Part I Polymers and Fillers

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1.1 Thermoplastics and Thermosets

Almost 85% of 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 decreases rapidly and the polymer exhibits liquid-like properties; amorphous thermoplastics are normally processed at temperatures well above their T_g . Glasstransition temperatures may be as low as 65 °C for polyvinyl chloride (PVC) and up to 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, $T_{\rm m}$, of the crystalline phase and the $T_{\rm g}$ 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 polyvinyl chloride (PVC). Next in performance and 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 being 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 due to their high T_g or T_m values (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 properties as well as 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]:

a) *Pre-shaping* 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.

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 $T_{\rm g}$ or $T_{\rm m}$ (thermoplastics) or by chemical reaction (thermosets).

b) *Shaping* operations, during which "structuring" occurs (morphology development and molecular orientation to modify and improve physical and mechanical properties). Principal shaping methods include die-forming, molding, casting, calendering, and coating.

c) *Post-shaping* 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 only applicable to thermosets and cross-linkable thermoplastics, while 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 commodity thermoplastics being used in extrusion process equipment to produce profiles, pipes and tubing, films, sheets, wires, and cables. Injection molding follows as the next most popular processing method, accounting for about 15% of all commodity thermoplastics processed. Other common methods include blow molding, rotomolding, thermoforming, and calendering.

Tab. 1-1	Principal	processing	methods	for thermo	plastics a	and thermosets

Thermoplastics	Thermosets/Cross-linkable thermoplastics
Extrusion – Pipe, tubing, sheet, cast film, profile – Blown film – Coextrusion, extrusion coating – Wire & cable coating – Foam extrusion	Compression Molding, Transfer Molding, Casting
Injection Molding, Resin Injection Molding (RIM)	Injection Molding, Resin Injection Molding (RIM)
Foam Molding – Structural – Expandable bead	Polyurethane Foam Molding
Thermoforming – Vacuum – Pressure forming	
Rotational Molding, Calendering	
	Open-Mold Reinforced Plastics – Lay-up – Spray-up – Filament Winding
	Closed-Mold Reinforced Plastics – Pultrusion – Resin transfer molding (RTM)

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 twenty years has not only stimulated machinery sales, but has 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 in-

to 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 powders, 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 continuous 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.

Important types of modified polymer systems include polymer composites, 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, particulates). Thus, they consist of two or more components and two or more phases. The additives may be continuous, e.g. 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. On the other hand, the additives may be discontinuous (short), as, for example, short fibers (say <3 cm in length), flakes, platelets, spheres or irregulars; these are dispersed throughout the continuous matrix. Such systems are usually based on a thermoplastic matrix and are classified as lower performance polymer composites compared to their counterparts with continuous additives; they form the topic of this book.

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 a glue. Wood is a composite of fibrous cellulose and lignin. Bone is a composite of collagen and other proteins and calcium phosphate salts. The shells of mollusks (Figure 1-1) are made of layers of hard mineral separated by a protein binder [5]. A similar platy structure providing a tortuous path for vapors and liquids can be obtained by embedding mica flakes in a synthetic polymeric matrix (Figure 1-2).



Fig. 1-1 A natural composite: the shell of a mollusk made up of layers of calcium salts separated by protein (reprinted from ref. [5]).



Fig. 1-2 A synthetic composite: SEM photograph of a cross-section of a fractured mica thermoset composite showing mica flakes with thickness $-2.5 \ \mu m$ separated by a much thicker polymer layer (courtesy of the author).

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, etc. For composites containing continuous reinforcements, mostly in thermosetting matrices, the long fibers or ribbons, when pre-arranged in certain geometric patterns, 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 that are amenable to much higher fiber contents, as used in high performance engineering polymers [6]. In this book, the term reinforcement will be mostly used for long, continuous fibers or ribbons, whereas the terms filler, performance filler or functional filler will mostly refer to short, discontinuous fibers, flakes, platelets or particulates.

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

- the properties of the additives (inherent properties, size, shape);
- composition;
- the interaction of components at the phase boundaries, which is also associated with the existence of a thick interface, known also 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 the 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 containing mostly 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 the presence of the primary continuous fiber reinforcement. The concentration and inherent properties of the additive, as well as its interaction with the matrix, are important parameters controlling the processability of the composite.

1.3.2

Effects of Fillers/Reinforcements – Functions

Traditionally, fillers were considered as additives, which, due to their unfavorable geometrical features, surface area or surface chemical composition, could only moderately increase the modulus of the polymer, while strength (tensile, flexural) remained unchanged or even decreased. Their major contribution was in lowering the cost of materials by replacing the more 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 1-3, the fiber "pinches" the polymer in its vicinity, reducing strain and increasing stiffness [7]. Reinforcing fillers are characterized by relatively high aspect ratio, α , defined as the ratio of length to diameter for a fiber, or the ratio of diameter to 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 1-4 (from ref. [7]) shows that maximizing *A*/*V* and 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 enhance and optimize not only the primary function of the filler (in this case its use as a mechanical property modifier), but may also introduce or enhance additional functions. New functions attained by substitution or modification of existing



Fig. 1-3 A cylindrical reinforcing fiber in a polymer matrix: a) in the undeformed state; b) under a tensile load (reprinted with permission of Oxford University Press from ref. [7]).



Fig. 1-4 Surface area-to-volume ratio, A/V, of a cylindrical particle plotted versus aspect ratio, a = l/d (reprinted with permission of Oxford University Press from ref. [7]).

fillers, thus broadening their range of applications, are illustrated by the examples below.

As described by Heinold [8], 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 a replacement for asbestos 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, while calcium carbonate proved to be 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 calcium carbonate to assist dispersion were found to enhance these functions and introduced other benefits such as improved processability, a means of imparting color, and reduced long term heat ageing. 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 a family of fillers imparting distinct new properties is given by the pearlescent pigments produced by platelet core-shell technologies [9]. These comprise platelets of mica, silica, alumina or glass substrates coated with films of oxide nanoparticles, e.g. TiO₂, Fe₂O₃, Fe₃O₄, Cr₂O₃ (Figure 1-5). In addition to conventional decorative applications, new functional applications such as solar heat re-

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Fig. 1-5 SEM photographs of mica flakes (left) and a cross-section of an anatase/mica pigment particle (right) [9].

flection, laser marking of plastics, and electrical conductivity are possible through selection of the appropriate substrate/coating combinations.

1.3.3 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 composites. For example:

a) Concentrations are usually expressed by volume, as volume fractions of filler, $V_{\rm f}$, and matrix $V_{\rm m}$, obtained from the volumes, $v_{\rm f}$ and $v_{\rm m}$, of the individual components:

$$V_{\rm f} = v_{\rm f} / (v_{\rm f} + v_{\rm m})$$
 (1-1)

$$V_{\rm m} = v_{\rm m} / (v_{\rm f} + v_{\rm m})$$
 (1-2)

$$V_{\rm f} + V_{\rm m} = 1$$
 (1-3)

b) 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:

$$\rho = V_f \rho_f + (1 - V_f) \rho_m \tag{1-4}$$

c) The total cost per unit weight of 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 composite, C_i [6].

$$C = V_{\rm f} \rho_{\rm f} / \rho \ C_{\rm f} + (1 - V_{\rm f}) \rho_{\rm m} / \rho \ C_{\rm m} + C_{\rm i} \tag{1-5}$$

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 such as

polypropylene, the term filler (implying cost reduction) may be a misnomer since manufacturing costs may offset the lower cost of most mineral fillers. For high 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.

1.3.4

Functional Fillers

1.3.4.1 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 which are used in reasonably large volume loadings in plastics. Pigments and elastomeric matrices are not normally included in this definition.

There is significant diversity in the chemical structures, forms, shapes, sizes, and inherent properties of the various inorganic and organic compounds that are used as fillers. They are usually rigid materials, immiscible with the matrix in both the 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). In a recent review [10], Wypych 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 barite.

Chemical Family	Examples
Inorganics	
Oxides	Glass (fibers, spheres, hollow spheres, flakes), MgO, SiO ₂ , Sb ₂ O ₃ ,
	Al ₂ O ₃
Hydroxides	$Al(OH)_3$, $Mg(OH)_2$
Salts	CaCO ₃ , BaSO ₄ , CaSO ₄ , phosphates
Silicates	Talc, mica, kaolin, wollastonite, montmorillonite, nanoclays, feldspar, asbestos
Metals	Boron, steel
Organics	
Carbon, graphite	Carbon fibers, graphite fibers and flakes, carbon nanotubes, carbon black
Natural polymers	Cellulose fibers, wood flour and fibers, flax, cotton, sisal, starch
Synthetic polymers	Polyamide, polyester, aramid, polyvinyl alcohol fibers

Tab. 1-2 Chemical families of fillers for plastics

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

 Tab. 1-3
 Particle morphology of fillers

A more convenient scheme, first proposed by Mascia [11] for plastics 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, anti-ageing characteristics, bioactivity, radiation absorption, warpage minimization, etc. Such attributes will be identified in subsequent sections of the book.

Primary Function	Examples of Fillers	Additional Functions	Examples of Fillers
Modification of mechanical properties	High aspect ratio: glass fibers, mica, nano- clays, carbon nanotubes, carbon /graphite fibers, aramid / synthetic / natural fibers Low aspect ratio: talc, CaCO ₃ , kaolin, wood flour, wollastonite, glass spheres	Control of permeability	Reduced permeability: impermeable plate-like fillers: mica, talc, nanoclays, glass flakes Enhanced permeability: stress concentrators for in- ducing porosity: CaCO ₃ , dis- persed polymers
Enhancement of fire retardancy	Hydrated fillers: Al(OH) ₃ , Mg(OH) ₂	Bioactivity	Bone regeneration: hydroxyapatite, tricalcium phosphate, silicate glasses

Primary Function	Examples of Fillers	Additional Functions	Examples of Fillers
Modification of electrical and magnetic properties	Conductive, non-conductive, ferromagnetic: metals, carbon fibers and nano- tubes, carbon black, mica	Degradability	Organic fillers: starch, cellulosic
Modification of surface properties	Antiblock, lubricating: silica, CaCO ₃ , PTFE, MoS ₂ , graphite	Radiation absorption	Metal particles, lead oxide, leaded glass
Enhancement of processability	Thixotropic, anti-sag, thickeners, acid scavengers: colloidal silica, bentonite, hydrotalcite	Improved dimensional stability	Isotropic shrinkage, reduced warpage: particulate fillers, glass beads, mica
		Modification of optical properties	Nucleators, clarifiers, irridescent pigments: fine particulates, mica/pigment hybrids
		Control of damping	Flake fillers, glass, BaSO ₄

1.3.4.2 Applications and Trends

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 is estimated to be about 15 million tons [12]. 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 [13].

Recent statistics (2001) suggest a combined demand for performance minerals for use in plastics for North America and Europe of about 4 million tons per annum, with an average annual growth to 2006 forecasted to be about 4.2% [13]. Data (not including glass products, natural fibers, or nanofillers, but including TiO₂) indicate the highest demand for ground calcium carbonate (60% of the total), followed by TiO₂ (13%), aluminum trihydrate (10%), and talc (10%). Kaolin, mica, wollastonite, and barites have a much smaller share of the market. When glass and natural fibers are included in the statistics, calcium carbonate accounts for 40% of the total market, glass for 30%, and other mineral fillers and natural fibers for 20%. Combinations of

fillers are also often used to impart specific combined properties not attainable with a single filler. Among polymers, PVC is still the plastic with the highest filler usage, followed by polyolefins, nylons, and polyesters.

Additional growth in the usage of functional fillers will undoubtedly stem from the current efforts towards: a) identifying new applications for composites containing nanofillers [14,15], b) developing composites containing ultrafine particles (dimensions < 3 μ m), the latter produced by special grinding methods [16], and c) the increased usage of natural fiber (flax, wood) composites, coupled with the expected significant growth in the use of nanoclay composites in the automotive industry. Some exciting new application areas for composites containing nanoclays, nanosilicates, carbon nanotubes, ultrafine TiO₂, talc, and synthetic hydroxyapatite are:

- as structural materials with improved mechanical properties, barrier properties, electrical conductivity, and flame retardancy;
- as high performance materials with improved UV absorption and scratch resistance;
- as barrier packaging for reduced oxygen degradation;
- as bioactive materials for tissue engineering applications.

Certain issues need to be addressed prior to further growth in the usage of these novel functional fillers. For example, the melt processing of nanocomposites and, to a certain extent, of composites containing natural fibers, still presents compounding problems related to feeding, dispersion, aspect ratio retention, and orientation of the reinforcement. Figure 1-6 shows complex agglomerates of commercial montmoril-



Fig. 1-6 SEM photograph of a montmorillonite agglomerate prior to its dispersion into high aspect ratio nanoplatelets; 7000x (courtesy of Dr. S. Kim, Polymer Processing Institute).

lonite that need to be exfoliated into nanoparticles by melt compounding. Furthermore, concerns have been raised relating to the safety of certain nanomaterials in a variety of products, since their inhalation toxicology has not yet been fully evaluated and few data exist on dermal or oral exposures [15,17].

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