PLASTICS

MATERIALS AND PROCESSING

A. BRENT STRONG

Plastics:
Materials and Processing

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Preface

The objective of *Plastics: Materials and Processing* is to introduce plastics to a broad cross section of readers who have a need to gain, improve, or refresh their knowledge of plastics. The book is intended for students of technology, engineering technology, and engineering, and for professionals in the plastics industry (such as technical and nontechnical managers, staff in plastics companies, foremen, and operators). The text emphasizes the fundamentals of plastics materials and processing, yet it is detailed enough to be a valuable reference for future consulting. This combination of fundamentals and details makes the book ideal as a textbook for an introductory course in plastics. The instructor can emphasize those topics that have special application for the class and can also assign additional reading to enhance the overall knowledge of the student in the entire field of plastics technology. After completion of the class, students can retain the book for future general reference. The book is also an excellent resource for seminars in plastics technology, as well as for company courses and personal study.

The book is not, however, a reference for design data and plastic properties. That role is fulfilled adequately by the several encyclopedias and handbooks of plastics that are published regularly and therefore can present more up-to-date data. *Plastics: Materials and Processing* is an excellent reference for fundamentals over a very broad spectrum of plastic materials and processes.

The book is written at a level appropriate for those who need to gain a basic understanding of plastics but have had no prior plastics experience. Another audience is production personnel who have had some operational knowledge of plastics through on-the-job training and want to gain additional technical background. They will find that the book discusses plastics at a valuable operational level and still provides an in-depth understanding from a nonoperational (theoretical) basis. College and university students will also appreciate this operational level for laboratory assistance and later understanding of workplace operations. Professionals who wish to gain knowledge of plastics will find the overview nature of the book useful in readily identifying topics of interest.

The text parallels an introductory plastics course taught for many years in the Department of Manufacturing Engineering and Technology at Brigham Young University. (Hence, the text itself, the objectives, problems, and format have been tried in practice and have been shown to help students succeed.) This is the only plastics course available for most of these manufacturing engineering and technology students, who have reported its value during later work experience in the plastics industry. The text provides a proper foundation for advanced courses in polymer synthesis, polymer properties, and plastics processing.

A background and basic understanding of high school or freshman chemistry, physics, and mathematics is suggested. A few important mathematical formulas are presented and used to show how the various variables are related, to enable important operational calculations to be made, and to illustrate the mathematical theory of key plastic properties. Molecular (chemical) formulas for many of the plastics materials are given, along with an introduction of basic organic chemistry that provides the reader the necessary background to readily understand molecular formulas. As the reader gains experience in plastics, these chemical formulas will serve as valuable references to a deeper understanding of the relationships among plastic structure, properties, and processing.

Plastics is a very broad category of materials. It includes most elastomers, adhesives, fibers, films, modified natural polymers (such as the cellulosics), and traditional commercial and engineering thermoplastics and thermosets. This book takes a broad view that allows the comparison of similar concepts and principles within all these similar materials.

Plastics are introduced at three levels of focus: (1) the molecular, (2) the micro (polymer chains and crystals), and (3) the macro (physical properties). Through knowledge of all three levels, readers can understand and predict the properties of the various plastics and their performance in products. Manufacturing methods for plastics and the changes in plastics properties that result from manufacturing are also related to the three levels.

Each chapter in the book has an introductory section that describes the major concepts of the chapter. The chapter then expounds the subject in qualitative and limited (no derivations) quantitative terms. Extensive figures and tables give visual and comparative understanding to the concepts. At the end of each chapter, a case study highlights in detail some important aspect of the chapter in a specific circumstance. Also at the end of the chapter is a summary of the major concepts and objectives. Questions then follow to test the reader's *understanding* (rather than mere recollection) of the principles presented in the chapter. A list of references is provided to assist the student in finding additional material on the subject of the chapter.

The learning of plastics is directly connected with the vocabulary of plastics. Not only are the concepts often expressed in unique terms, but the industry communicates in these terms. Therefore, terms that have unique meanings in plastics technology are italicized when they are introduced in the body of the text and defined briefly when they are used. Furthermore, all of these new terms are included in the index for easy reference. A valuable cost estimating form for injection molding parts is also included as an appendix.

Plastics has many highly interrelated topics. Ideally, topics such as molecular interactions, crystallinity, thermal transitions, steric effects, processing methods, and product applications should all be perceived simultaneously in order to gain the best appreciation of each. Simultaneous perception is, however, very difficult when the topics are new. This book, of necessity, presents the material in a linear fashion. However, for best understanding, the book should be reexamined in a rapid, overall reading so that the whole picture of plastics can be appreciated. The structure of the book—with the chapter outlines and summaries, case studies, questions, and appendix—is intended to assist in gaining that overall view.

Contents

CHAPTER ONE

INTRODUCTION TO PLASTICS

CHAPTER OVERVIEW

This chapter examines the following concepts:

- Definition of plastics
- History of plastics
- Raw material supply and pricing
- Strategic materials
- The plastics industry
- Uses of plastics in modern society

DEFINITION OF PLASTICS

Plastics is not a uniformly defined term and there certainly is no general agreement on the definition. Some writers and organizations prefer to define plastics in a relatively narrow sense, focusing on specific properties (such as formability) or a specific group of related materials. Others prefer to define plastics more broadly, examining properties, processing, and design characteristics. This book uses a relatively broad definition to enable the reader to see the fundamental similarities of many related materials that come under this definition and the processes used to form them.

Plastics is a general term that describes materials composed principally of very large molecules (called *polymers*) that are synthetically made or modified from small components (called *monomers*). Plastics are solids that, in some stage have been shaped by flow or molding in the liquid, molten, or softened form. (The word *plastics* comes from the Greek *plastikos,* which means to form or mold.) The definition of plastics can be illustrated in a systematic classification diagram (called a taxonomy), as shown in Figure 1.1. Since several of the terms used to define plastics may be new, some additional definitions and explanations are given.

Molecules are groups of atoms (such as carbon, hydrogen, oxygen, nitrogen, and others) joined together into specific arrangements that impart certain properties to the various groups. A more detailed introduction to atoms, molecules, and bonding is given in the chapter on Polymeric Materials (Molecular Viewpoint), but a brief overview is useful here to understand the basic

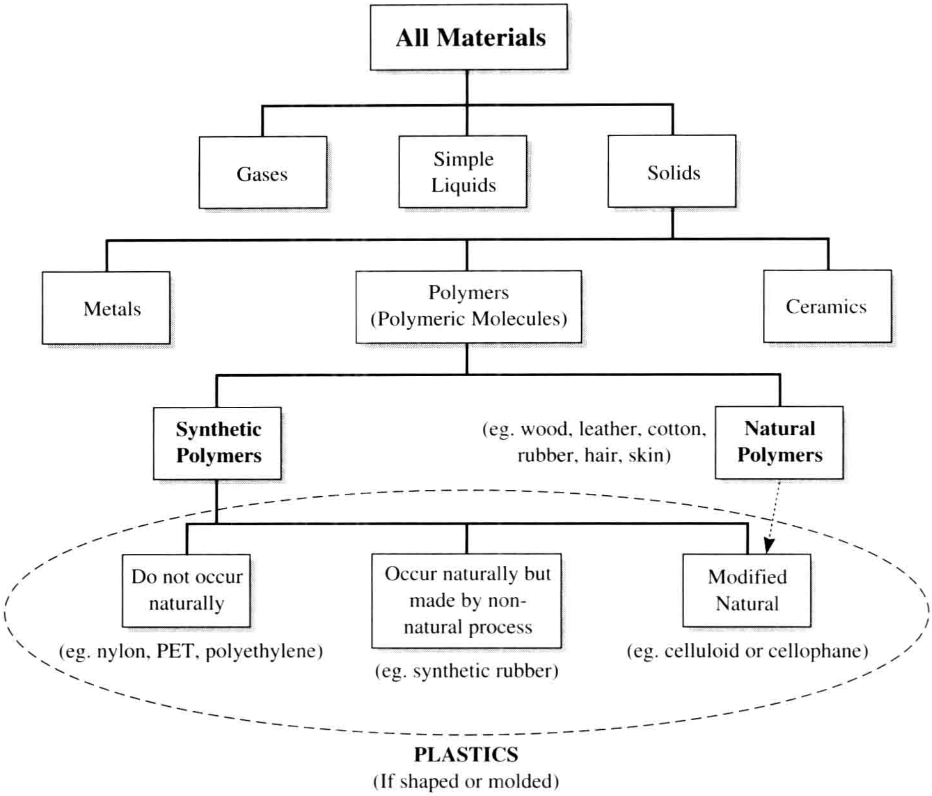

Figure 1.1 Diagram illustrating the definition of plastics.

nature of polymers. In chemistry, groups having the same arrangement of atoms have the same properties, and no group of atoms having a different arrangement has these same properties. If a molecular group is broken into smaller segments (so that it is no longer a molecule), some or all of the characteristic properties of that group are lost. **Therefore, a molecule is the smallest collection of atoms that possesses the characteristic properties of a group.** Even though these molecular structures cannot be seen, even with the strongest microscope, reasoning and sophisticated analytical tools have enabled chemists to deduce the structures of the molecules.

The science of chemistry is the study of the reactions and properties of various molecules and atoms. We will discuss the reactions of molecules rather than atoms because molecular reactions are more important for plastics, but the general concepts are the same. When two or more molecules react together, new molecules with different properties from the reactant molecules are formed. The molecules are said to have been chemically combined into a new molecule.

These chemical reactions are usually represented as two or three molecules reacting together to form a single, or perhaps a few, new molecules. In reality, a very large number of identical molecules react to form a great number of identical, new molecules. When many molecules of the same type are combined together, the properties that are usually measured are for the large collection of molecules. These properties are called *collective* or *bulk properties* of the material. The bulk properties are determined by both the molecular properties (properties that depend upon the molecular nature of the material—such as chemical reactivity) and the collective properties (properties that depend upon the interaction of the molecules—such as crystal formation). Subsequent chapters examine both the molecular and bulk properties of plastics because understanding many properties of plastics, such as mechanical strength, melting point, and solvent reactivity, depends upon understanding both the molecular and the bulk nature of plastic materials.

By the use of certain chemical reactions, some molecules can be combined into chains. This is illustrated in Figure 1.2. These chains are called *polymers* or *polymeric molecules.* (The word polymer means many parts or units. The parts or units are, of course, the small molecules that combine.) Another term that is widely applied to polymeric molecules is *macromolecules* (from the Greek *makros* meaning long or large). The chains become new molecules with properties that are different from those of the original individual units, even though the individual units might all be the same. These molecular chains can be short, in which case the molecule is likely to be a gas or a liquid at room temperature. These short molecular chains are usually not considered polymers. An example of a short-chain molecule would be cooking oil. Long-chain molecules (polymers) are usually solids. When the chains are long, often containing thousands of units, the polymer could be a plastic (provided other definitional conditions are met) and might be called a

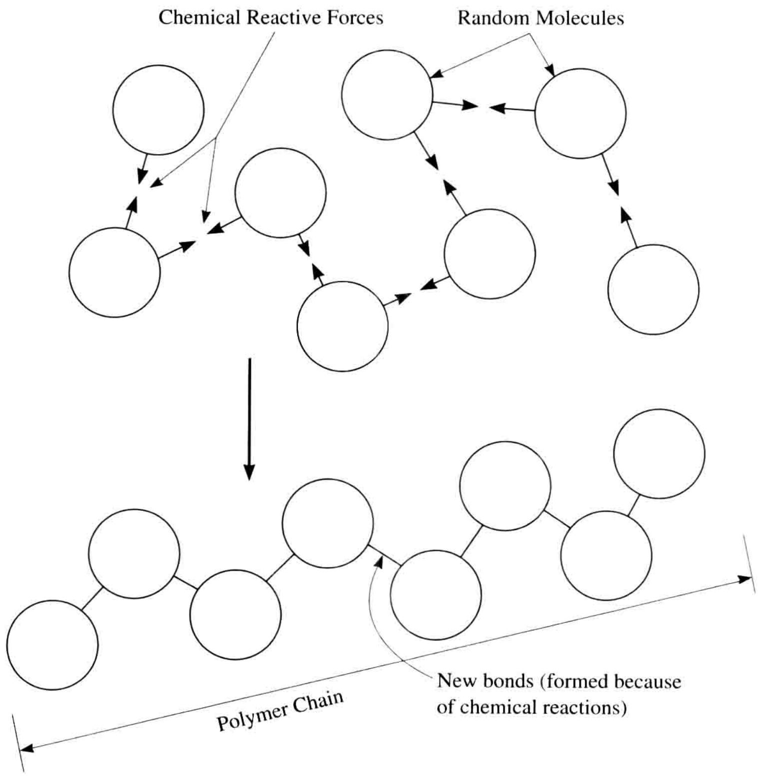

Figure 1.2 Illustration of small molecules combined into a polymer chain.

giant molecule. All plastics are giant molecules, although some giant molecules are naturally occurring and are not, therefore, plastics by the definition given above.

Polymeric molecules usually form (polymerize) as flakes or granules, although some can be viscous liquids. At this stage the polymeric material is called a *resin*. In some cases the flakes or granules are formed into some intermediate shape (such as small pellets) but these can also be called resins because they are subsequently shaped. Some shaping processes use the liquid materials to form the final shaped part. These liquid materials would also be called resins. Hence, a resin is any liquid or solid material that is later formed into a shaped plastic part. Because of this close connection between the terms resins, plastics and polymers, these terms are sometimes used interchangeably, although correctly used there are differences. To summarize: polymers are any material made up of molecular chains; plastics are synthetic, long-chain polymers that can be or have been shaped; and resins are solids or liquids that are subsequently shaped into a plastic part.

Synthetic materials are those that are man-made or man-altered. Since this book is about plastics, only synthetic polymeric materials will be considered.

Three classes of synthetic polymeric materials can be identified. The first class is synthetic polymeric materials that **do not occur naturally.** Many examples of this class can be given including nylon, polyester, polyethylene, and most of the common plastics in use today. The second class is synthetic polymeric materials that **occur naturally but can also be made by a non-natural process.** In this case both natural and synthetic types of the same material can exist. The natural and synthetic materials are often distinguished from each other as with natural and synthetic rubber. The third class of synthetic polymeric materials are those **naturally-occurring materials that are modified so substantially that the identity or basic nature of the material is changed.** This third class can be called naturally-derived synthetic materials. These materials were important in the early development of the plastics industry. An example of this type is cellophane, which is derived from cellulose (wood pulp).

HISTORY OF PLASTICS

The history of mankind's use of polymers and eventual development of plastics has followed a general pattern of events.

1. Discovery of the polymer. (This usually implies a naturally-occurring polymer, but some recent discoveries of synthetic polymers were made in the laboratory unintentionally.)
2. Use of the polymer. (The early applications are usually based upon the obvious properties of the polymer and require little modification of the material.)
3. Realization of deficiencies of the material and attempts at modification, usually by trial and error.
4. Investigation of the properties of the material and development of a conceptual view or model of the material's basic nature. (This step may take many years.)
5. Systematic modification based upon the properties and basic nature that have been developed.

Alternately, synthetic materials might be made that mimic the properties of the natural polymer, or in latter cases, development of synthetic materials that do not have natural analogues but have useful properties in their own right. Most plastics have followed the development pattern described, and for those that haven't, the deviations from the pattern are, in themselves, instructive on how new materials are developed.

Since the beginning of history, mankind has benefited from naturally-occurring polymers. These polymers have provided the raw materials for satisfying basic needs such as clothing (cotton, wool, silk, flax, fur), shelter (lumber, asphalt), food (starch, protein), and many higher needs such as communication (papyrus, wood pulp), music (strings, glues, reeds, lacquers), decoration (amber), defense and war (arrows, spears, bows), and recreation (rubber). Most of these polymers could be used with only minor modifications such as weaving the wool or cutting and shaping of wood.

Ancient people found that some natural polymers could be made more useful by making slightly greater changes to the polymer material. For instance, the flax plant could be beaten with rocks or between rollers to crush the cell structure and allow the long fibers to be separated from the rest of the plant. These long flax fibers were then woven into linen cloth. Even when more extensive modifications were made, such as the soaking of hides in tannic acid (tanning of leather) to prevent hardening when they dried, little change was made to the resultant material except cutting, shaping, sewing, and other changes in physical shape. Many of these polymers are still important today.

While most of these natural materials would not be considered plastics (they are neither molded as liquids nor are they synthetic), some natural materials were molded in ways similar to modern plastics. For instance, the sap or resin from resinous trees like pines and firs was found to harden if left to stand in the air and could therefore be placed into a mold of some desired shape and allowed to solidify. The solid part could be removed and it would retain the shape of the mold. Jewelry, amulets, and idols were made by this method. Modern plastics that are first liquids and then harden in molds in a process called casting, are called *resins* after the tree sap analogy.

An ancient natural polymer used in plastic-like processes is lac, which is a resin from certain shrubs that forms the basis of shellac or lacquer. The use of lac as a wood coating material was known and reported in about 1000 B.C. and was described in detail by explorers to India in the sixteenth century. Modern paints employ the same basic principles of drying from a solvent base as did ancient lac.

Natural rubber is another polymer that was described by sixteenth century explorers. The natives of Central and South America had found that by coagulating the latex (water suspension) sap from certain trees, a flexible, bouncy material was produced. Rubber was then investigated by scientists to determine the nature of this unusual behavior. For instance, in 1820, Thomas Hancock discovered that if the rubber was highly sheared or masticated, it became formable and hence capable of flow. In 1826, Michael Faraday, one of the founders of modern day electrical theory, performed elemental analysis on rubber and established the correct relationship between the number of carbon and hydrogen atoms. In 1839, Charles Goodyear discovered that natural rubber heated with sulphur retained its elasticity over a wider range of temperatures than the raw material and that it had greater resistance to solvents. This process came to be called *vulcanization.* If very large amounts of sulphur were added, the rubber stiffened significantly. This material is known as hard rubber. Later, others extracted several materials from natural rubber and characterized these, eventually breaking down the rubber into its basic chemical constituents. These were then recombined and, in 1897, an elastic, rubberlike material was synthesized. Hence, in the case of natural rubber, the steps in the pattern of polymer discovery—use, characterization, modification, and synthesis—were followed. Natural rubber is generally not considered to be a plastic, but highly modified natural rubber and synthetic rubbers would be plastics.

In the nineteenth century, wood pulp, plant fibers, or cotton fibers (all made of cellulose, a natural polymer) were treated with nitric acid to form a highly explosive material called gun cotton or more commonly today, nitrocellulose. It was used as a substitute for gun powder in both the American Civil War and in World War I. If the nitrocellulose had a lower nitrogen content, it was less explosive and could be molded or formed into a film or a shaped part after dissolving in a solvent, shaping and then allowing the solvent to evaporate. This highly modified cellulose became known as Parkesine. If treated with camphor, nitrocellulose became pliable and could be formed directly (with little or no solvent) and was known as Celluloid. Celluloid was used for early motion picture films, waterproofing coatings, combs and other molded items, and coating billiard balls (slightly explosive if impacted very hard). Celluloid, invented in 1868 by John Wesley

Hyatt, is considered to be the first commercial plastic. It was soon discovered that treatment of nitrocellulose with other acids and solvents resulted in quite different materials that could also be pressed into films or forced through small holes to form continuous fibers. These became known as cellophane and rayon. By the definition of plastics given at the beginning of this chapter, these *highly modified* natural polymers are viewed as plastics, that is, polymers that are substantially made (or modified) by synthetic (non-natural) processes.

Near the end of the nineteenth century and the beginning of the twentieth century, key postulates on the molecular structure of polymers were made that gave impetus to the development of new, wholly synthetic polymers. The synthetic fabrications then led to other, improved or expanded structural postulates. For instance, in 1877, Fredrich Kekulé, a pioneer in modern organic chemistry, proposed that natural organic substances consist of very long chains of molecules from which they derive their special properties. In 1893, Emil Fischer proposed a chain structure for cellulose that was followed shortly thereafter by the synthesis of a long, linear molecule based on sugar by Hermann Leuchs, an associate of Fischer. This synthesis confirmed many of the features of the Kekulé and Fischer structures of natural polymers.

Chemists also began to synthesize and explore the properties of polymers that were built up from small molecules rather than derived from natural polymers, although the syntheses were largely done by trial and error. One of the earliest developed (early 1900s) wholly synthetic polymers was phenolic (named Bakelite by Leo Bakeland, the inventor). It was formed by mixing and heating phenol and formaldehyde, two easily obtained, widely used chemicals. The process resulted in a resin that could be shaped (molded) and then, with time and elevated temperature, solidified into a hard material with excellent thermal and electrical insulating capabilities. The material is still used as handles for cooking pans and electrical switches although other plastics now compete for these applications. Shortly thereafter other polymers based upon formaldehyde were synthesized, some of which found use as coatings for paper and wood and are still widely used in kitchen countertops (Formica) and for the adhesive in particle board lumber and plywood.

Several other polymers were then found by mixing simple gases under extreme conditions (usually high heat and pressure) to form powdery solids. This synthesis method is today called the *addition, chain-growth, or free radical polymerization,* which will be described in detail in the chapter on Polymeric Materials (Molecular Viewpoint). The most common example of this was the reacting of ethylene gas to form polyethylene. Other polymers made during this time and by similar processes were polyvinyl chloride (PVC), polystyrene, and polymethyl methacrylate. The processes were poorly understood with successful results often coming only because of fortuitous accidents. For instance, the discoverers of polyethylene had great difficulty duplicating their original successful synthesis. After much investigation they discovered that a trace amount of oxygen was necessary for the reaction to proceed and that in the original experiment a small leak in the apparatus had provided this small oxygen source. In most of these cases the polymeric natures of the products were not well understood, despite the early work of Kekulé and Fischer. (Many scientists believed that the solid products of small molecules were simply small molecules held tightly together by physical, not chemical, forces and were therefore different from the naturally occurring polymers.)

The structural model for modern, wholly synthetic plastics can be traced to the proposed structure of a polymer by Herman Staudinger in 1924. He proposed that a polymer was a linear structure consisting of small units held together by normal chemical bonds. This structure model was disputed by many leading chemists of those days. However, the emergence of x-ray diffraction and of the ultracentrifuge were key analytical tools that were used to investigate the structure of polymers and eventually confirmed the Staudinger structure.

This well-defined structural model led to a decision by the DuPont Company in the early 1930s to make a polymer entirely from small molecules with specific, and preconceived,