

# Functional Fillers for Plastics

*Edited by Marino Xanthos*



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## Preface

It is generally accepted that growth in plastics consumption and the development of new and specialized applications are related to advances in the field of multicomponent, multiphase polymer systems. These include composites, blends and alloys and foams. Fillers are essential components of multiphase composite structures; they usually form the minor dispersed phase in a polymeric matrix.

Increased interest in the use of discontinuous fillers as a means to reduce the price of molding compounds began about 30 years ago when increasing oil prices made necessary the replacement of expensive polymers with less costly additives. When such additives had also a beneficial effect on certain mechanical properties (mostly modulus and strength) they were also known as reinforcing fillers. Since that time, there has been a considerable effort to extend the uses (and functions) of existing fillers by: a) particle size and shape optimization, b) developing value-added materials through surface treatments and c) developing efficient methods for their incorporation in plastics.

The term “filler” is very broad and encompasses a very wide range of materials. We arbitrarily define in this book as fillers a variety of natural or synthetic solid particulates (inorganic, organic) that may be irregular, acicular, fibrous or flakey and are used in most cases in reasonably large volume loadings in plastics, mostly thermoplastics. Continuous fibers or ribbons are not included. Elastomers are also not included in this definition as well as many specialty additives that are used at low concentrations (e.g. pigments, lubricants, catalysts, etc).

Among the best known handbooks on fillers that appeared in the English language in the past 25 years are the detailed works edited by Katz and Milewski (1978, 1987) and Zweifel (2001) and the monograph compiled by Wypych (2000). This present volume is not intended to be a handbook listing individual fillers according to their generic chemical structure or name but rather a comprehensive and up-to-date presentation, in a unified fashion, of structure /property/ processing relationships in thermoplastic composites containing discontinuous fillers that would help the identification of new markets and applications. For convenience, fillers are grouped according to their primary functions that include modification of: a) mechanical properties, b) flame retardancy, c) electrical and magnetic properties, d) surface properties and e) processability. For each filler there is always a series of additional functions. Examples include degradability enhancement, bioactivity, radiation absorption,

damping enhancement, enhancement of dimensional stability, reduced permeability and reduced density.

*Functional Fillers* has been the focus of International Conferences such as those organized annually by Intertech Corp. in N. America and Europe over the past 10 years and attended by the editor and several contributing authors of this book and the biannual “Eurofillers” Conference. Judging from the interest generated from these conferences it became clear that there is a need for a volume that would capture the current technologies applicable to “commodity” fillers and compare them with new technologies and emerging applications that would reflect the multifunctional character of new or modified existing fillers. Examples of advances in the latter category include nanoplatelets of high aspect ratio produced by exfoliation of organoclays, nanoscale metal oxides, carbon nanotubes, ultrafine talc, TiO<sub>2</sub> and hydroxyapatite particles, ceramers and ormosils, new rheology modifiers and adhesion promoters, and increased usage of natural fibers. This volume is expected to address the needs of engineers, scientists and technologists involved in the industrially important sector of polymers additives and composites.

The book is divided into three main parts:

Part I, entitled *Polymers and Fillers*, contains a general introduction to polymer composites, a review of the parameters affecting mechanical and rheological properties of polymers containing functional fillers and an overview of mixing and compounding equipment along with methods of filler incorporation in molten and liquid polymers.

Part II focuses on the use of *Surface Modifiers and Coupling Agents* to enhance the performance of functional fillers and includes sections on silanes, titanates, functionalized polymers and miscellaneous low molecular weight reactive additives.

Part III on *Fillers and their functions* describes in a systematic manner the most important inorganic and organic functional fillers with examples of existing and emerging applications in plastics. Fillers have been grouped into seven families, each family representing the primary function of the filler. The families and the corresponding fillers covered in this book are:

- *High Aspect Ratio Mechanical Property Modifiers* with detailed description of glass fibers, mica flakes, nanoclays, carbon nanotubes/nanofibers and carbon fibers, and natural fibers, Chapters 7–11.
- *Low Aspect Ratio Mechanical Property Modifiers* with detailed description of talc, kaolin, wollastonite, wood flour, and calcium carbonate, Chapters 12–16.
- *Fire Retardants* with emphasis on metal hydroxides but also inclusion of antimony oxide, ammonium polyphosphate, borate salts and low melting temperature glasses, Chapter 17.
- *Electrical and Magnetic Property Modifiers* with emphasis on carbon black but also inclusion of metal particles and various magnetic fillers, Chapter 18.
- *Surface Property Modifiers* with further division into: a) solid lubricants/tribological additives that include molybdenite, graphite, PTFE and boron nitride and b) antiblocking fillers such as silica, Chapter 19.
- *Processing Aids* including rheological modifiers such as MgO and fumed silica, and process stabilizers such as hydrotalcites, Chapter 20.

Under *Specialty Fillers* (Chapters 21–23) a variety of multifunctional inorganics are discussed. They include: a) *glass and ceramic spheres* with primary functionalities as rheology modifiers and enhancers of dimensional stability (solid spheres) or weight reduction (hollow spheres), b) a variety of phosphate, carbonate and silicate calcium salts and specialty glasses that show *bioactivity* in tissue engineering applications and, c) *in-situ* generated fillers such as *organic-inorganic hybrids* with important functions as mechanical property or surface modifiers, depending on the system.

For commercially available fillers, contributing authors to chapters of Part III have been asked to broadly adhere to a uniform pattern of information that would include: a) production methods of the respective filler, b) its structure and properties, c) a list of major suppliers, information on availability and prices, d) a discussion of environmental/toxicity issues including applicable exposure limits proposed by regulatory agencies, and e) a concluding section on applications that considers both primary and secondary functions of each filler and presents specific data on properties and information on current and emerging markets.

Many authors used government and company websites as sources for updated Material Safety Data Sheets (MSDS) and information on the threshold limit values (TLV) for the airborne concentration of filler dusts in the workplace. Reliable information on possible risks to human health or the environment is extremely important to current and potential users of existing fillers, or new fillers of different origin and different particle size/shape characteristics. It should be recognized that health issues have been responsible in the past for the withdrawal from certain plastics markets of natural and synthetic fibrous fillers with unique properties such as chrysotile asbestos, microfibers, whiskers and the recently mandated very low content of crystalline silica in mineral fillers.

In presenting the different topics of this book, efforts were made to produce self-contained chapters in terms of cited references, abbreviations and symbols. Although this may have resulted in duplication of information, it should be useful to readers interested in only certain chapters of the book. All Tables, Figures and Equations are labeled in terms of the chapter where they first appear to facilitate cross-referencing.

The authors who contributed to this book all have significant credentials in the field of fillers and reinforcements for plastics and represent industry, academe, consulting and R&D organizations. Their different backgrounds and insight reflect on their chapter contents, style of presentation and the emphasis placed on the information presented. I would like to thank my colleagues from the Polymer Processing Institute (Drs. Davidson, Patel, Todd), from industry (Drs. Ashton, Dey, Mack and Weissenbach, and Messrs. Duca, Kamena and Monte), from academic institutions (Drs. Flaris, Iqbal, Mascia and Rethon), from US Government laboratories (Drs. Clemons and Caulfield), and our doctoral students at the New Jersey Institute of Technology (Ms. Chouzouri and Mr. Goyal) for their hard work and excellent cooperation and patience during the long editing process. Special thanks are due to my friends and coworkers for many years in the field of polymer composites, Dr. Leno Mascia of Loughborough University, UK and Dr. Ulku Yilmazer of Middle East Technical University, Turkey for reading Chapters 1 and 2 and offering many useful suggestions for their improvement. Finally, many thanks to Dr. Michael Jaffe of NJIT for

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This book was largely completed during a sabbatical leave of the editor/contributing author from the New Jersey Institute of Technology in 2003-2004.

Fort Lee, NJ, USA, November 2004

*Marino Xanthos*

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**Part I**  
**Polymers and Fillers**





# 1

## Polymer and Polymer Composites

*Marino Xanthos*

### 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  $T_g$ . Glass-transition 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,  $T_m$ , 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 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  $T_g$  or  $T_m$  (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 calendaring.

**Tab. 1-1** Principal processing methods for thermoplastics 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, Calendaring	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).

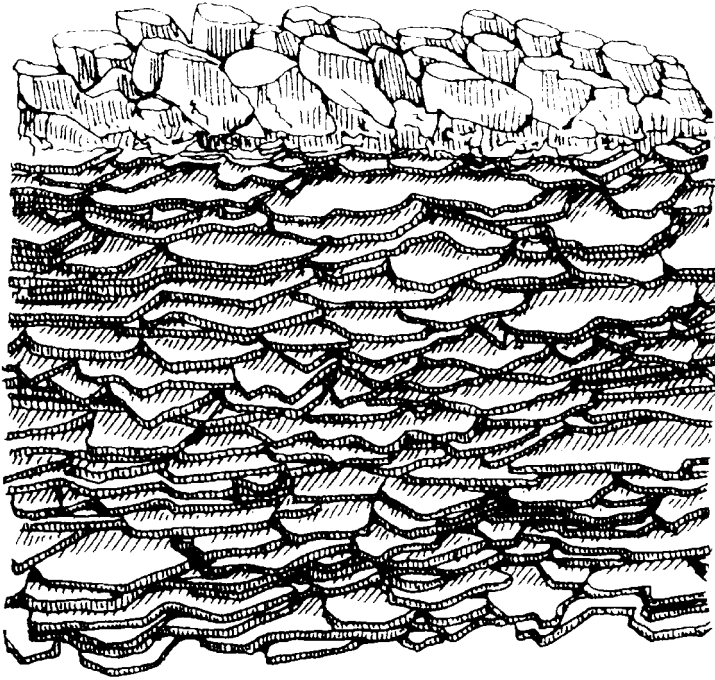


Fig. 1-1 A natural composite: the shell of a mollusk made up of layers of calcium salts separated by protein (reprinted from ref. [5]).

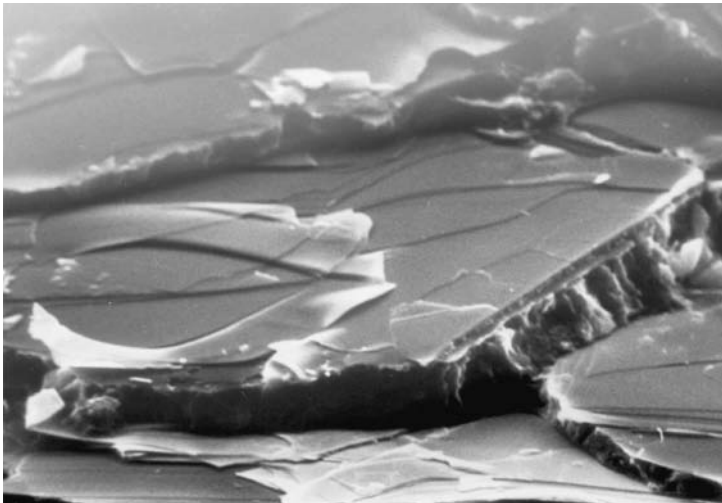


Fig. 1-2 A synthetic composite: SEM photograph of a cross-section of a fractured mica thermoset composite showing mica flakes with thickness  $\sim 2.5 \mu\text{m}$  separated by a much thicker polymer layer (courtesy of the author).

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 semi-structural 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) re-