaSO_4$) that is available in particle sizes from 1 to 20 μm. It is used as a filler when a high specific gravity is required of the polymer article. Typical polymer loading levels are 25–100 phr for articles such as stoppers and seals.

Crystalline silica (SiO_2) from sand or quartz can be ground and used as a degrading or extending filler for low cost polymer articles. To minimize the health hazards of exposure to airborne crystalline silica, particle sizes are large, normally ranging from 2 to 20 μm. Naturally occurring silica (SiO_2) or dolomite is often referred to as diatomaceous earth since the primary deposits are the exoskeletons formed by diatoms that have extracted silicic acid from sea water and formed amorphous silica shells. Diatomaceous earth is usually very high in surface area because the shells retain the radial and/or rod-like structures of the living creature. The largest deposits are several million years old and have been partially converted to crystalline silica over time. Diatomaceous earth obtained from sedimentary rocks often contains up to 30% organic matter and inorganic impurities such as sand, clay and soluble salts (54) requiring separation or treatment to remove crystalline content, which could represent a health hazard. Biogenic silica is used as a semireinforcing filler or as a solid carrier for liquid compounding ingredients.

Kaolin clay (55,56), also called Kaolinite or China clay, is hydrous aluminum silicate [$Al_2Si_2O_5(OH)_4$] consisting of platelets with alternating layers of silica and alumina in the structure. The fine particles of clay are formed by the weathering of granite. Clay deposits are classified as primary, secondary and tertiary. Primary deposits are mixtures of clay and granite that are found where the clay was originally weathered. They contain only 40–50% particles <2 μm in diameter. Secondary deposits are formed when fine particles from primary deposits are carried by water flow and are deposited in a new location. Tertiary deposits are the most important commercial deposits due to their fine particle size with >80% of the particles being <2 μm in diameter. Their high purity results when water carries the fine particles of a secondary deposit to a new location. The most significant deposits of tertiary clay in the world are found in the southeastern United States, in Cornwall, United Kingdom, in the Amazon region of Brazil, and in Australia. Clay is broadly divided into soft and hard clay in that they produce softer and harder polymer compounds, respectively, at a given loading level. Because clay is mined as a fine particle-size material, it does not require significant grinding for use in polymers. There are five basic processes for producing clay for polymer reinforcement from the mined form (*1*) Air-floated clay, in which the ore is milled to break up lumps and air classified, is the least expensive form of clay and imparts moderate reinforcement. (*2*) Water-washed clay involves gravity separation of impurities, bleaching, magnetic separation to improve color properties, and centrifuging to produce the desired particle size range to impart higher reinforcement by the control of pH, color and particle size. (*3*) Delaminated kaolin uses chemical and/or mechanical means to break apart the platelet structure of the clay, which further increases the available surface area and reinforcement properties. (*4*) Metakaolin is partially calcined by heat treating to 600°C. (*5*) Calcined clay is formed by heating to 1000°C, which produces a very white, high surface area mineral with an inert surface.

Clay is a widely used filler for polymer compounds of all types including components of tires such as fiber adhesive compounds, and the entire range of nontire polymer applications where good reinforcement, moderate cost and good processability is desired. Clays are usually added to polymer compounds at levels of 20–150 phr. The aspect ratio of clay is between 4 and 12 with average particle size ranging from 0.5 to 2.3 μm.

Talc [$Mg_3Si_4O_{10}(OH)_2$] is a platelet form of magnesium silicate with a high aspect ratio, 5–20. Because the platelets can orient in the extrusion process, it provides polymer extrudates with smooth surfaces that can be extruded at high rates. It is commonly used in compounds, which have critical surface appearance such as exterior automotive components or consumer goods. Talc is used in tires in white sidewall compounds to provide a smooth appearance to the buffed sidewall. The large platelets of talc provide a barrier to gas and moisture permeability in compounds which allows talc to be used in applications such as hydraulic and automotive hoses, barrier films and tire innerliners. Talc is usually used in addition to other fillers with total filler content of 30–150 phr. The average particle size of talc ranges from 5 to 8 μm.

Mica is a generic name given to a family of hydrous potassium aluminum silicates having similar physical properties. Mica is a common rock forming mineral and is found around the world. Muscovite and phlogopite micas are most commonly used. Muscovite mica, $K_2Al_4(Al_2Si_6O_{20})(OH)_4$, has a layer structure composing of three planes and has an average particle size of 5 μm. The center is a pseudo-octahedral gibbsite plane that is chemically bonded to two tetrahedra silica planes. Phlogopite mica, $K_2(Mg, Fe)_6(Al_2Si_6O_{20})(OH,F)_4$, with the same structure as that for Muscovite mica, and is opaque to ultraviolet (uv) radiation. Phlogopite mica has a particle size of 20 μm and has an aspect ratio from 30 to 100 similar to that of muscovite mica. The largest usage of mica is in polyolefins. The high aspect ratio of mica could provide enhancements in properties as stiffness, tensile strength, dimensional stability, and heat deflection temperature.

4.2. Nanoclays. Nanocomposites are materials that contain nanofillers, or fillers of nanometer dimensions. The successful synthesis of nylon–clay nanocomposites (57–59) ushered in nylon nanocomposites that could attain high modulus, heat distortion temperature, dimensional stability, impermeability, and strength with only a few percent modified clay nanofillers. Although it has been long known that polymers could be mixed with appropriately modified clay minerals and synthetic clays, the field of polymer-layered silicate nanocomposites has gained tremendous momentum since the initial publications. The nylon–clay nanocomposites have since been commercialized and were utilized for automotive timing-belt covers and packaging barrier films.

The layered silicates used in nylon–clay nanocomposites are 2:1 phyllosilicates with layers made up by fusing two silica tetrahedra to an edge-shared octahedral sheet of aluminum hydroxide. Isomorphic substitution within the layers, such as Al^{3+} replaced by Mg^{2+}, generates negative charges defined by the charge exchange capacity (CEC). Stacking of the layers leads to a gap between layers called the interlayer or gallery that is pristinely filled with exchangeable hydrated alkali metal cations to counterbalance these negative charges. Ion exchange of these alkali metal cations with various organic cations, such as alkyl ammonium cationic surfactants, could render the normally hydrophilic silicate surface hydrophobic. These layered silicates, or phyllosilicates, intercalated by organic cations are called organosilicates.

Commonly used 2:1 phyllosilicates include hectrite, saponite, montmorillonite, and synthetic mica. These silicates are stacks of layers of 1 nm in thickness and about 50 nm (hectrite), 170 nm (saponite), 200 nm (montmorillonite), and 1,230 nm (synthetic mica) in length (63). In particular, naturally occurring montmorillonite with CEC ranging from 0.9 to 1.2 mequiv/g, depending on the mineral origin, is most frequently used and was the type employed in the initial nylon–clay nanocomposites. Organosilicates consisting of alkyl ammonium-exchanged montmorillonites are also commercial.

The nylon–clay nanocomposites were prepared by *in situ* polymerization in the presence of organically modified, with aminolauric acid, montmorillonite. The reaction between nylon monomer and modified montmorillonite rendered nylon chains end-tethered though aminolauric acid to the silicate surface leading to exfoliated silicates (61). However, not all polymer nanocomposite systems could be produced via *in situ* polymerization processes due to the chemical sensitivity of polymerization catalysts. Direct melt blending of hydrophilic polymers with montmorillonite in its pristine state or polymers with surfactantintercalated montmorillonite was found to be possible to deliver polymer intercalated or exfoliated nanocomposites (60,62).

Commercial organosilicates based on montmorillonites are effective agglomerates of smaller, primary particles consisting of 10–20 layers in a coplanar orientation. Those primary particles are usually referred to as the tactoids. The first step of melt mixing is to break up the agglomerates of organosilicates to their primary particles through diffusion of polymer chains into the agglomerates. This, in turn, will provide fillers from micron in size with aspect ratios of about 1 to fillers of submicron, 0.1–0.2 μm, with aspect ratios of $\sim$20. The ultimate goal in melt mixing is to diffuse polymers into the silicate galleries to completely exfoliate organosilicates leading to fillers of 1-nm thick with aspect ratios of $\sim$200.

4.3. Synthetic Fillers. Synthetic fillers are generally manufactured by precipitation of soluble materials under carefully controlled conditions to provide tailored properties. They may be found as colloidal particles that may be spherical, ellipsoid, rod, or tube shaped, as aggregates which are covalently bonded groupings of individual particles, or as agglomerates that are loosely held associations of aggregates physically interacting. Reinforcement properties are a function of the colloidal particle size and shape, the aggregate dimensions and morphology, and the ability of agglomerates to break down during mixing. Additionally, the composition and surface chemistry of the filler plays a significant role.

Precipitated calcium carbonate is formed by dissolving limestone and precipitating $CaCO_3$ as very fine particles using carbon dioxide (Aroganite Process) or sodium carbonate (Solvay Process). Typical particle sizes range from 0.02 to 2 μm. Most commercially available precipitated calcium carbonate is spherical colloidal particles or aggregates consisting of a few spherical particles. Additional shapes and aggregates of varying morphology are possible and provide increased reinforcement. Precipitated calcium carbonate is used as a semi-reinforcing filler in shoe products and industrial polymer goods, particularly when resistance to alkali solutions is needed. The low moisture content and good reinforcement allow precipitated calcium carbonate to be used in wire and cable insulation applications.

Zinc oxide, which is formed from the burning of zinc metal, was the first non-black filler used for reinforcement of rubber compounds. Although zinc oxide and magnesium oxide are still used as a reinforcing filler in some specialty compounds, particularly those that require heat resistance, their role in rubber compounding in the last several decades is that of an activator for the sulfur cure system or as curatives for chloroprene rubber compounds.

The rutile form of titanium dioxide (TiO_2) is an important filler for white and colored polymer articles. The ability of the titanium dioxide particle to scatter light provides high whiteness and opacity to polymer, which gives the filler particle the ability to cover background colors. The anatase crystalline form of titanium dioxide is also used.

Alumina trihydrate ($Al_2O_3 \cdot 3H_2O$), ATH, is an intermediate mineral that is formed in the conversion of bauxite to aluminum. The major types of ATH are ground and precipitated. The alumina trihydrate is ground and classified using the same procedures as other minerals, and is available in particle sizes from <1 μm to several micrometers in diameter. Alumina trihydrate is used to provide flame-retardant properties to polymer articles and to suppress smoke formation. The water of hydration of the ATH crystal is released beginning at 230°C, which absorbs heat and provides water vapor to cool the polymer article and disperse smoke.

Amorphous silica (64) consists of ultimate particles of the inorganic polymer $(SiO_2)_n$ where a silicon atom is covalently bonded in a tetrahedral arrangement to four oxygen atoms. Each of the four oxygen atoms is covalently bonded to at least one silicon atom to form either a siloxane (—Si—O—Si—) or a silanol (—Si—O—H) functionality. Surface silanol groups can be isolated from one another such that hydrogen bonding between the silanols cannot occur, vicinal to one another promoting the formation of intramolecular hydrogen bonding, or geminal to one another where two silanol groups are bonded to the same silicon atom. Particulate silicas are made by precipitation from aqueous solution. The physical and chemical properties of precipitated silicas can vary according to the manufacturing process. Reinforcement and control of suspension pH, temperature, and salt content can vary the ultimate particle and aggregate sizes of silicas precipitated from solution. The surface area, as determined by nitrogen (16) or cetyltrimethylammonium bromide, CTAB adsorption (65), is a function of the ultimate particle size. Ultimate particles can range from 5 to 50 nm in diameter. Aggregates are 3D clusters of ultimate particles covalently bonded to one another via siloxane bonds, and range in size up to 500 nm in diameter. Aggregates can physically agglomerate through intermolecular hydrogen bonding of surface silanol groups of one aggregate to a silanol group of another aggregate affording structures up to ~100 μm in diameter. The median agglomerate particle size is generally 20–50 μm in diameter, but can be reduced in size by milling to ~1 μm. Precipitated silica is prepared from an alkaline metal silicate solution, such as sodium silicate in a ratio of ~2.5–3.3 SiO_2:Na, but using lower concentrations of silicate than is used in silica gel preparation (66). In the absence of a coagulant, silica is not precipitated from solution at any pH value (66). Silica is precipitated by adding acid to sodium silicate to reduce the pH value of the hot suspension to a pH value of 9 to 10, where the concentration of sodium ion exceeds approximately 0.3 N. Sulfuric acid is normally used to neutralize sodium silicate and precipitate silica.

Because of its small particle size and complex aggregate structure, precipitated silica imparts the highest degree of reinforcement to elastomer compounds among all of the non-black particulate fillers. This superior reinforcement is employed in a variety of polymer compounds for shoe soles, industrial polymer goods and tires (67–69). Precipitated silica is used in shoe soles for its resistance to wear and to tearing, its non-scuffing characteristics, and in order to obtain compounds with light color, or even a transparent material. Precipitated silica is used to improve the tear strength and resistance to flex fatigue (cracking, cut-growth) and heat aging in a wide variety of manufactured rubber goods including conveyor and power transmission belts, hoses, motor and dock mounts, and bumper pads. Rubber rolls that utilize the abrasion resistance, stiffness, and nonmarking characteristics of precipitated silica, are important for use in paper processing and the dehulling of grains, particularly rice (70).

Amorphous pyrogenic or fumed silicas are generally less dense and of higher purity than silicas precipitated from solution. They are much less hydrated and are sometimes completely anhydrous, with the surface silanol group density ranging from 2 to 4/nm^2 of surface area. The $SiCl_4$ can be burned with methane (CH_4) or hydrogen (H_2) gases to produce SiO_2, H_2O, and HCl, an important commercial method (71). Particle size is controlled by combustion conditions during the flame hydrolysis. Pyrogenic silicas with surface areas <300 m^2/g are essentially nonporous, while those with higher surface areas can have some porosity. They generally contain a few hundred ultimate particles fused into branched-chain, 3D aggregates (71). Pyrogenic silicas in the 100–2000-nm particle size range are common (72). Pyrogenic silica is used in applications which require a low level of surface water per unit surface area of the silica, primarily as a reinforcement in adhesives, sealants (73) and elastomer compounds based on silicone polymers (74,75). They are used as a thixotropic agent, free flow, antistatic agent, carrier, coating additive, and antifoaming agent (76).

Amorphous silicates (77) are precipitated from aqueous blends of soluble silicate, typically sodium silicate, and soluble salts of other metals. The most important types for reinforcement of elastomers are aluminosilicates with mixed Al_2O_2 and SiO_2 structures, magnesium aluminosilicates and calcium silicates. The silicates have surface areas and resultant reinforcement that span the range from the highest surface area clays ($\sim$30 m^2/g) to the lower end of the precipitated silicas ($\sim$100 m^2/g).

4.4. Nanoscale Oxides and Metals.

Using vapor-phase plasma-based techniques, precipitation sol–gel reaction or simple grinding, nanoscale metal oxides are being produced in competition with existing fumed oxide products (78). Based on physical vapor synthesis methods developed in the 1980s, zinc oxide nanoparticles are produced for use as a sunscreen and fungicide in personal care and cosmetics products. Using a pulsed plasma process, nanometals, such as aluminum and silver nanoparticles, and nanoscale oxides, are being produced. Potential commerical markets for nanometals include aluminum nanoparticles in explosives and pyrotechnics and silver nanoparticles in electronics and medicines.

4.5. Carbon Fillers.

The application of carbon black in rubber compounds is over a hundred years old. Unlike the well known crystalline forms of carbon, such as diamond and graphite, carbon black is amorphous and is a manufactured product (79,80). Carbon blacks are prepared by incomplete combustion of hydrocarbons or by thermal cracking. Presently, almost all rubber-reinforcing blacks are manufactured by the oil furnace process. A fuel is burned in an excess of air to produce finely divided carbon. Furnace blacks have low oxygen contents with neutral or alkaline surfaces. In the thermal process, oil or natural gas is cracked in an absence of oxygen to produce unoxidized blacks of small surface areas, or thermal blacks.

Many grades of carbon blacks are manufactured for various applications. These include blacks of higher surface area, different internal porosity, and higher surface oxidation. There are also electrical conductive blacks, such as acetylene black. The American Society of Testing Materials (ASTM) has established a carbon black classification system based on particle size and surface oxidation, ASTM D1765. The degree of surface oxidation affects the cure time of carbon-black filled rubber compounds. The "N" denotes normal curing blacks and the "S" refers to slow curing blacks. After N or S, the first number of the three-digit suffix identifies the particle size and the remaining two digits are assigned arbitrarily. Specifications are given both in terms of analytical processes of characterizing the black and of resulting physical properties of carbon-black filled rubbers prepared in standard recipes. In accordance to the designation, N550 black, for example, denotes a normal-curing carbon black with particle size in the range of 40–48 nm.

Carbon black owes its reinforcing character to the size, shape and surface chemistry of the aggregate structures that consists of primary particles essentially spherical in shape that are chemically bonded to one another (80). The two most important properties of carbon black are surface area and structure. Surface area depends inversely upon the size of the primary particles, and is one measure of the area available for physical interaction with the polymer. Surface area ranges from 10–140 m^2/g with thermal blacks having the lowest values based on nitrogen adsorption via ASTM D4820. The structure of carbon black depends on the size and grouping of these primary particles in the aggregate. The more primary particles in the aggregate, the higher structure of the carbon black due to the more complex shape and void volume (porosity). Structure varies from 35 to 130 $cm^{-3}/100$ g as measured by dibutylphthalate oil absorption via ASTM D2414. Surface activity refers to the strength of the carbon black/polymer interaction either from physical adsorption or chemisorption. The small (2–3%) but significant amount of non-carbon heteroatoms, such as hydrogen, oxygen and sulfur, that are present on the carbon black surface results in surface activity differences. During mechanical mixing with polymers, it is desirable to minimize the presence of agglomerates. Aggregate structures are not thought broken down into primary particles by simple mechanical processes.

Carbon blacks are extensively used in rubbers and elastomers, in loading from 10 to 150 phr, for improvements in stiffness, strength, processability, and abrasion resistance (79). Particle size and concentration are optimized based on balances in mixing–compounding, heat build up, property improvement, and cost. Carbon black fillers, without considering the electrical conductive blacks, are used in plastics predominantly as pigment or colorant.

4.6. Carbon Nanotubes.

Carbon nanotubes are graphene cylinders end capped with pentagonal rings. They were discovered in 1991 (81) during the arc-evaporation synthesis of fullerenes. The arc-evaporation method produces only multilayered tubes. Multiwalled nanotubes were first produced in 1983 before their structure was fully understood. These multiwalled nanotubes are sold in commercial quantities for electrostatic discharge control in polymers for electronic and automobile applications. Addition of metals to the graphite electrodes was found in 1993 (82) to synthesize single-layer-wall carbon nanotubes. An alternative method of preparing single-walled nanotubes was developed in 1996 (83) leading to the commercialization of single-walled carbon nanotubes, or buckytubes. Single-walled nanotubes have fewer defects and much improved performance compared to multiwalled tubes. The use of single-walled tubes in flat panel displays, conductive plastics, and high performance fibers are recent application developments.

5. Economic Aspects

Sales of fillers worldwide were estimated to be on the order of 10^6 t and $9 billion for 1990, with paint (42%), paper (21%), and plastics (16%) as the principal consumers on a dollar basis. When viewed on a volume basis, paint and paper are even at 37% each, plastics use 21%, and rubber 6%. Titanium dioxide represented 67% of the dollar volume, with 60% of its use in paint. The filler industry appeared to approach market saturation in 1998 (84) before the introduction of nano-fillers. The nanomaterials business, at the present time, consists of three lines; nanoclays, nanoscale oxides and metals, and carbon nanotubes. The most established market now is nanoclays. The nanomaterials market is expected to increase by 12.8%/year, to $900 million by 2005 (85). The global market for coupling agents used in plastics grew at about 7% in 2001 and was expected to reach $300 million (86). The coupling agent market has three major categories: silanes, which make up ~85% of demand; organometallics acount for 10%; and maleated polyolefins have 5%.

6. Health and Safety Factors

The principal hazard involved in the handling and use of many fillers is inhalation of airborne particles (dusts) in the respirable size range, ie, 10 μm and below. Filler dusts may be classified as nuisance particulates, fibrogens, and carcinogens. Nuisance particulates are dusts that have a long history of little adverse effect on the lungs and do not produce significant organic disease or toxic effect when exposures are kept under reasonable control. The American Conference of Governmental and Industrial Hygienists (AC-GIH) establishes TLVs for the airborne concentration of many fillers in workroom air (87). A new manner of occupational and environmental legislation is aimed at the hazards of ultrafine particles, and OSHA regulations effective in 1992 regulate the total workplace, including nonproduction areas (88). In addition, concern for the toxicity of many metals and their compounds is limiting the use of many fillers, eg, Pb, Co, Cr, and Ba compounds, and possibly the use of certain organometallic surface coatings. Suppliers have information on proper usage and handling of their products. The use of NIOSH–OSHA-approved dust masks or respirators is required when dust concentrations exceed permissable exposure limits. It has been reported that because of concerns by some international agencies over the possibility that crystalline silica might be a carcinogen, a 0.1% max silica (crystalline) specification has been mandated in mineral fillers (89).

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