PLASTICS
Materials and Processing

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Third Edition

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Contents

Preface

This edition retains the general objectives and format of the previous edition with some important additions and reorganizations to clarify some topics. The principal objective of *Plastics: Materials and Processing, Third Edition*, 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 resource for future reference. 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 overall knowledge of the entire field of plastics technology. 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, handbooks of plastics, and computer databases that are published regularly and can therefore present more up-to-date data.

The text parallels an introductory plastics course taught for many years 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 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 in and a 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 to 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 category of materials that traditionally includes commercial and engineering thermoplastics and thermosets. If a broad view of plastics is taken, elastomers and highly modified natural polymers can also be included. This book takes the broad view, thus allowing comparisons of similar concepts and principles within all these related 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 that chapter's 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 **boldfaced** 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 and gathered into a glossary. A valuable cost estimating form for injection molding parts is also included as an appendix (Appendix 2).

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.

New Features

In the second edition, some concepts were reorganized so that the flow is easier for the reader. For instance, the tooling chapter of the first edition was distributed into tooling sections in each of the processing chapters, thus integrating tooling and processing for each process. Similarly, the testing section was put into the chapters where properties of plastics are discussed. The chapter on design was moved to immediately follow the chapters on properties, thus giving an immediate example of how the properties can be used in specific examples.

The second edition had several new charts and figures, which not only improved on previous charts but also allowed some concepts to be understood in a broader overall view, often better than was done with text only. A glossary of new terms was added to each chapter.

A form (Design Matrix) that can be copied and used for designing new plastic parts was added as an appendix. A case study in the chapter on design illustrates, in detail, how to use this form.

Brief characteristics of the major plastics are printed inside the front and back covers for easy reference and comparison.

New and Expanded Third Edition

The world of plastics continues to expand and change. To reflect that change, several new topics have been added to the book so that it will remain current. The following are some of the more important of those additions:

- Conductive polymers
- Nano technology
- Biodegradable polymers
- Bio-based raw materials
- Twin-sheet thermoforming
- Health considerations of plasticizers

The following changes have been made to the features of the book:

- Added appendix on properties of engineering materials
- Added appendix on plastics identification chart
- Added appendix on process procedures—startup, steady-state, and shutdown, including information on safety
- Added appendix on machining guidelines for plastics
- Added appendix on MSDS sample sheet and form
- Combined all the glossaries from each chapter into a single glossary at the end of the book
- Added many photos of processes that correlate to diagrams of the process
- Added many photos showing typical products made from each material and by each process
- Upgraded numerous figures
- Significantly expanded several chapters
- Reorganized the order of the chapters to simplify reading
- Reorganized each of the processing chapters to identify advantages, disadvantages, and costs of each process so that comparisons between processes would be easier
- Expanded the chapter questions

An expanded online Instructor's Manual has also been prepared. It contains answers to all the questions as well as several laboratory procedures that have proven to work well. To

access the online Instructor's Manual, go to **www.prenhall.com**. Instructors can search for a text by author, title, ISBN, or by selecting the appropriate discipline from the pull down menu at the top of the catalog home page. To access supplementary materials online, instructors need to request an instructor access code. Go to **www.prenhall.com**, click the **Instructor Resource Center** link, and then click Register Today for an instructor access code. Within 48 hours of registering you will receive a confirming e-mail including an instructor access code. Once you have received your code, go to the site and log on for full instructions on downloading the materials that you wish to use.

I hope that you enjoy reading the book as much as I have enjoyed writing it.

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CHAPTER ONE

Introduction to Plastics

CHAPTER OVERVIEW

This chapter examines the following concepts:

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

DEFINITIONS OF PLASTICS AND POLYMERS

Plastics does not have a commonly agreed-upon definition. Some prefer to define plastics in a relatively narrow sense, focusing on specific properties (such as formability). Others prefer to define plastics more broadly, viewing collectively properties, processing, and design characteristics of a group of related materials. This book uses a relatively broad definition, with the objective of assisting the reader to appreciate the fundamental similarities among a large group of related materials.

Plastics *are materials composed principally of large molecules (polymers) that are synthetically made or, if naturally occurring, are highly modified.* This definition of plastics can be illustrated in a systematic classification diagram, as shown in Figure 1.1. In addition to their similar nature as synthetic polymers, *all plastic materials have the property that at some stage, they have been or can be readily formed or molded into a useful shape.* (The word *plastic* comes from the Greek *plastikos*, which means "to form or mold.")

As Figure 1.1 shows, all materials can be classified as gases, simple liquids, or solids, with the understanding that most materials can be converted from one state to another through heating or cooling. If only materials that are structural solids at normal temperatures are examined, three major types of materials are encountered: metals, polymers, and ceramics. The polymer materials can be further divided into **synthetic polymers** and **natural polymers.**

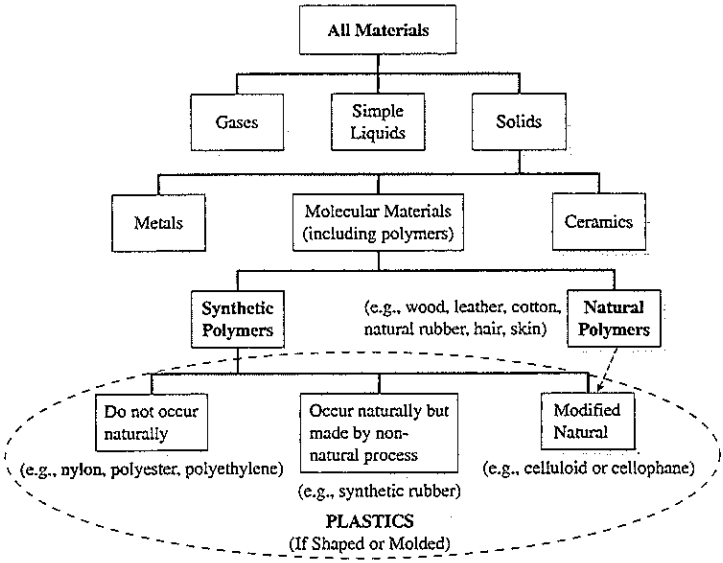

Figure 1.1 Diagram illustrating the definition of plastics.

Most synthetic polymers are those that do not occur naturally and are represented by materials such as nylon, polyethylene, and polyester. Some synthetic polymers could be manufactured copies of naturally occurring materials (such as synthetic rubber) or even natural polymers that have been so radically modified that they no longer possess the general properties of the original natural polymer, such as celluloid or cellophane, which are derived from cellulose. Therefore, natural rubber is not a plastic but is considered as a reference material in the chapter on elastomers. (Some narrow definitions of plastics exclude all elastomers from the plastics group.) Hence, by our definition, *plastics include all non-naturally occurring polymers, all synthetic elastomers, and all highly modified natural polymers*, as shown in the circled area within Figure 1.1.

Definition of Polymers

A detailed explanation of polymers is given in Chapter 2, on the molecular nature of materials. However, a simple understanding of polymers can be gained by imagining them to be like a chain or, perhaps, a string of pearls, where the individual pearls represent small

molecules that are chemically bonded together. Therefore, a polymer *is a molecule made up of smaller molecules that are joined together by chemical bonds*. The word *polymer* means "many parts or units." The parts or units are the small molecules that combine. The result of the combination is, of course, a chainlike molecule (polymer). Usually the polymer chains are long, often consisting of hundreds of units, but polymers consisting of only a few units linked together are also known and can be commercially valuable.

All **molecules**, whether the small type or the large type that result when particular small molecules join together, are made up of **atoms** (such as carbon, hydrogen, oxygen, or nitrogen). When any small molecule is formed, the atoms join together into a specific arrangement that is characteristic of the particular molecule. The types of atoms and their arrangement determine the properties of the molecule. For instance, the small molecule called methane (natural gas) always has one carbon and four hydrogens, which are arranged in a tetrahedral (pyramid) shape. Another small molecule, ethylene, is a gas derived from petroleum that always has two carbons and four hydrogens arranged so that two hydrogens are connected to each carbon and the carbons are also linked to one another in a planar arrangement. Ethylene is one type of small molecule that can be combined into very long chains to make polymers (polymeric molecules), whereas methane cannot be readily combined to form polymers. Plainly, ethylene and methane are different small molecules and have different chemical properties.

Therefore, the **chemical properties** of a molecule determine the types of reactions into which the molecule can enter. In the example of ethylene and methane, the ethylene is more chemically reactive under the conditions needed to form polymers. The reasons for this chemical reactivity and the nature of the chemical reactions that take place are a major study of chemists and are beyond the scope of this book. However, some specific examples are given in the chapter on the molecular (chemical) nature of polymers, especially concerning the reactions that take place when small molecules combine to form polymers. For now, the polymer-forming process can be understood in general terms by examining Figure 1.2, where the combining of small molecules to create a polymer is depicted. Note that each small molecule has two reactive forces, thus allowing each small molecule to be bonded to two others and a long chain to be formed.

The chains formed are called *polymers*, or *polymeric molecules*. 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 small molecules, 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 liquid at room temperature. These short molecular chains are sometimes called **oligomers**. An example of a short-chain molecule would be cooking oil. Long-chain molecules are usually solids or viscous liquids. 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 *giant molecule*. All plastics are giant molecules, although some giant molecules are naturally occurring and are not, therefore, plastics by the definition used in this book.

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

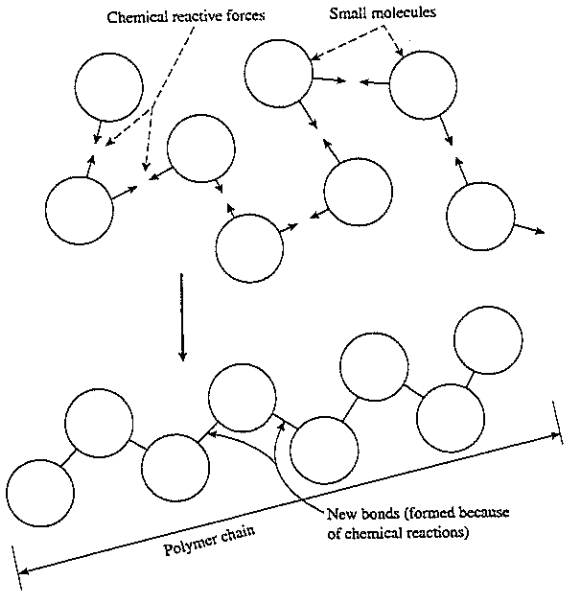

Figure 1.2 Illustration of small molecules combined into a polymer chain.

molecules of the same type are combined, 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.

Another term that is often associated with polymers and plastics is *resin*. Although no definition for resin is universally accepted, a convenient definition is *a* **resin** *is a polymer that has not yet been formed into its final useful shape*.

When initially made, polymers are usually **viscous liquids** or, if solid, are **granules (powders)** or **flakes**. In some cases the granules or flakes are formed into some intermediate shape (such as small **pellets**), but these can also be called resins because they are later formed into a shaped plastic part. Because of this close connection between the terms *resins*, *plastics*, and *polymers*, they 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.

HISTORY OF PLASTICS

The history of humankind'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 discoveries of synthetic polymers were made in the laboratory unintentionally.)
2. Use of the polymer. (The early applications were usually based upon the obvious properties of the polymer and required 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 or synthesis of materials that might 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.

A time summary of the history of plastics is given in Table 1.1.

Since the beginning of history, people have 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), and 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 the 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 in a natural polymer, 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.

Although most of these natural materials would not be considered plastics (they are not 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. The modern term *resin* comes from this tree-sap analogy.

An ancient natural polymer used in plasticlike 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

Table 1.1 History of Plastics

Year	Event
Pre-1800	People discovered and used natural polymers (examples: wool, cotton, leather, wood, silk, flax, lacquers, rubber) with little modification of the polymer.
1839	Charles Goodyear discovered the process for vulcanizing natural rubber.
1868	Celluloid was invented by John Wesley Hyatt. This is considered to be the first plastic because it was made by substantially modifying a natural polymer and then molding the resulting material into new shapes.
1877	Fredrich Kekulé proposed the chain model for polymers.
1893	Emil Fischer and Hermann Leuchs proposed a chain structure for cellulose and then synthesized the molecule, thus confirming their proposed structure.
1909	Leo Baekeland announced the invention of phenolic resin, the first polymer made from purely synthetic materials.
1924	The polymer chain structure for synthetic polymers was proposed by Herman Staudinger.
1925–1940	Several polymers made by the addition polymerization method were introduced (examples: PVC, PMMA, PS, PE, PVAc, PAN, SAN).
1934	Nylon and the condensation polymerization process were invented by Wallace Carothers.
1940–1950	Several polymers made by the condensation polymerization method were introduced (examples: PET, unsaturated polyester).
1950–1955	Low-pressure catalysts were developed by K. Ziegler and G. Natta.
1955–1970	Many polymers made by a variety of methods were introduced (examples: PC, silicones, PPO, acetals, epoxies, polyurethanes).
1955–1970	Composite materials were developed using synthetic resins and strong, stiff reinforcements such as fiberglass, carbon fiber, and aramid fibers.
1970–1990	Production and development of new manufacturing methods for plastic parts were expanded, resulting in lower prices, improved quality, and applications where other materials, such as wood and metal, had previously been used.
1990–2005	Resins with sophisticated structures were developed, giving special properties such as high thermal resistance, low flammability, light sensitivity, electrical conductivity, biodegradability, and biocompatibility.
1990–2005	Several new catalysts that significantly improved the properties of many resins were developed, thus further expanding the capabilities of plastics.

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 sap from

certain trees, a flexible, bouncy material was produced. In 1839, Charles Goodyear discovered that natural rubber heated with sulphur retained its elasticity over a wider range of temperatures than the raw rubber 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 not strictly considered 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 World War I. If the nitrocellulose had a lower nitrogen content, it was less explosive and could be treated with camphor to become pliable and moldable. This material was known as celluloid. Celluloid was used for early motion picture films, waterproofing coatings, combs and other molded items, and making 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 cellulose 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 (nonnatural) processes.

Near the end of the nineteenth century and the beginning of the twentieth century, key postulates on the molecular structure of polymers were formed 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 some 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 by Hermann Leuchs, an associate of Fischer, of a long, linear molecule based on sugar. 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 these early 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 is described in detail in Chapter 2, "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 (PS), and polymethyl methacrylate (PMMA). The processes were poorly understood; successful results often came 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 structurally 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 structural model was disputed by many leading chemists of those days. However, the emergence of X-ray diffraction and of the ultracentrifuge provided key analytical tools 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, properties. DuPont hired Wallace Carothers, from Harvard University, to make a material that had properties similar to natural silk. After several years of experimentation and development, the polymer that we now call nylon was created. Even more important, Carothers developed a new process for making polymers and clarified the supporting molecular structure model. Within a short time, this knowledge of the nylon polymerization process (called *condensation polymerization* or *stepwise polymerization*) led to the development and understanding of additional processes for fabricating other polymers by simply varying the type of small molecules used as the starting materials. These polymerization processes will be discussed in more detail in Chapter 2.

The combination of good structural models and several polymerization methods (addition and condensation), coupled with the needs of World War II and the postwar consumer boom, resulted in rapid developments of many new polymers and hundreds of diverse new applications for plastics. Polytetrafluoroethylene, or PTFE (Teflon®), was discovered (by accident) and then synthesized and became an important material for wire insulation, chemical-resistant, and nonstick applications. Other developments in plastics included synthetic rubber; scratch-resistant, weatherable, transparent plastics for aircraft, buildings, and packaging; lightweight, low-cost, nonflammable, nonwrinkling fibers for clothes, carpets, and other textile applications; sophisticated coatings and packaging materials for food

wrappings and containers as well as paints; unique electrical devices and insulators; and structural materials for buildings, aircraft, and automobiles. Plastics successfully replaced traditional materials (such as wood and metal) in many applications but occasionally with less than acceptable results before the long-term behavior of the plastic was well understood. Hence, plastics developed a reputation for being "cheap" and short-lived. In some applications, however, plastics were indispensable and filled the requirement better than any other material. An example would be wire insulation, which combined flexibility with the good electrical insulative capability of plastics. Improvements in plastics materials and use in more appropriate applications have largely removed their negative image.

Catalysts developed by Ziegler and Natta allowed low-cost production of high-density polyethylene and polypropylene, which began to be produced in large volumes. Investigations surrounding the use of these catalysts further illuminated the processes of polymerization, and the resulting polymeric structure was refined. The concepts of crystallinity in polymers and the dependence of properties on molecular structure were understood at a much deeper and more meaningful level. These concepts led to other catalysts, improved processing methods, and stronger, longer-lasting, and less expensive polymers. Some of these polymers were new materials, but in some cases new plastic materials were made by blending or combining previously known polymers.

The combining of plastics with fiber reinforcement materials, usually ceramics or metals, but occasionally very strong and stiff polymers, provided further advances in properties available to society. These combinations of materials, called *composites*, were easily formable because of the plastic material but were very strong and stiff because of the reinforcements. Fiberglass-reinforced plastic, carbon fiber epoxy, and carbon-carbon composites are typical examples that have been used extensively in automotive, aerospace, and sports applications.

Other areas of polymer development include electrically conductive polymers, light-sensitive polymers, biodegradable plastics, biocompatible plastics for medical applications, and derivation of plastic feedstocks from sources other than petroleum, such as coal and plant materials.

Although the developments in plastic materials have been astounding, the developments in the processing, fabrication, and analysis of plastics have been equally important. A multitude of plastic-manufacturing methods are now available, each with one or more particular advantages. These processes allow plastic materials to be shaped inexpensively and accurately while achieving desired functionality or desired material characteristics and optimal performance. New equipment and new methods are still the subject of extensive development efforts.

This history of plastics began with people's use of and curiosity about natural polymers. Improvement of these natural polymers was inevitable. Over time, fortuitous events led to the discovery and characterization of synthetic polymers. Eventually, the underlying concepts of polymer synthesis, structure, and properties were so well understood that polymers could be made to fill specific end-use requirements. Today, the development, characterization, and fabrication of polymers involves chemists, mathematicians, statisticians, design engineers, and manufacturing engineers, among others. In many cases, the tasks of these experts overlap, which may facilitate the advancement of the field of plastics as the skill levels required for further advancements continue to increase.

RAW MATERIAL SUPPLY AND PRICING

Although the history of plastics begins with natural polymers, modern plastics are generally made from small molecules and built up into polymeric chains rather than by converting existing natural polymers into plastics. The small molecules used to make most plastics have been derived chiefly from crude oil. (The major exception is plastics based upon the molecule ethylene where about half of the ethylene is derived from natural gas, although the rest of the ethylene is from crude oil.) The plastics component of crude oil is approximately 2% of the total volume of crude oil consumed (Figure 1.3). Plastics can also be obtained from coal, trees, and other plant products (corn, nut husks, soy, oats, tree sap), as well as from other naturally occurring materials (fish, animals, algae).

Even though crude oil continues to be the most common source for the chemicals that are used to make plastics, some resin manufacturers have embarked upon a campaign to identify chemicals and polymerization methods that are completely renewable and bio-based. Some of these innovations have identified raw materials from natural sources, such as ethanol from corn syrup or polyols from soybeans, which are then used to make polymers in the traditional way. Some of these polymers derived from wholly natural and renewable raw materials have already been made into commercial polymers.

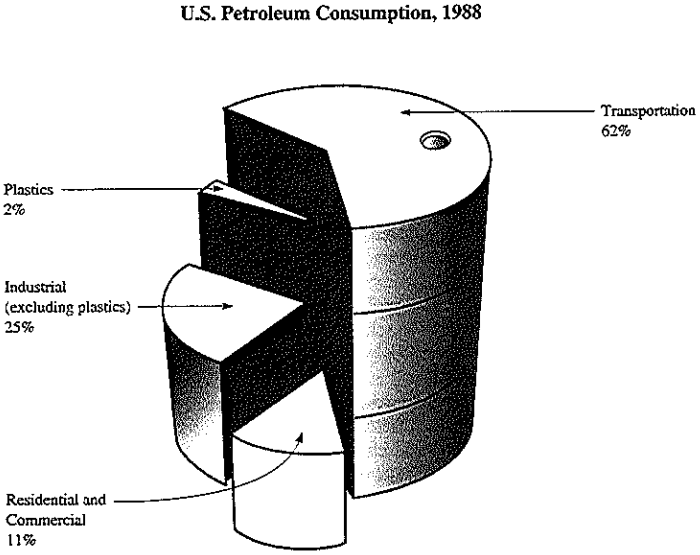

Figure 1.3 Plastics as a component of petroleum consumption in the United States.

Other efforts to make bio-based polymers are much more daring. These methods are exploring the creation of polymers directly from natural materials (such as corn) through the use of genetically engineered bacteria. In some of these cases, the raw materials are waste products of the bacteria, and in other cases, the polymers are actually made by the bacteria and are stored as food reserves. Still other researchers are genetically modifying plants, often followed by cloning, to produce polymers that can be extracted for commercial use. These efforts could produce totally new polymer species with unique properties beyond those expected of bio-derived materials. The major problem to date is cost and yield. However, as our ability to manipulate plants genetically improves, the natural production of these materials will increase and become competitive in cost and overall performance with petroleum-derived polymers.

The advantages of using bio-based materials are numerous. (We should remember, however, that oil-based products are also bio-based—it is just that the plants that gave us the oil lived a long time ago.) What should be focused on is not the origin of the raw materials, but, rather, the nature of the resulting polymer. If that polymer is not compatible with biological entities, it should be considered synthetic and should not be mixed with biological materials in the waste stream. It should be recycled in a totally synthetic waste stream. Likewise, if the polymer is synthesized so that it is compatible with biological systems, it should be recycled within the biological waste stream and not be mixed with synthetic materials. By keeping these two waste streams (biocompatible and synthetic) separate, numerous environmental problems, such as unwanted degradation and pollution of the biosphere, can be largely avoided.

Clearly, using modern bio-based materials can potentially reduce the pollution associated with transporting and refining oil. The new products could also eliminate the price fluctuations of plastic raw materials that have become commonplace with petroleum-based products. Stable raw material prices can add significant profits for resin producers because of improved control over inventories and the potential of lower prices from agricultural sources. In light of all these advantages, at least one major chemical company, DuPont, has stated its desire to develop a bio-based feedstock supply for each of its existing products and to explore the properties and applications of wholly new bio-based polymers.

While plastics continue to be largely oil-based, prices of raw materials for plastics are dependent on the price of oil, but not to the same extent as fuels, which comprise the largest use of crude oil. Other factors such as production costs, capacities, and demand generally have a greater influence on costs. For instance, the costs of polyethylene (PE) and polyvinyl chloride (PVC) are low (approximately one-fourth) compared to the costs of polycarbonate (PC) and polyethylene terephthalate (PET), yet the amount of crude oil contained in all of them is not much different. The differences in price arise from differences in the processes and, eventually, in the amount of the plastics produced (price-volume relationship). The process complexity is dependent upon costs of raw materials, costs of nonpetroleum components, costs of equipment, variations and complexity of the processing conditions, labor, environmental protection costs, and energy consumed. Table 1.2 gives the prices of various plastics in 2005, showing the high variability of prices, with a range of $0.48 per pound for polyethylene to $6.70 per pound for polytetrafluoroethylene (PTFE) and $33.00 per pound for polyetheretherketone (PEEK).

Table 1.2 Prices of Various Plastics (2005)

Plastic Type	PE	PS	PET	PA (nylon)	PC	PTFE	PEEK
Price ($/pound)	0.75	0.86	0.79	1.40	1.75	6.70	33.00

For a new plastic material, the pricing pattern has usually been to sell it for uses that place a high value on the properties of the plastic so that high prices can be justified. As time goes on, the manufacturer of the plastic develops more economical methods of manufacture and the price drops, which allows the development of other uses. Eventually, the volume and market stability warrant the erection of a full-size manufacturing facility rather than the semiworks or pilot plant that are initially used. The economies of scale and inevitable competition usually result in a dramatic price reduction for the plastic over the subsequent few years and then a leveling off of the price as the process and consumption (demand) become stable and the major uses are identified and demonstrated. The long-term price then becomes a function of the complexity of the process and the volume (as already discussed). The price-volume relationship is illustrated in Figure 1.4 for several plastic and nonplastic materials. The general linearity of the curve in this figure confirms the strong price-volume dependence of all these materials. The deviations from the line, which are generally small, suggest that the process complexity is a factor in the price, although it is a secondary factor.

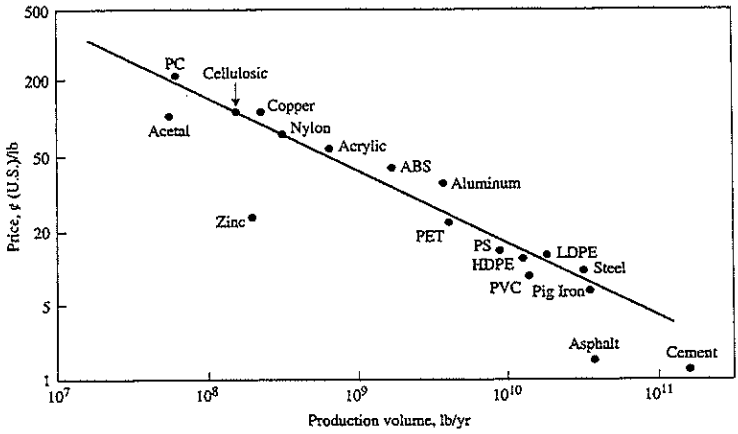

Figure 1.4 Price-volume relationship for plastics and other selected materials (1998 data).