

Part One

Polymers and Fillers

1

Polymers and Polymer Composites

Marino Xanthos

1.1

Thermoplastics and Thermosets

Almost 85% of the polymers produced worldwide are thermoplastics [1]. They can be divided into two broad classes, amorphous and crystalline, depending on the type of their characteristic transition temperature. Amorphous thermoplastics are characterized by their glass transition temperature T_g , a temperature above which the modulus rapidly decreases and the polymer exhibits liquid-like properties; amorphous thermoplastics are normally processed at temperatures well above their T_g . Glass transition temperatures may be as low as 65 °C for polyvinyl chloride (PVC) and as high as 295 °C for polyamideimide (PAI) [1]. Crystalline thermoplastics or, more correctly, semicrystalline thermoplastics can have different degrees of crystallinity ranging from 20 to 90%; they are normally processed above the melting temperature T_m of the crystalline phase and the T_g of the coexisting amorphous phase. Melting temperatures can be as high as 365 °C for polyetherketone (PEK), as low as 110 °C for low-density polyethylene (LDPE), and even lower for ethylene–vinyl acetate (EVA) copolymers [1]. Upon cooling, crystallization must occur quickly, preferably within a few seconds. Additional crystallization often takes place after cooling and during the first few hours following melt processing.

Over 70% of the total production of thermoplastics is accounted for by the large-volume, low-cost commodity resins: polyethylenes (PE) of different densities, isotactic polypropylene (PP), polystyrene (PS), and PVC. Next in performance and in cost are acrylics, acrylonitrile–butadiene–styrene (ABS) terpolymers, and high-impact polystyrene (HIPS). Engineering plastics such as acetals, polyamides, polycarbonate, polyesters, polyphenylene oxide, and blends thereof are increasingly used in high-performance applications. Specialty polymers such as liquid-crystal polymers, polysulfones, polyimides, polyphenylene sulfide, polyetherketones, and fluoropolymers are well established in advanced technology areas because of their high T_g or T_m (290–350 °C).

Common thermosetting resins are unsaturated polyesters, phenolic resins, amino resins, urea/formaldehyde resins, polyurethanes, epoxy resins, and silicones. Less

common thermosets employed in specialized applications are polybismaleimides, polyimides, and polybenzimidazoles. Thermosetting resins are usually low-viscosity liquids or low molecular weight solids that are formulated with suitable additives known as cross-linking agents to induce curing and with fillers or fibrous reinforcements to enhance both properties and thermal and dimensional stability. It has been frequently stated that in view of their excessive brittleness many thermosets would have been nearly useless had they not been combined with fillers and reinforcing fibers.

1.2

Processing of Thermoplastics and Thermosets

The operation by which solid or liquid polymers are converted to finished products is generally known as polymer processing. Polymer processing consists of several steps [2]:

- 1) *Preshaping* operations involving all or some of the following individual operations:
 - handling of particulate solids (particle packing, agglomeration, gravitational flow, compaction, and others);
 - melting or heat softening;
 - pressurization and pumping of the polymer melt;
 - mixing for melt homogenization or dispersion of additives;
 - devolatilization and stripping of residual monomers, solvents, contaminants, and moisture.The common goal of the above operations is to deliver thermoplastics or cross-linkable thermosets in a deformable fluid state that will allow them to be shaped by a die or mold; thereafter, they can be solidified by cooling below T_g or T_m (thermoplastics) or by a chemical reaction (thermosets).
- 2) *Shaping* operations during which “structuring” occurs (morphology development and molecular orientation that modify and improve physical and mechanical properties). Principal shaping methods include die forming, molding, casting, calendaring, and coating.
- 3) *Postshaping* operations, such as decorating, fastening, bonding, sealing, welding, dyeing, printing, and metallizing.

Following the explosive development of thermoplastics after World War II, many improvements and new developments have led to today’s diversity of polymer processing machines and technologies. Some processes are unique to thermoplastics; some are applicable only to thermosets and cross-linkable thermoplastics, whereas others, after certain modifications, can be applied to both thermoplastics and thermosets. Table 1.1, adapted from Ref. 3, summarizes the principal processing/shaping methods. For thermoplastics, extrusion is the most popular with approximately 50% of all the commodity thermoplastics being used in extrusion process equipment to produce profiles, pipe and tubing, films, sheets, wires, and cables. Injection molding follows as the next most popular processing method, accounting for

Table 1.1 Principal processing methods for thermoplastics and thermosets.

Thermoplastics	Thermosets/cross-linkable thermoplastics
Extrusion	Compression molding, transfer molding, casting
Pipe, tubing, sheet, cast film, profile	Injection molding, resin injection molding
Blown film	Polyurethane foam molding
Coextrusion, extrusion coating	Open mold reinforced plastics
Wire and cable coating	Lay-up
Foam extrusion	Spray-up
Extrusion blow molding	Filament winding
Injection molding, injection blow molding, resin injection molding (RIM)	Closed mold reinforced plastics
Foam molding	Pultrusion
Structural	Resin transfer molding (RTM)
Expandable bead	
Thermoforming	
Vacuum	
Pressure forming	
Rotational molding, calendering	

about 15% of all the commodity thermoplastics processed. Other common methods include blow molding, rotomolding, thermoforming, and calendering.

The range of processes that may be used for fabricating a plastic product is determined by the scale of production, the cost of the machine and the mold, and the capabilities and limitations of the individual processes. For example, complex and precise shapes can be achieved by injection molding, hollow objects by blow molding or rotational molding, and continuous lengths by extrusion. Processing methods for thermosets, particularly those related to reinforced thermosets involving liquid polymers, are often quite different from those employed for thermoplastics.

Increased polymer consumption over the past 20 years has not only stimulated machinery sales but also led to a parallel growth in the usage of a large variety of liquid and solid modifiers including fillers and reinforcements [4]. Significant advances have been made to accommodate such additives by improving the efficiency of polymer mixing/compounding equipment. Thermoplastic resin compounders combine the polymer(s) with the modifiers in high-intensity batch mixers and continuous extruders (mostly twin-screw extruders), and the material is then pumped into a pelletizer to produce the feed for subsequent shaping operations (see Chapter 3). Thermosetting resin suppliers compound heat-sensitive resins with fillers, additives, and/or pigments in a variety of mixers to produce molding compounds in such forms as powder, granules, and pastes to be fed into the molding equipment.

1.3

Polymer Composites

Modification of organic polymers through the incorporation of additives yields, with few exceptions, multiphase systems containing the additive embedded in a contin-

uous polymeric matrix. The resulting mixtures are characterized by unique microstructures or macrostructures that are responsible for their properties. The primary reasons for using additives are

- Property modification or enhancement.
- Overall cost reduction.
- Improving and controlling of processing characteristics.

In addition to polymer composites that are introduced in this chapter, important types of modified polymer systems include polymer–polymer blends and polymeric foams.

1.3.1

Types and Components of Polymer Composites

Polymer composites are mixtures of polymers with inorganic or organic additives having certain geometries (fibers, flakes, spheres, and particulates). Thus, they consist of two or more components and two or more phases. The additives may be continuous, for example, long fibers or ribbons; these are embedded in the polymer in regular geometric arrangements that extend throughout the dimensions of the product. Familiar examples are the well-known fiber-based thermoset laminates that are usually classified as high-performance polymer composites, or as *macrocomposites* based on the length of the fibers or ribbons. On the other hand, additives may be discontinuous (short), for example, short fibers (say, <3 cm in length), flakes, platelets, spheres, or irregulars (millimeter to micrometer size); fibers and flakes are usually dispersed in different orientations and multiple geometric patterns throughout the continuous matrix forming *microcomposites*. Such systems are usually based on a thermoplastic matrix and are classified as lower performance polymer composites compared to their counterparts with continuous additives. When the fibers, platelets, or spheres as the dispersed phase are of nanoscale dimensions (see, for example, hydrotalcite nanoplatelets in Figure 1.1), the materials are known as *nanocomposites*. They differ from microcomposites in that they contain a significant number of interfaces available for interactions between the intermixed phases [5]. As a result of their unique properties, nanocomposites have a great potential for advanced applications. Microcomposites and, to a lesser extent, nanocomposites form the topic of this book.

Composites may also be classified based on the origin (*natural* versus *synthetic*) of the matrix or filler. Nature uses composites for all her hard materials. These are complex structures consisting of continuous or discontinuous fibrous or particulate material embedded in an organic matrix acting as glue. Wood is a composite of fibrous cellulose and lignin. Bone is a composite of collagen and other proteins and calcium phosphate salts. Spider silk consists of organic nanocrystals in an organic amorphous matrix. The shells of mollusks (Figure 1.2) are made of layers of hard mineral separated by a protein binder [6]. A similar platy structure providing a tortuous path for vapors and liquids can be obtained in a microcomposite containing mica flakes embedded in a synthetic thermoset polymeric matrix (Figure 1.3).

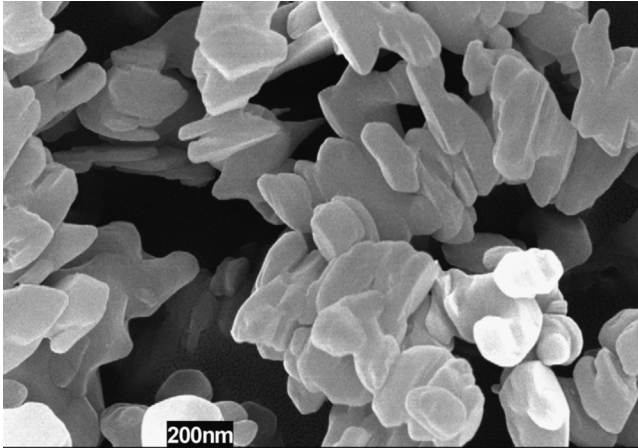


Figure 1.1 Scanning electron micrograph of hydrotalcite, a synthetic anionic nanoclay. (Courtesy of Dr. T.G. Gopakumar, Polymer Processing Institute.)

Composites can also be classified on the basis of the intended application. For example, one can distinguish between two types of *biocomposites*. Biocomposites for ecological applications are combinations of natural fibers or particulates with polymer matrices from both nonrenewable and renewable resources and are characterized by environmental degradability. Biocomposites for biomedical applications are combinations of biostable or degradable polymers with inert or bioactive

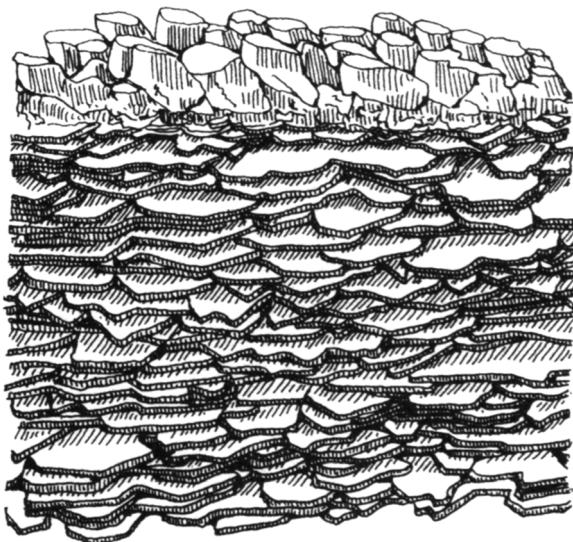


Figure 1.2 Natural microcomposite composite: the shell of a mollusk made of layers of calcium salts separated by protein. (Reprinted with permission from Ref. [6].)

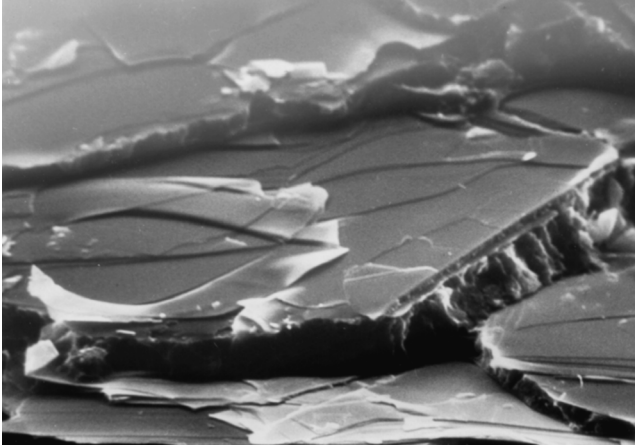


Figure 1.3 Synthetic microcomposite: scanning electron micrograph photo of cross section of fractured mica thermoset composite showing mica flakes with a thickness of about $2.5\ \mu\text{m}$ separated by a much thicker polymer layer.

fillers intended for use in orthopedics, bone regeneration, or tissue engineering applications.

Additives for polymer composites have been variously classified as reinforcements, fillers, or reinforcing fillers. Reinforcements, being much stiffer and stronger than the polymer, usually increase its modulus and strength. Thus, mechanical property modification may be considered as their primary function, although their presence may significantly affect thermal expansion, transparency, thermal stability, and so on. *Continuous* composites contain long fiber or ribbon reinforcements mostly in thermosetting matrices; when prearranged in certain geometric patterns, they may become the major component of the composite (they can constitute as much as 70% by volume in oriented composites). For *discontinuous* composites, the directional reinforcing agents (short fibers or flakes) are arranged in the composite in different orientations and multiple geometric patterns, which are dictated by the selected processing and shaping methods, most often extrusion or injection molding. In this case, the content of the additive does not usually exceed 30–40% by volume. It should be noted, however, that manufacturing methods for continuous oriented fiber thermoplastic composites are available resulting in much higher fiber contents, as used in high-performance engineering polymers [7]. In this book, the term reinforcement will be mostly used for long, continuous fibers or ribbons, whereas the term filler, performance filler, or functional filler will mostly refer to short, discontinuous fibers, flakes, platelets, or particulates.

1.3.2

Parameters Affecting Properties of Composites

In general, parameters affecting the properties of polymer composites, whether continuous or discontinuous, include

- the properties of the additives (inherent properties, size, and shape);
- the composition;
- the interaction of components at the phase boundaries, which is also associated with the presence of a thick interface, also known as the interphase; this is often considered as a separate phase, controlling adhesion between the components;
- the method of fabrication.

With regard to methods of fabrication, all processes in Table 1.1 that are applicable to unfilled, unmodified thermoplastics can also be used for discontinuous systems (with the exception of expandable bead molding). In addition to thermoforming, hot stamping of reinforced thermoplastic sheets mostly containing randomly oriented continuous or discontinuous fibers is used for the production of large semistructural parts. Fillers can also be used in the thermoset processes in Table 1.1, often in combination with the primary continuous fiber reinforcement. The content and inherent properties of the additive, as well as its physical/chemical interactions with the matrix, are important parameters controlling the processability of the composite.

1.3.3

Effects of Fillers/Reinforcements: Functions

Traditionally, most fillers were considered as additives, which, because of their unfavorable geometrical features, surface area, or surface chemical composition, could only moderately increase the modulus of the polymer, whereas strength (tensile, flexural) remained unchanged or even decreased. Their major contribution was in lowering the cost of materials by replacing the most expensive polymer; other possible economic advantages were faster molding cycles as a result of increased thermal conductivity and fewer rejected parts due to warpage. Depending on the type of filler, other polymer properties could be affected; for example, melt viscosity could be significantly increased through the incorporation of fibrous materials. On the other hand, mold shrinkage and thermal expansion would be reduced, a common effect of most inorganic fillers.

The term reinforcing filler has been coined to describe discontinuous additives, the form, shape, and/or surface chemistry of which have been suitably modified with the objective of improving the mechanical properties of the polymer, particularly strength. Inorganic reinforcing fillers are stiffer than the matrix and deform less, causing an overall reduction in the matrix strain, especially in the vicinity of the particle as a result of the particle–matrix interface. As shown in Figure 1.4, the fiber “pinches” the polymer in its vicinity, reducing strain and increasing stiffness [8]. Reinforcing fillers are characterized by relatively high aspect ratio α , defined as the ratio of length over diameter for a fiber or the ratio of diameter over thickness for platelets and flakes. For spheres, which have minimal reinforcing capacity, the aspect ratio is unity. A useful parameter for characterizing the effectiveness of a filler is the ratio of its surface area A to its volume V , which needs to be as high as possible for effective reinforcement. Figure 1.5 (from Ref. 8) shows that maximizing A/V and

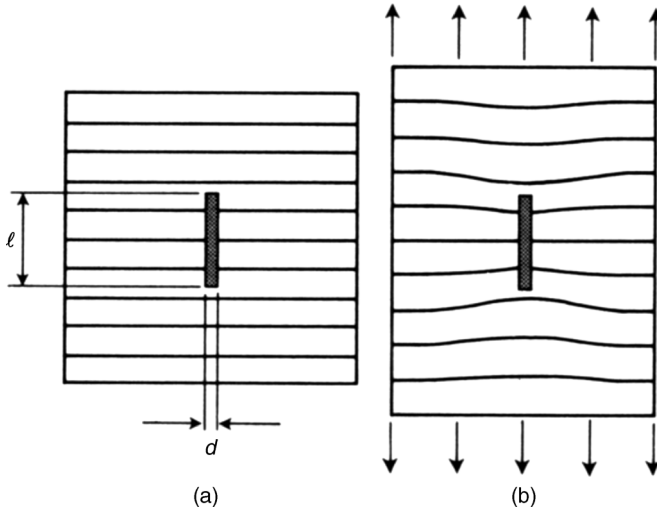


Figure 1.4 A cylindrical reinforcing fiber in a polymer matrix: (a) in the undeformed state; (b) under a tensile load. (Reprinted with permission from Ref. [8].)

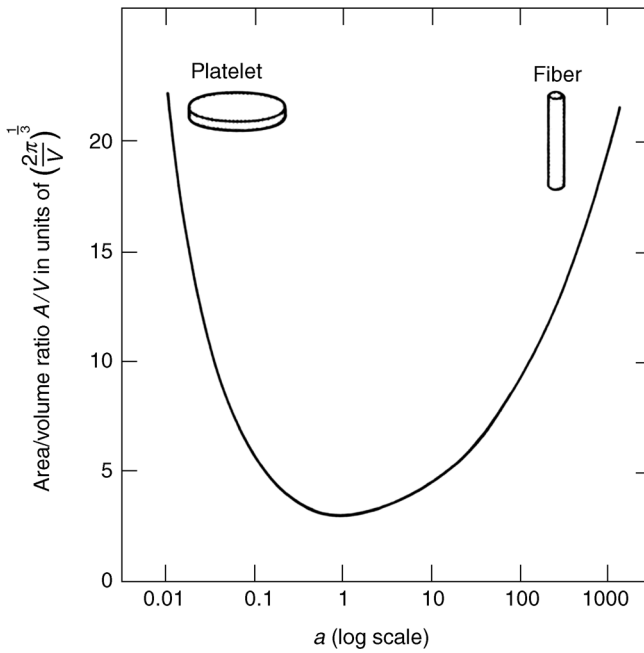


Figure 1.5 Surface area-to-volume ratio A/V of a cylindrical particle plotted versus aspect ratio $\alpha = l/d$. (Reprinted with permission from Ref. [8].)

particle–matrix interaction through the interface requires $\alpha \gg 1$ for fibers and $1/\alpha \ll 1$ for platelets.

In developing reinforcing fillers, the aims of process or material modifications are to increase the aspect ratio of the particles and to improve their compatibility and interfacial adhesion with the chemically dissimilar polymer matrix. Such modifications may not only enhance and optimize the primary function of the filler (in this case, its use as a mechanical property modifier) but also introduce or enhance additional functions. New functions attained by substitution or modification of existing fillers, thus broadening their range of applications, are illustrated in the examples below.

As described by Heinold [9], the first generation of fillers soon after the commercialization of polypropylene included talc platelets and asbestos fibers for their beneficial effects on stiffness and heat resistance. The search for an asbestos replacement due to health issues led to calcium carbonate particles and mica flakes as the second-generation fillers. Mica was found to be more effective than talc for increasing stiffness and heat resistance, whereas calcium carbonate was less effective in increasing stiffness but increased the impact resistance of PP homopolymers. Surface modification of mica with coupling agents to enhance adhesion and stearate modification of the calcium carbonate to assist dispersion were found to enhance these functions and introduce additional benefits such as improved processability, a means of controlling color, and reduced long-term heat aging. Other fillers imparted entirely different functions. For example, barium sulfate enhances sound absorption, wollastonite enhances scratch resistance, solid glass spheres add dimensional stability and increase hardness, hollow glass spheres lower density, and combinations of glass fibers with particulate fillers provide unique properties that cannot be attained with single fillers.

An additional example of families of fillers imparting distinct new properties is given by the pearlescent pigments produced by platelet core–shell technologies [10]. These comprise platelets of mica, silica, alumina, or glass substrates coated with films of oxide nanoparticles, for example, TiO_2 , Fe_2O_3 , Fe_3O_4 , and Cr_2O_3 (Figure 1.6). In addition to conventional decorative applications, new functional applications such as solar heat reflection, laser marking of plastics, and electrical conductivity are possible through the proper selection of substrate/coating combinations.

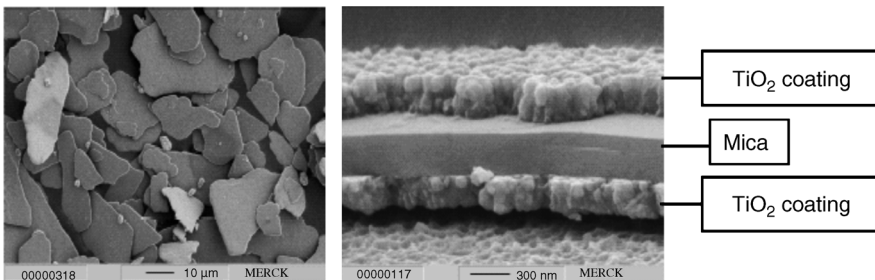


Figure 1.6 Scanning electron micrograph of mica flakes and a cross section of an anatase/mica pigment particle [10].

1.3.4

Rules of Mixtures for Composites

Rule of mixtures equations (often modified according to the type, shape, and orientation of the reinforcement/filler) are commonly used to describe certain properties of the composites. For example

- 1) Concentrations are usually expressed by volume, as volume fractions of filler V_f and matrix V_m , obtained from the volumes v_f and v_m of the individual components:

$$V_f = v_f / (v_f + v_m), \quad (1.1)$$

$$V_m = v_m / (v_f + v_m), \quad (1.2)$$

$$V_f + V_m = 1. \quad (1.3)$$

- 2) Volume fractions are also used to predict a theoretical density of the composite ρ , based on the respective densities of the components and assuming a total absence of voids:

$$\rho = V_f \rho_f + (1 - V_f) \rho_m. \quad (1.4)$$

- 3) The total cost per unit weight of the composite C can also be calculated from the volume fractions and the costs of the individual components and the cost of compounding per unit weight of the composite C_i [7]:

$$C = V_f \rho_f / \rho C_f + (1 - V_f) \rho_m / \rho C_m + C_i. \quad (1.5)$$

After introducing incorporation costs, the cost of the composite may be higher or lower than that of the unfilled polymer. For low-cost commodity plastics, the term filler (implying cost reduction) may be a misnomer since manufacturing costs may offset the lower cost of most mineral fillers. For higher cost specialty high-temperature thermoplastics, the final cost of, for example, glass fiber-reinforced polyetherimide is usually less than that of the unmodified polymer.

Rule of mixtures equations are also used to describe mechanical, thermal, and other properties as shown in Chapter 2.

1.3.5

Functional Fillers**1.3.5.1 Classification and Types**

The term filler is very broad and encompasses a very wide range of materials. In this book, we arbitrarily define as fillers a variety of solid particulate materials (inorganic, organic) that may be irregular, acicular, fibrous, or plate-like in shape and that are used in reasonably large volume loadings in plastics. Pigments and elastomeric matrices are normally not included in this definition.

There is a significant diversity in chemical structures, forms, shapes, sizes, and inherent properties of the various inorganic and organic compounds that are used as

Table 1.2 Chemical families of fillers for plastics.

Chemical family	Examples
Inorganics	
Oxides	Glass (fibers, spheres, hollow spheres, and flakes), MgO, SiO ₂ , Sb ₂ O ₃ , Al ₂ O ₃ , and ZnO
Hydroxides	Al(OH) ₃ and Mg(OH) ₂
Salts	CaCO ₃ , BaSO ₄ , CaSO ₄ , phosphates, and hydrotalcite
Silicates	Talc, mica, kaolin, wollastonite, montmorillonite, feldspar, and asbestos
Metals	Boron and steel
Organics	
Carbon, graphite	Carbon fibers, graphite fibers and flakes, carbon nanotubes, and carbon black
Natural polymers	Cellulose fibers, wood flour and fibers, flax, cotton, sisal, and starch
Synthetic polymers	Polyamide, polyester, aramid, and polyvinyl alcohol fibers

fillers. They are usually rigid materials, immiscible with the matrix in both molten and solid states, and, as such, form distinct dispersed morphologies. Their common characteristic is that they are used at relatively high concentrations (>5% by volume), although some surface modifiers and processing aids are used at lower concentrations. Fillers may be classified as inorganic or organic substances and further subdivided according to chemical family (Table 1.2) or according to their shape and size or aspect ratio (Table 1.3). Wypych [11] reported more than 70 types of particulates or flakes and more than 15 types of fibers of natural or synthetic origin that have been used or evaluated as fillers in thermoplastics and thermosets. The most commonly used particulate fillers are industrial minerals, such as talc, calcium carbonate, mica, kaolin, wollastonite, feldspar, and aluminum hydroxide. The most commonly used fibrous fillers are glass fibers and, recently, a variety of natural fibers. Carbon black has long been considered a nanofiller. More recent additions, rapidly moving to commercial markets, are nanoclays such as montmorillonite and hydrotalcite, a variety of oxides, and nanofibers such as single- or multiple-wall carbon nanotubes. Graphene sheets and halloysite nanotubes are potential additives in

Table 1.3 Particle morphology of fillers.

Shape	Aspect ratio	Example
Cube	1	Feldspar and calcite
Sphere	1	Glass spheres
Block	1–4	Quartz, calcite, silica, and barite
Plate	4–30	Kaolin, talc, and hydrous alumina
Flake	50–200 + +	Mica, graphite, and montmorillonite nanoclays
Fiber	20–200 + +	Wollastonite, glass fibers, carbon nanotubes, wood fibers, asbestos fibers, and carbon fibers

advanced nanocomposites; the first are single layers of carbon atoms tightly packed in a honeycomb structure [12], whereas the second are naturally occurring nanotubes produced by surface weathering of aluminosilicate minerals [13].

A more convenient scheme, first proposed by Mascia [14] for plastic additives, is to classify fillers according to their specific function, such as their ability to modify mechanical, electrical, or thermal properties, flame retardancy, processing characteristics, solvent permeability, or simply formulation costs. Fillers, however, are multifunctional and may be characterized by a primary function and a plethora of additional functions (see Table 1.4). The scheme adopted in this book involves classification of fillers according to five primary functions, as follows:

- mechanical property modifiers (and further subdivision according to aspect ratio);
- fire retardants;
- electrical and magnetic property modifiers;
- surface property modifiers;
- processing aids.

Additional functions may include degradability enhancement, barrier characteristics, antiaging characteristics, bioactivity, radiation absorption, warpage minimization, and so on. Such attributes for certain fillers will be identified in subsequent chapters of the book.

1.3.5.2 Applications, Trends, and Challenges

Global demand for fillers/reinforcing fillers including calcium carbonate, aluminum trihydrate, talc, kaolin, mica, wollastonite, glass fiber, aramid fiber, carbon fiber, and carbon black for the plastics industry has been estimated to be about 15 million tons [15]. Primary end-use markets are building/construction and transportation, followed by appliances and consumer products; furniture, industrial/machinery, electrical/electronics, and packaging comprise smaller market segments. Flexural modulus and heat resistance are the two critical properties of plastics that are enhanced by the inclusion of performance minerals. Automotive exterior parts, construction materials, outdoor furniture, and appliance components are examples of applications benefiting from enhanced flexural modulus. Automotive interior and underhood parts, electrical connectors, and microwaveable containers are examples of applications requiring high-temperature resistance. Environmental acceptance and improved sustainability of automotive parts are attributes of composites containing natural fibers. Life cycle assessment studies [16] tend to support the position that natural fiber composites are environmentally superior to glass fiber composites.

Recent statistics (2007) estimate the U.S. demand for fillers and extender minerals to a total of 3.2 million tons per annum [17]. Annual growth rates are estimated to be 2–3% with much higher rates for fire retardant fillers such as aluminum hydroxide (5.5–7%). Data (not including glass products and natural fibers but including TiO_2 and organoclays) indicate the highest demand for ground calcium carbonate followed by TiO_2 and aluminum trihydrate. Talc, kaolin, mica, wollastonite, silica, barites, and organoclays have a much smaller share of the market.

Table 1.4 Fillers and their functions.

Primary function	Examples of fillers	Additional functions	Examples of fillers
Modification of mechanical properties	High aspect ratio: glass fibers, mica, nanoclays, carbon nanotubes, carbon/graphite fibers, and aramid/synthetic/natural fibers Low aspect ratio: talc, CaCO ₃ , kaolin, wood flour, wollastonite, and glass spheres	Control of permeability	Reduced permeability: impermeable plate-like fillers: mica, talc, nanoclays, glass flakes Enhanced permeability: stress concentrators for inducing porosity: CaCO ₃ and dispersed polymers Bone regeneration: hydroxyapatite, tricalcium phosphate, and silicate glasses
Enhancement of fire retardancy	Hydrated fillers: Al(OH) ₃ and Mg(OH) ₂	Bioactivity	Organic fillers: starch and cellulosic fibers
Modification of electrical and magnetic properties	Conductive, nonconductive, and ferromagnetic: metals, carbon fiber, carbon black, and mica	Degradability	Metal particles, lead oxide, and leaded glass
Modification of surface properties	Antiblock, lubricating: silica, CaCO ₃ , PTFE, MoS ₂ , and graphite	Radiation absorption	
Enhancement of processability	Thixotropic, anti-sag, thickeners, and acid scavengers: colloidal silica, bentonite, and hydrotalcite	Improved dimensional stability Modification of optical properties Control of damping	Isotropic shrinkage and reduced warpage: particulate fillers, glass beads, and mica Nucleators, clarifiers, and iridescent pigments: fine particulates and mica/pigment hybrids Flake fillers, glass, and BaSO ₄

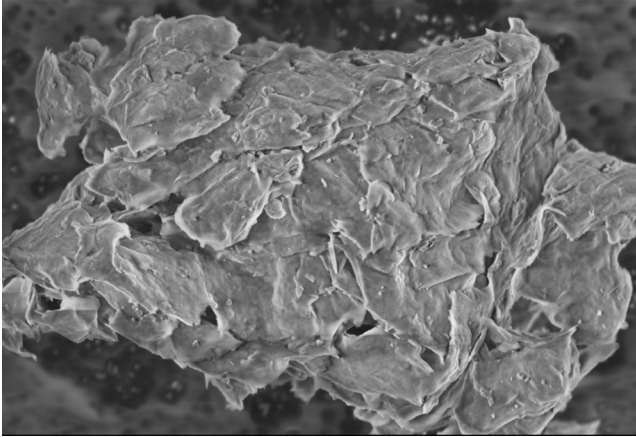


Figure 1.7 Scanning electron micrograph of montmorillonite agglomerate (a natural cationic clay) prior to its dispersion into high aspect ratio nanoplatelets. 7000 \times . (Courtesy of Dr. S. Kim, Polymer Processing Institute.)

There are a significant number of technological advances that will undoubtedly contribute to the additional growth in the usage of certain functional fillers: for example, for wood-filled plastics, introduction of specially configured counter-rotating twin-screw extruders with vent zones to remove moisture [18]; for mica and talc, development of new grinding technologies to retain the lamellarity and aspect ratio of the plate-like fillers [19] and for other minerals to produce ultrafine particles by special grinding methods [20]; for deagglomeration, dispersion, and exfoliation of agglomerated nanoclays (see, for example, Figure 1.7), particularly in high-temperature thermoplastic matrices, clay modification with additives such as ionic liquids [21] having higher thermal stability than the existing alkylammonium modifiers; in addition, melt compounding in extruders with improved screw configuration, and optional ultrasonic assistance or the use of supercritical fluids; for carbon nanotube composites, appropriate interfacial modification to improve dispersion and adhesion and minimize deagglomeration; also, equipment/process modification to ensure the desired orientation and maintain the high aspect ratio.

Some new exciting application areas for composites containing cationic or anionic nanoclays, nanooxides, carbon nanotubes, ultrafine TiO_2 , talc, and synthetic hydroxyapatite are

- 1) structural materials with improved mechanical, thermal, and barrier properties, electrical conductivity, and flame retardancy;
- 2) high-performance materials with improved UV absorption and scratch resistance;
- 3) barrier packaging for reduced oxygen degradation;
- 4) multifunctional fillers that could release in a controlled manner corrosion sensing additives, corrosion inhibitors, insecticides, active pharmaceutical ingredients, and so on;
- 5) bioactive materials for tissue engineering applications.

Concerns have been raised regarding the safety of certain nanomaterials in a variety of products, since their inhalation toxicology has not been fully evaluated yet and few data exist on dermal or oral exposures [22, 23]. The environmental, health, and safety (EHS) issues may be related to real risks, perceptual risks, and/or the lack of clear regulations. Current practices by some material suppliers are to supply precompounded masterbatches of nanoclays or nanofibers, slurries of nanoparticles, or high bulk density dispersible powders. Note that there is a significant amount of ongoing work in government, industrial, and academic laboratories that seeks to identify and address potential EHS risks of nanomaterials. Recent advances are described in Refs [24, 25].

References

- Xanthos, M. and Todd, D.B. (1996) Plastics processing, in *Kirk-Othmer Encyclopedia of Chemical Technology*, vol. 19, 4th edn, John Wiley & Sons, Inc., New York, pp. 290–316.
- Tadmor, Z. and Gogos, C.G. (2006) *Principles of Polymer Processing*, 2nd edn, John Wiley & Sons, Inc., Hoboken, NJ, pp. 14–17.
- Xanthos, M. (2000) Chapter 19: Polymer processing, in *Applied Polymer Chemistry: 21st Century* (eds C.E. Carraher and C.D. Craver), Elsevier, Oxford, UK, pp. 355–371.
- Xanthos, M. (1994) Chapter 14: The physical and chemical nature of plastics additives, in *Mixing and Compounding of Polymers: Theory and Practice* (eds I. Manas-Zloczower and Z. Tadmor), Carl Hanser Verlag, Munich, pp. 471–492.
- Ajayan, P.M., Schadler, L.S., and Braun, P.V. (eds) (2003) *Nanocomposite Science and Technology*, Wiley-VCH Verlag GmbH, Weinheim, pp. 77–144.
- Vogel, S. (1998) *Cats' Paws and Catapults*, W.W. Norton & Co., New York, pp. 123–124.
- Raghupathi, N. (1990) Chapter 7: Long fiber thermoplastic composites, in *Composite Materials Technology* (eds P.K. Mallick and S. Newman), Hanser Publishers, Munich, pp. 237–264.
- McCrum, N.G., Buckley, C.P., and Bucknall, C.B. (1997) *Principles of Polymer Engineering*, 2nd edn, Oxford University Press, New York, pp. 242–245.
- Heinold, R. (1995) Broadening polypropylene capabilities with functional fillers. Proceedings of the Functional Fillers 95, Intertech Corp., Houston, TX.
- Pfaff, G. (2002) Chapter 7: Special effect pigments, in *High Performance Pigments* (ed. H.M. Smith), Wiley-VCH Verlag GmbH, Weinheim, pp. 77–101.
- Wypych, G. (2000) *Handbook of Fillers*, ChemTec Publishing, Toronto, Canada.
- Jacoby, M. (2009) Graphene: carbon as thin as can be. *C&EN*, 87 (9), 14–20.
- Lvov, Y. and Price, R. (2009) Halloysite Nanotubes. Accessed May 2009 at <http://www.sigmaaldrich.com/materials-science/nanomaterials/nanoclay-building/halloysite-nanotubes.html>.
- Mascia, L. (1974) *The Role of Additives in Plastics*, Edward Arnold, London, UK.
- Mahajan, S. (2003) Proceedings of the Functional Fillers for Plastics, Intertech Corp., Atlanta, GA, October 2003.
- Joshi, S.V., Drzal, L.T., Mohanty, A.K., and Arora, S. (2004) Are natural fiber composites environmentally superior to glass fiber reinforced composites? *Composites Part A*, 35, 371–376.
- Blum, H.R. (2008) Functional fillers: a solution towards polymer sustainability & renewability. Proceedings of the Functional Fillers for Plastics, PIRA Intertech Corp., Atlanta, GA, September 2008.
- Wood, K.E. (2007) Wood-filled composites jump off the deck. *Compos. Technol.*, 13.6, 25–29.
- Roth, J. (2008) Influencing functional properties by different grinding methods. Proceedings of the Functional Fillers for

- Plastics, PIRA Intertech Corp., Atlanta, GA, September 2008.
- 20 Holzinger, T. and Hobenberger, W. (2003) *Ind. Miner.*, **443**, 85–88.
- 21 Ha, J.U. and Xanthos, M. (2009) Functionalization of nanoclays with ionic liquids for polypropylene composites. *Polym. Compos.*, **30** (5), 534–542.
- 22 Cheetham, A.K. and Grubstein, P.S.H. (2003) *Nanotoday*, 16–19.
- 23 Warheit, D.B. (2004) *Mater. Today*, 32–35.
- 24 Wetzel, M.D. (2008) Environmental, health and safety issues and approaches for the processing of polymer nanocomposites. Proceedings of the 66th SPE ANTEC, vol. 54, pp. 247–251.
- 25 Hussain, S.M. *et al.* (2009) Toxicity evaluation for safe use of nanomaterials: recent advancements and technical challenges. *Adv. Mater.*, **21** (126), 1549–1559.