Susan E. M. Selke
John D. Culter
Rafael A. Auras
Muhammad Rabnawaz

Plastics Packaging

Properties, Processing, Applications, and Regulations

4th Edition

HANSER

Selke, Culter, Auras, Rabnawaz
Plastics Packaging

Susan E. M. Selke
John D. Culter
Rafael A. Auras
Muhammad Rabnawaz

Plastics Packaging

Properties, Processing, Applications, and Regulations

4th Edition

HANSER
Hanser Publishers, Munich

The Authors:

Susan E. M. Selke, Professor Emeritus, School of Packaging, Michigan State University, 448 Wilson Rd., Rm. 135, East Lansing, MI 48824-1223

John D. Culter, President, Advanced Materials Engineering Inc., 1231 Silver Lakes Blvd., #132, Naples, FL 34114-9232

Rafael A. Auras, Professor, School of Packaging, Michigan State University, 448 Wilson Rd., Rm. 145, East Lansing, MI 48824-1223

Muhammad Rabnawaz, Assistant Professor, Michigan State University, 448 Wilson Rd., Rm. 145, East Lansing, MI 48824-1223

Distributed by
Carl Hanser Verlag
Postfach 86 04 20, 81631 München, Germany
Fax: +49 (89) 98 48 09
www.hanserpublications.com
www.hanser-fachbuch.de

Cataloging-in-Publication Data is on file with the Library of Congress

Editor: Dr. Julia Diaz Luque
Production Management: Cornelia Speckmaier
Cover concept: Marc Müller-Bremer, www.rebranding.de, München
Cover design: Max Kostopoulos
Typesetting: Eberl & Kœsel Studio GmbH, Krugzell, Germany
Printed and bound by CPI Ebner & Spiegel GmbH, Ulm
Printed in Germany

ISBN: 978-1-56990-822-8
eBook ISBN: 978-1-56990-823-5

Preface

This book is intended to provide a basic understanding of plastic packaging materials. It covers the properties of common packaging plastics, and relates these properties to the chemical structure of the polymers. Common processing methods for transforming plastic resins into packages are covered.

In this book, we discuss the uses of plastics in packaging. Although this is not a course in chemistry or materials science, we attempt to stress the relationship between chemical structure and packaging material properties. We expect the reader to have some knowledge of chemistry and physics. The major purpose of this book is to provide the students in the School of Packaging with reading material on plastics for packaging; however, we hope that it can also be useful to packaging professionals responsible for writing specifications, designing, fabricating, testing, and controlling the quality of plastic materials. We also hope to trigger the readers' curiosity to pursue further studies in the exciting world of packaging materials.

This fourth edition updates information from the third edition. We have expanded and updated the discussion of biobased plastics such as PLA, PBS, and PHA, plastics recycling, life cycle assessment, and a variety of other topics. We have expanded the discussion of migration, added some new topics such as foam blow molding, and fixed a few errors that, despite our best efforts, still crept in.

We have deliberately included some information that goes well beyond what normally would be included in an introductory level packaging course, in order to make it available for the more advanced student and for the practitioner. The "Study Questions" at the end of each chapter are intended to serve as review of the main concepts, and also to stimulate thought about aspects of plastics that have not been thoroughly covered. Answers to quantitative questions are provided in parentheses after the question.

One of the significant changes in this fourth edition is the addition of two new co-authors, Dr. Rafael Auras and Dr. Muhammad Rabnawaz. Both are faculty in the School of Packaging at Michigan State University, and experts in plastics packaging. John Culter and Susan Selke hope to pass the torch to them for further editions of this textbook.

Content

1 Introduction

1.1 Historic Note

The first man-made plastic, a form of cellulose nitrate, was prepared in 1838 by A. Parker and shown at the Great International Exhibition in London in 1862. It was intended to be a replacement for natural materials such as ivory and was called parkesine. In 1840, Goodyear and Hancock developed the "vulcanization" procedure that eliminated tackiness and added elasticity to natural rubber. The change in the properties of the natural rubber was obtained by the addition of sulfur powder that produced additional chemical bonds in the bulk of the rubber.

In 1851, hard rubber, or ebonite, was commercialized. In 1870 a patent was issued to J. Hyatt, of New York, for celluloid, a type of cellulose nitrate with low nitrate content produced at high temperature and pressure. This was the first commercially available plastic and the only one until the development of Bakelite by Baekeland in 1907. Bakelite is the first of the entirely synthetic plastics and consisted of a resin obtained by the reaction of phenol and formaldehyde.

The exact nature of plastics, rubber, and similar natural materials was not known until 1920, when H. Staudinger proposed a revolutionary idea: all plastics, rubber, and materials such as cellulose were polymers or macromolecules. Before Staudinger's theory, the scientific community was very confused about the exact nature of plastics, rubbers, and other materials of very high molecular weight. To most research workers in the 19th century, the finding that some materials had a molecular weight in excess of 10,000 g/mol appeared to be untrustworthy. They confused such substances with colloidal systems consisting of stable suspensions of small molecules.

Staudinger rejected the idea that these substances were organic colloids. He hypothesized that the high molecular weight substances known as polymers were true macromolecules formed by covalent bonds. Staudinger's macromolecular theory stated that polymers consist of long chains in which the individual monomers (or building blocks) are connected with each other by normal covalent bonds. The

unique polymer properties are a consequence of the high molecular weight and long chain nature of the macromolecule. While at first his hypothesis was not readily accepted by most scientists, it eventually became clear that this explanation permitted the rational interpretation of experiments and so gave to industrial chemists a firm guide for their work. An explosion in the number of polymers followed. Staudinger was awarded the Nobel Prize in 1953. It is well established now that plastics, as well as many other substances such as rubber, cellulose, and DNA, are macromolecules.

Since 1930, the growth in the number of polymers and their applications has been immense. During the 1930s, industrial chemical companies initiated fundamental research programs that had a tremendous impact on our society. For example, Wallace Carothers, working at DuPont de Nemours and Co., developed diverse polymeric materials of defined structures and investigated how the properties of these materials depend on their structure. In 1939 this program resulted in the commercialization of nylon.

A commercial process for the synthesis of polyethylene was successfully developed in the 1930s by ICI (Imperial Chemical Industries), in England. In 1955, K. Ziegler in Germany and J. Natta in Italy developed processes for making polyethylene at low pressure and temperature using special catalysts. They were awarded the Nobel Prize, Ziegler in 1964 and Natta in 1965, for their contributions in the development of new polymerization catalysts with unique stereo-regulating powers. Linear polyethylene produced using solution and gas technologies was introduced in the 1970s. The continuous development of new polymers resulted in additional breakthroughs in the mid-1980s and early 1990s. Single-site catalysts, which were originally discovered by Natta in the mid-1950s, were commercialized for syndiotactic polystyrene in 1954, polypropylene in 1984, and polyethylenes in the early 1990s. These catalysts permit much greater control over the molecular weight and architecture of polyolefins such as polyethylene and polypropylene. Table 1.1 shows the approximate introduction dates for some common plastics.

Table 1.1 Approximate Dates of Introduction for Some Common Plastics

Date	Polymer	Date	Polymer
1907	Phenol-formaldehyde resins	1952	Polyethylene, linear
1927	Polyvinyl chloride	1955	Polypropylene
1927	Cellulose acetate	1957	Polycarbonate
1930	Styrene-butadiene rubber	1957	LLDPE – linear low density polyethylene
1936	Polymethyl methacrylate	1964	Ionomer resins
1936	Polyvinyl acetate	1965	Polyimides
1938	Polystyrene	1970	Moldable elastomers
1938	Nylon 66	1972	Acrylonitrile copolymers
1939	Polyvinylidene chloride	1972	Ethylene vinyl alcohol
1941	Polytetrafluoroethylene	1974	Aromatic polyamides
1942	Polyesters, unsaturated	1978	PET – polyethylene terephthalate
1942	Polyethylene, branched	1983	PEEK – polyether ether ketone PES – polyether sulfone
1943	Butyl rubber	1985	Liquid crystal polymers
1943	Nylon 6	1990	PHBV – polyhydroxy butyrate
1943	Fluoropolymers	1992	Metallocene polymers
1943	Silicones	1994	PEN – polyethylene naphthalate
1947	Epoxies	2000	PLA (for packaging) – polylactic acid
1948	ABS resins – acrylonitrile-butadiene-styrene	2012	PEF – polyethylene 2,5-furandicarboxylate

Today, dozens of different synthetic plastics are produced throughout the world by hundreds of companies. In 2018, world production of plastics totaled about 359 million metric tons [1]. U.S. resin production in 2019 was about 55 million metric tons (121 billion lbs) [2].

■ 1.2 Role of Plastics in Packaging

The term plastics is used instead of polymer to indicate a specific category of high molecular weight materials that can be shaped using a combination of heat, pressure, and time. All plastics are polymers, but not all polymers are plastics. In this text, we will discuss the major plastics that are useful as packaging materials. To a limited extent, we will discuss cellophane, which is a wood-based material that is a polymer, but not a plastic. We will also discuss adhesives, which are polymers and

may or may not be plastics, but which are very useful in the fabrication of plastic and other types of packaging.

Packaging started with natural materials such as leaves. From there, it progressed to fabricated materials such as woven containers and pottery. Glass and wood have been used in packaging for about 5000 years. In 1823, Durand in England patented the "cannister," the first tin-plate metal container. The double seamed three-piece can was in use by 1900. Paper and paperboard became important packaging materials around 1900. As soon as plastic materials were discovered, they were tried as packaging materials, mainly to replace paper packaging. Use of cellophane, which is a polymer but not truly a plastic, predated much of the use of plastics.

The use of plastics in packaging applications began, for the most part, after World War II. Polyethylene had been produced in large quantities during the war years, and it became commercially available immediately after the war. Its first application had been as insulation for wiring in radar and high frequency radio equipment. It was soon found that it could be formed easily into various shapes useful for packaging. An early application was in bread bags, replacing waxed paper. Polyethylene coatings replaced wax in heat-sealable paperboard. As a coating, it was also combined with paper to replace waxed paper and cellophane. The driving force behind the expansion of polyethylene use was to obtain a resealable package as well as a transparent material that allowed the product to be visible. Polyethylene remains the leading packaging plastic because of its low raw material price, versatile properties, and its ease of manufacture and fabrication.

The growth of plastics packaging has accelerated rapidly since the 1970s, in large part because of one of the main features of plastics—low density. This low density made the use of plastics attractive because of the weight savings, which translates into energy savings for transportation of packaged goods. In addition, plastic packages are usually thinner than their counterparts in glass, metal, paper, or paperboard. Therefore, conversion to plastic packaging often permits economies of space as well as of weight. Savings in the amount of distribution packaging needed may also result. Another important property is the relatively low melting temperatures of plastics compared to glass and metals. Lower melting temperatures mean less energy is required to produce and fabricate the materials and packages. While use of plastics in all applications has grown rapidly during this period, the growth in packaging has outpaced the growth in other sectors. Packaging is the largest single market for plastics. In 2018, packaging accounted for about 33% of the uses of the major thermoplastic resins in the U.S. (42% if exports were excluded) [3]. As shown in Figure 1.1, packaging accounted for 39.9% of all plastics used in Europe in 2018 [4]. Figure 1.2 shows how use has evolved over time.

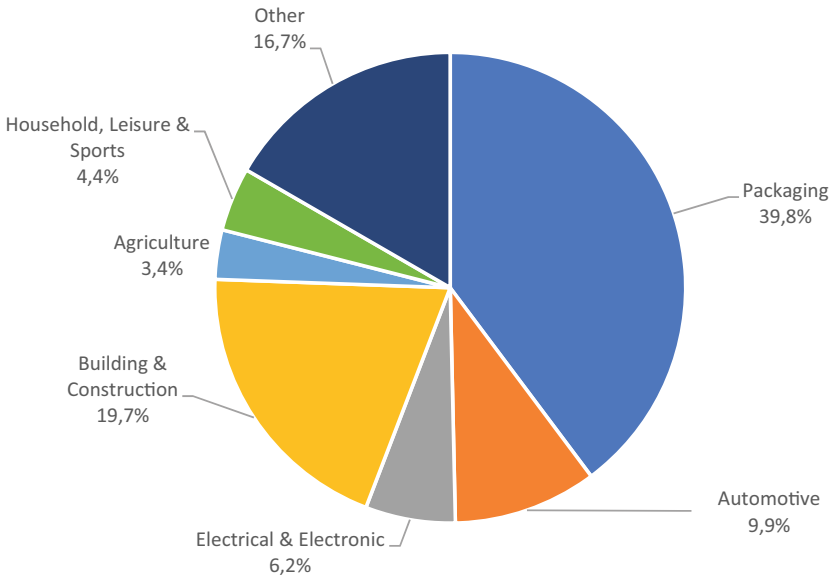


Figure 1.1 Major markets for plastics in Europe, 2018 [4]

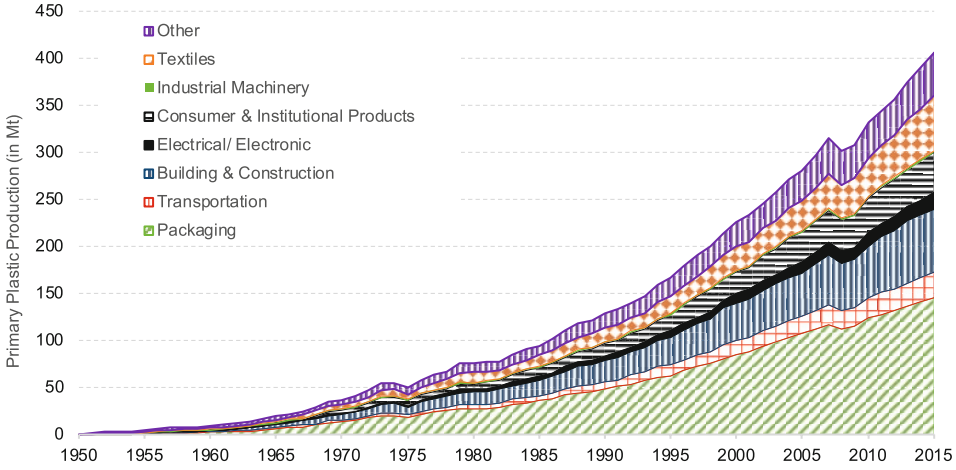


Figure 1.2 History of plastics use (adapted from [4])

Many of the early applications of plastics were in food packaging. The substitution of plastic films for paper in flexible packaging led to the development of many new combinations of materials, and to the use of several polymers together to gain the benefit of their various attributes. The development of flexible packaging for foods picked up speed in the late 1940s and 1950s as the prepared foods business began to emerge. Milk cartons using polyethylene coated paperboard were intro-

duced in the 1950s. Here the driving force was economics: glass was more expensive in a systems sense, breakage of glass on line required extensive cleaning, and returnable bottles brought all sorts of foreign objects into an otherwise clean environment.

In industrial packaging, plastics were used early on as a part of multiwall shipping sacks that replaced bulk shipments, drums, and burlap sacks. Again, polyethylene film is the predominant material used. Cement in 110 kg (50 lb) bags became a major application of polyethylene film in the industrial sector. The polyethylene liner protects the cement from moisture that would cause it to solidify. Another large use of plastics in industrial packaging is as cushioning to protect goods from vibration and impact during shipping. Polystyrene, polyurethane, and polyethylene foams, along with other polymers that are used as cushioning, compete against paper-based cushioning materials.

Medical packaging has been another big user of plastics. As converting techniques improved, so that accurate molding of small vials could be accomplished at low cost, and as new polymers became available with the necessary characteristics, plastics have been substituted for glass in many applications. As medical procedures became more complex, more disposable kits were introduced, designed to have complete sets of equipment for specific procedures. These kits require special packaging to keep the parts organized and easily usable. Here thermoformed trays became standard, so that kits of pre-sterilized, disposable instruments and supplies, in the proper varieties and amounts, can be readily assembled. Plastic packaging allows the sterilization to occur after the package is sealed, thus eliminating the possibility of recontamination after sterilization, as long as the package remains intact. Sterilization with ethylene oxide is facilitated by the use of spunbonded polymeric fabrics. Radiation sterilization depends on the use of polymers that retain their integrity after exposure to ionizing radiation.

The energy crisis in the 1970s, while at first leading to attacks on plastics as users of precious petroleum, actually accelerated the movement to plastic packaging because of the weight reduction possible. Many metal cans and glass bottles were replaced by plastic cans and bottles, and in many cases changes in package design moved the product out of rigid packaging altogether, into flexible packaging, which more often than not was made of plastic. Similarly, some metal drums were replaced by plastic drums. A major driving force was to reduce the fuel used for transportation of both packages and packaged goods by reducing the weight of the package. One important example is the introduction of the plastic beverage bottle.

Environmental concerns of the 1980s and early 1990s, caused by littering issues and a perceived lack of landfill space, caused a major rethinking of the plastic packaging in use. Companies that used plastics had to defend the uses that were in place and justify new applications. The result was a more responsible approach to

packaging in general by most companies. As politicians and the public became more informed about the truth concerning plastics and the environment, the issues receded from the forefront for a time. Today, plastic packaging has earned its position as one of the choices of the package designer. More recently, concerns about plastic litter in the ocean and microplastics entering the food chain have fueled a resurgence in concerns especially about "single-use" plastic packaging.

Decisions about which material(s) should be used require consideration of (1) product protection requirements, (2) market image, (3) cost, and (4) environmental issues.

1.3 Book Structure

This book is intended to provide (1) an introduction to the plastics used in packaging, (2) discussion of how their use relates to their properties, and (3) explanation of how these properties relate to their chemical structure, along with (4) an introduction to converting these plastic resins into useful packages. We have used much of the material in this book in our undergraduate course on plastics packaging at the School of Packaging, Michigan State University.

Chapter 2 provides some introductory concepts and definitions. Chapter 3 looks at the relationship between the chemical and physical structure and the properties of plastics. Chapter 4 provides a description of the plastics commonly used in packaging. Chapter 5 looks at the other ingredients that go into a plastic resin. Chapter 6 examines adhesion, adhesives, and heat sealing. Chapter 7 covers conversion of plastic resins into film and sheet forms. Chapter 8 examines how film and sheet can be modified by lamination and by coating. Chapter 9 discusses flexible packaging and Chapter 10 covers thermoforming. Chapter 11 discusses injection molding of plastics, with a special look at closures, rotational and compression molding, and tubes. Chapter 12 looks at formation of plastics into bottles and other containers by blow molding. Chapter 13 looks at distribution packaging, with an emphasis on foams and cushioning. Chapter 14 looks at the barrier characteristics and other mass transfer characteristics of packaging and how they relate to the shelf life of products. In Chapter 15, we examine various laws and regulations impacting packaging choices. Finally, Chapter 16 looks at environmental issues associated with plastic packaging, including biodegradable and biobased plastics.

Throughout the book, long examples are placed in boxes. Most chapters end with a set of study questions. In many cases, the answers can be found (or calculated) from the material in the chapter. In other cases, answering the questions requires the reader to put together information from several previous chapters. Sometimes,

the questions are intended to stimulate thinking in preparation for what will be discussed in subsequent chapters and cannot be answered completely with only the information that has already been presented. The correct solutions to quantitative questions are included.

1.4 References

[1] Statista, Global Plastic Production from 1950 to 2018 (in million metric tons), *https://www.statista.com/statistics/282732/global-production-of-plastics-since-1950/*, accessed 5/26/20

[2] American Chemistry Council, 2019 Resin Situation and Trends, (2020), *https://plastics.americanchemistry.com/Plastics-Statistics/ACC-Situation-and-Outlook-Resins.pdf*, accessed 5/26/20

[3] Statista, Distribution of Thermoplastic Resin Sales in the United States in 2018 by Major Markets, *https://www.statista.com/statistics/625952/thermoplastic-resin-sales-and-captive-use-in-the-us-distribution-by-major-market/*, accessed 5/26/20

[4] Association of Plastics Manufacturers in Europe, Plastics – The Facts 2019, *https://www.plasticseurope.org/en/resources/market-data*, accessed 5/26/20

2 Basic Concepts and Definitions

2.1 Terminology

The plastic materials we use in packaging are polymers and macromolecules. Before beginning the discussion and description of polymer structures and properties, we should define these and some related terms. Mastering these terms will provide the reader with a terminology useful for understanding many of the polymer properties described in the rest of the book. Some of these concepts were learned in basic chemistry courses, but now will be applied to polymers. Additional terms will be defined in subsequent chapters.

2.1.1 Macromolecule

Polymers belong to the group of materials called macromolecules, which simply means very large molecules, and can be defined as compounds made of a very large number of atoms chemically connected by covalent bonds (Figure 2.1). The relative molecular mass (also referred to as molecular weight) of macromolecules ranges from several hundred to millions of daltons (g/mol). Therefore, the chemical and mechanical properties of macromolecules are in large part determined simply by the very large size of the molecules. Polymers form a large group of materials that include plastics, adhesives, rubbers, fibers, and surface coatings, as well as cellulose, deoxyribonucleic acid (DNA), and ribonucleic acid (RNA).

In a macromolecule, the atoms that are linked together by covalent bonds and run through the whole molecule form the backbone, or main chain. The backbones of a large number of polymers (about 75%) are formed entirely by carbon atoms (C–C backbone). However, there are polymers whose molecular backbones include carbon and oxygen (polyesters); silicon, carbon and oxygen (silicone rubbers and resins); or nitrogen, carbon and oxygen (nylons, also called polyamides).

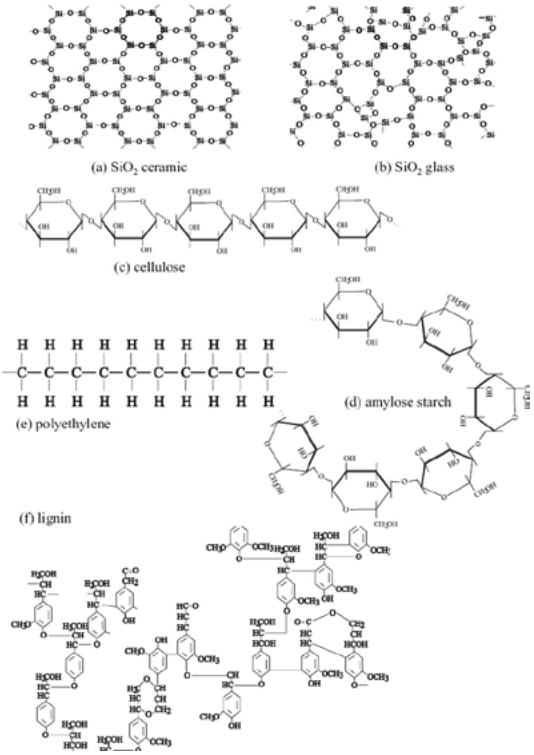


Figure 2.1
Examples of macromolecules

2.1.2 Polymer

A polymer is defined by the International Union of Pure and Applied Chemistry (IUPAC) as a substance made of large molecules that is characterized by the multiple repetition of one or more species of atoms or group of atoms (called monomers or constitutional units) linked to each other covalently in amounts sufficient to provide a set of properties that do not vary markedly with the addition or removal of one or a few of the constitutional units. IUPAC and many other authorities consider macromolecule and polymer to be synonyms; others define polymer as a macromolecule that consists of multiple repetitions of monomer(s). With this definition, enzymes are macromolecules but not polymers, since they are very large molecules made by the nonrepetitive combination of 20 amino acids.

Although the possible number of polymers is theoretically limitless, the economics of their production and processing, as well as the physical and chemical properties they have, restrict the number of commercial importance to a few dozen (see Figure 2.2), and in packaging applications the number of polymers used is even smaller. The polymers most commonly used in packaging are polyolefins, specifically polyethylene and polypropylene. Polystyrene, polyvinyl chloride, and polyethylene terephthalate (PET) are also among the most commonly used packaging polymers.

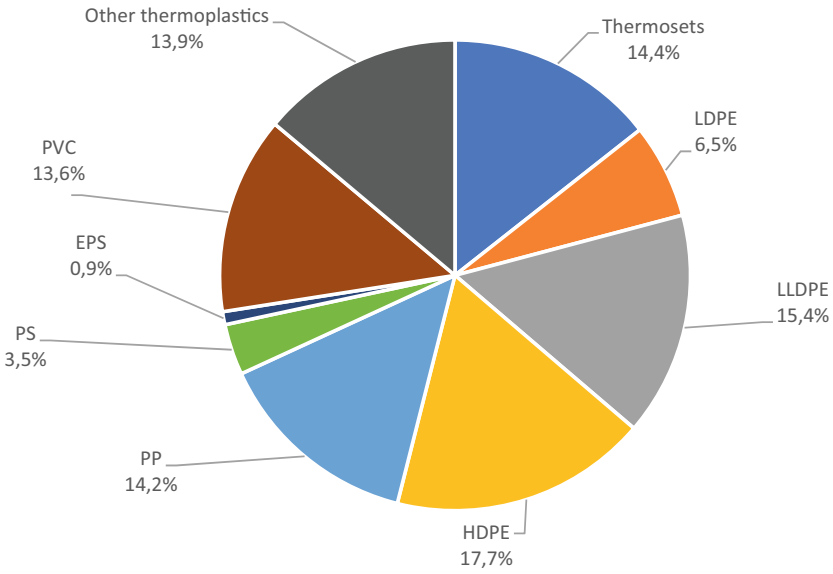


Figure 2.2 Plastics use in the United States by resin type, 2018 [1]

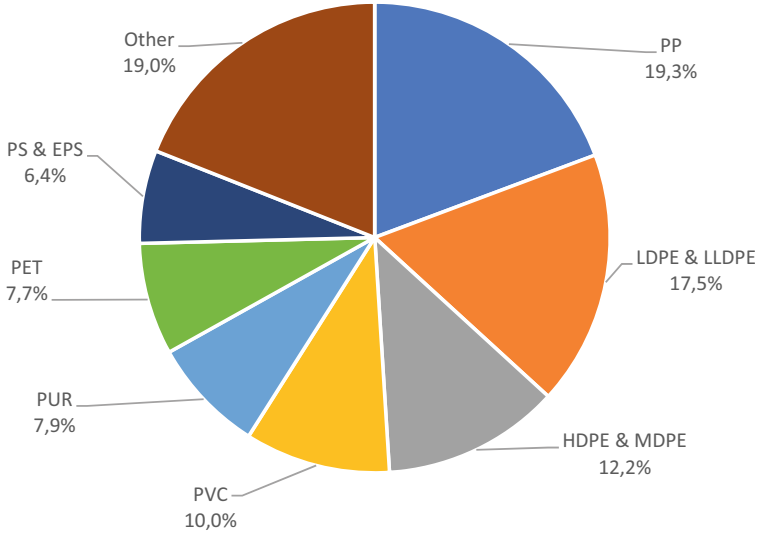


Figure 2.3 Plastics use in Europe by resin type, 2018 [2]

2.1.3 Plastic

Plastics are a special group of polymers with characteristics that differentiate them from fibers, rubbers, adhesives, and other materials that are also polymers. The main characteristic of plastics is their ability, while solid in the finished state, to be made to flow and be molded using controlled heat and pressure at relatively low temperatures, as compared to glass and metals. Plastics are, then, materials capable of being deformed continually without rupture by a stress which exceeds a yield value during processing. The plastic is easily shaped into the desired form by increasing the temperature and pressure to soften it and mold it into a new shape. On cooling, the plastic becomes hard and is able to retain the new shape. The distinctions between plastics, fibers, adhesives, and rubbers are not always clear. The same type of polymer may belong to more than one group, depending on its molecular weight and on how it is processed. Currently, for example, new catalyst technology is causing a blurring of the boundaries between rubbers and plastics.

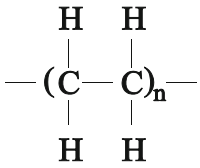
Some plastics, called *thermoplastics*, are able to repeatedly undergo this shape-changing treatment. Others, known as *thermosets*, can be shaped only once because they form irreversible covalent bonds between chains during the "setting" process and consequently will no longer melt and flow. Vulcanized rubber is an example of a thermoset polymer. Thermoset polymers tend to have relatively high chemical resistance and excellent mechanical properties. However, the vast majority of plastics used in packaging are thermoplastics. An emerging category of plastics is covalent adaptable networks (sometimes also referred to as vitrimers), which bear reversibly bonded structures in their network; they behave like thermosets at room temperature but can be melt-processed like thermoplastics at elevated temperature. However, these are still in an early stage of development.

2.1.4 Monomer

A monomer is the unit, made of a simple molecule, or a compound constituted of such molecules, from which polymers are produced by a chemical polymerization reaction. For example, ethylene (CH_2=CH_2) is the monomer used to produce polyethylene. Propylene (CH_3–CH=CH_2) is polymerized to form polypropylene, and vinyl chloride (CH_2=CHCl) is polymerized to form polyvinyl chloride. As illustrated, polymer names are often formed by prefixing the term "poly" to the monomer name.

2.1.5 Constitutional Unit

The constitutional unit is the smallest chemical unit whose repetition completely describes the main chain structure. For example, in polyethylene (PE),

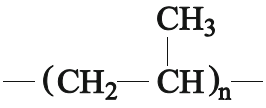


CH_2=CH_2 is the monomer, since polyethylene is formed by the polymerization of ethylene molecules. However, the group CH_2 is the smallest unit that completely describes PE, and therefore is the constitutional unit.

It will be noted that in this and other depictions of the structure of polymer molecules, we have not indicated the species at the ends of the molecules. The polymers, of course, do not have dangling bonds at the ends. However, because the molecules are so large, the groups at the end generally are insignificant in determining behavior. Further, there are a variety of possible ending groups, including hydrogens, groups with double bonds, and initiator residues. Therefore we are following the common convention in polymer science of leaving the end structures unspecified.

2.1.6 Homopolymer

A homopolymer is a polymer formed from only one type of monomer. For example, homopolymer polypropylene is formed only from propylene monomers, so it has the following structure:



2.1.7 Copolymer

A copolymer is a polymer composed of two or more different types of monomers. For example, if E represents ethylene and P propylene, a copolymer of E and P might have the following structure:

–PPEEEPPPPEPEEEE–

Copolymers can have a variety of structures, depending on the number and arrangement of the monomeric units. A random structure, illustrated above, typically results when the comonomers are introduced into the polymerization reactor at the same time and allowed to react randomly. Other important structures are alternating, block, and graft copolymers. The chemical structure has a significant effect on the final copolymer properties. We will discuss this topic in Section 3.3. Many plastics used in packaging are copolymers.

In condensation polymerization, the reaction usually starts with two different types of monomers but these polymers are not considered copolymers. The main reason is that these two monomers are able to react only with each other, so it takes both to form a polymer. Most often, in packaging applications, these belong to either the amide or the polyester family. Copolyesters and copolyamides incorporate a third monomer.

■ 2.2 Polymer Nomenclature

Precise chemical names for polymers are frequently long and unwieldy, so a system of generally accepted abbreviations has arisen. Table 2.1 lists the names of a number of common homopolymers and copolymers, along with the abbreviations commonly used for them. Polymer chemists usually use parentheses in the name to contain the monomer, or repeating unit; for example poly(acrylonitrile) or poly(ethylene). However, in many fields, including packaging, it is common to omit the parentheses, and refer simply to polyacrylonitrile or polyethylene. Similarly, chemists would typically denote a copolymer as poly(monomer 1-co-monomer 2), such as poly(ethylene-co-vinyl acetate), but in other fields it is common to drop both the co- and the poly- and refer to the polymer simply as ethylene vinyl acetate. In some cases, a slash is used to separate the monomers, so the name becomes ethylene/vinyl acetate, as shown in Table 2.1.

The names of some plastics, particularly condensation polymers (see Section 3.8), do not follow this customary pattern. For example, as we shall see in Chapter 4, nylons (or polyamides) have a unique numbering system related to their structure. Polycarbonate is another polymer whose name does not accurately reflect the monomer used to produce it. In this and some other cases, a generic family name is so closely associated with a particular member of a polymer family, that this family name is often used as if it represented only that particular plastic. For example, the term polyester is often used interchangeably with PET, and vinyl interchangeably with PVC. It is also common, for some copolymers, to totally ignore the comonomer in naming the plastic, or to not specify what comonomer is used. For example, we refer to high impact polystyrene, or HIPS, when it is actually a copoly-

mer. Similarly, we talk about polyvinylidene chloride, PVDC, as a packaging material, although we never use the homopolymer, and the name, in fact, represents a whole family of copolymers.

Table 2.1 Common Plastics

Homopolymer	Abbreviation
Cellulose acetate	CA
Epoxy	EP
Polyamide	PA
Polyacrylonitrile	PAN
Polybutyl acrylate	PBA
Polybutylene terephthalate	PBT
Polycarbonate	PC
Polyethylene	PE
High density polyethylene	HDPE
Low density polyethylene	LDPE
Polyethylene terephthalate	PET
Polyethylene furanoate	PEF
Polyethylene naphthalate	PEN
Polymethyl acrylate	PMA
Polymethyl methacrylate	PMMA
Polypropylene	PP
Polystyrene	PS
Polytetrafluoroethylene	PTFE
Polyurethane	PU
Polyvinyl acetate	PVA
Polyvinyl alcohol	PVOH
Polyvinyl chloride	PVC
Polyvinylidene chloride	PVDC
Copolymer	**Abbreviation**
Acrylonitrile/butadiene/styrene	ABS
Ethylene/ethyl acrylate	E/EA
Ethylene/propylene	E/P
Ethylene/vinyl acetate	EVA
Ethylene/vinyl alcohol	EVOH
Linear low density polyethylene	LLDPE
Vinyl chloride/ethylene	VC/E
Vinyl chloride/ethylene/methyl acrylate	VC/E/MA
Vinyl chloride/vinyl acetate	VC/VA
Vinyl chloride/vinylidene chloride	VC/VDC

2.3 Interatomic and Intermolecular Forces in Polymers

Because of the very large size of polymer molecules, both interatomic and intermolecular forces play a crucial role in their formation and properties. A brief review of the most important atomic forces follows.

2.3.1 Interatomic Forces

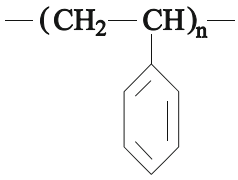
Interatomic forces are the forces that bond atoms together, forming molecules. These forces connect atoms like carbon C, hydrogen H, oxygen O, and nitrogen N, making possible the construction of the very large polymer molecules. In polymeric materials, we find two types of interatomic bonds: covalent bonds, which are very common, and ionic bonds, which are very rare.

2.3.1.1 Covalent Bonds

A covalent bond consists of two electrons shared by two adjacent atoms, with each atom contributing one electron. The bond is formed when the orbitals of the two atoms overlap and form a hybrid. We represent this bond by a dash between the symbols for the two elements, for instance, C–C. The covalent bond is the predominant bond in polymers, linking the atoms of carbon (and also oxygen and nitrogen when present) to form the backbone of the polymer chain. Covalent bonds also link hydrogen, oxygen, carbon, and other atoms in the side groups onto the backbone chain. The angle formed by three carbon atoms C–C–C in a linear chain measures 109.5°, as is predicted by orbital hybridization theory. The C–C–C angle is partially responsible for the elastic behavior of polymers, as the bond angle and hence the dimensions of the molecular segments can be affected by stress.

Atoms can be joined by one or more covalent bonds. If two pairs of electrons are shared, the bond is referred to as a double bond; for instance, C=C. Three shared pairs of electrons result in a triple bond. Many polymers contain six-member carbon rings that are often described as containing alternating single and double bonds that can switch positions with one another. While this description is not totally accurate, it is useful in understanding some of the unique properties of these materials. This type of bond is referred to as aromatic, and polymers contain-

ing these structures are called aromatic polymers. A common example of an aromatic polymer is polystyrene:



When atoms are joined by a single covalent bond, they are not "locked in place," but can rotate around the bond. Ease of rotation is one of the factors that influence the properties of the polymer, as will be discussed later. Rotation is not possible about double or triple bonds or within ring structures because of the characteristics of the electron orbitals.

Electron sharing between dissimilar atoms is not always equal. When one atom in the pair has a higher affinity for the shared electrons than the other atom, the bond is known as a polar covalent bond. For example, in a carbon-chlorine bond such as in polyvinyl chloride, the chlorine has a higher electron affinity than carbon, so it gets a disproportionate share of the electrons, resulting in the C–Cl bond being a polar covalent bond. The importance of this polarity will be discussed in Section 2.3.2. Electron sharing between identical atoms, such as C–C or O–O, is nonpolar.

Table 2.2 shows the energy necessary to break covalent bonds between atoms. As the energy increases, the molecule becomes stronger and more stable. Conversely, the least energetic bonds indicate the points where the molecule is most susceptible to degradation or other chemical change.

Table 2.2 Energies of Covalent Bonds

Bond	Energy (kJ/mol)	Bond	Energy (kJ/mol)
C–C	347	C≡N	891
C=C	614	C–H	414
C–O	360	C–F	439
C=O	715	C–Cl	326
C–N	293	O–O	146
C=N	614	O–H	460

2.3.1.2 Ionic Bonds

An ionic bond results when the affinity of two atoms for their shared electrons is so unequal that it results in actual transfer of one or more electrons from the atom with the lowest attraction, the electropositive atom, to the atom with the highest

attraction, the electronegative atom. This transfer results in the formation of a positive ion and a negative ion. Oppositely charged ions in the substance are then attracted to each other by electrostatic attractions. Ionic bonds are common in many substances (salts, for example) but are rarely found in plastics. They are present in the side chains in certain polymers, however, and convey some unique and useful properties. For example, Na^+ and Zn^{++} when used to neutralize carboxylic groups, $-COO^-$, and bonded to hydrocarbon chains such as polyethylene, produce polymers called ionomers.

2.3.2 Intermolecular and Intramolecular Forces

When atoms and molecules approach one another closely, they begin to exert forces on one another that do not result from the sharing or transfer of electrons. These forces are known as intermolecular forces if the forces are between two neighboring molecules and are called intramolecular forces if they are between different parts of the same molecule. These forces are much weaker than covalent or ionic bonds but are very important to the properties of polymers because the huge size of polymer molecules results in a proportionally huge number of these attractions.

Intermolecular forces are often referred to as *secondary bonds* or secondary forces, while covalent and ionic bonds are referred to as *primary bonds*. The primary bonds determine the molecular structure of the material. The secondary forces are responsible for its physical nature. Gases have relatively weak secondary forces, liquids have stronger ones, and solids have the strongest secondary forces. When a solid is heated and melts, the heat is providing the energy necessary to disrupt the secondary forces sufficiently to allow flow. An "ideal gas" can be described as a (hypothetical) substance with no ability to form secondary bonds.

There are three primary categories of secondary forces, also called van der Waals forces: dispersion forces, induction forces, and dipole forces – from weakest to strongest. These forces are highly sensitive to the distance between the molecules, with an approximate range of action between 3 and 5 Å (1 Å = 1×10^{-10} m). This distance range, as we will see, is crucial in the adhesion of polymers and in polymer surface preparation for adhesion, which are very important in packaging. The strength of secondary forces decreases proportionally to the 6^{th} power of the distance separating the molecules. The cohesive energy density, which indicates the amount of energy required, per unit volume, to move a molecule far enough away from its neighbors that no significant intermolecular forces remain, is a useful parameter for measuring secondary forces. Several important polymer properties, such as solubility, miscibility, viscosity, surface tension, and friction, as well as adhesion between two materials, are largely determined by the strength and

type of intermolecular forces. Table 2.3 summarizes the relationship between intermolecular forces and the mechanical characteristics of polymers.

Table 2.3 Importance of Intermolecular/Intramolecular Forces in the Mechanical Characteristics of Polymers

Intermolecular/ Intramolecular Forces	Cohesive Energy Density	Typical Polymer Characteristics
Small	Low	Relatively flexible rubbery behavior, high permeability. Ex: PE, PP
Medium	High	Stiffer, plastic behavior. Ex: PET
Large	Higher	High resistance to stress, high strength, good mechanical properties, low permeability. Ex: nylon, EVOH

2.3.2.1 Dispersion Forces

Dispersion forces, also called London forces or London dispersion forces, are the most prevalent type of intermolecular forces. They are found in all polymers (and all other substances as well), resulting from the natural fluctuation of the electron cloud in an atom that causes time-varying partial positive and negative charges. These charges sum to zero over time, but at any instant lead to electrostatic attractions between neighboring atoms with opposite charges. Dispersion forces are the weakest type of secondary forces, and are typically about 0.4–0.8 kJ/mol.

2.3.2.2 Induction Forces

Induction forces are found only when polar atoms are present, such as in ethylene/vinyl acetate copolymer. Polar atoms are those with a partial (or full) positive or negative charge resulting from polar or ionic bonds (as discussed in Section 2.3.1). The positive and negative charges in polar atoms can induce a corresponding fluctuation of the electrons in neighboring nonpolar atoms, thereby creating temporary polarity in these neighbors, and resulting in electrostatic attraction between the atoms. Induction forces are intermediate in strength between dispersion forces and dipole forces.

2.3.2.3 Dipole Forces

A permanent electrical dipole is formed wherever there is a polar bond, resulting in an asymmetric distribution of positive and negative charges in a molecule. The attractions between the permanent partial positive charges and partial negative charges in neighboring molecules are the strongest of the van der Waals forces, reaching up to 8 kJ/mol. The characteristics of PVC, for example, are largely determined by its strong secondary forces, which result from the C–Cl dipoles.

2.3.2.4 Hydrogen Bonds

Hydrogen bonds are the strongest type of secondary forces. While they can be regarded as a subcategory of dipole forces, their strength and unique characteristics generally result in classifying these forces in a special group, distinct from the ordinary van der Waals forces. Hydrogen bonds can reach strengths as high as 40 kJ/mol; they result from the attraction between a strongly electronegative atom and a hydrogen that is covalently bonded to a strongly electronegative atom. Fluorine, oxygen, nitrogen, and to a lesser extent chlorine, have very high electron affinities. A hydrogen atom attached to one of these atoms has an unusually high excess positive charge and the electronegative atom itself has an unusually high excess negative charge. The attraction between such a hydrogen and a neighboring electronegative atom is thus unusually strong, and can take on some of the characteristics of a very weak covalent bond. In fact, in 1999, evidence of actual electron-sharing in some hydrogen bonds was reported. Hydrogen bonds play an important role in the intermolecular forces of polymers such as polyamides (nylons) and ethylene/vinyl alcohol.

■ 2.4 Properties Determined by Chemical Composition

The properties of polymers are strongly influenced both by their chemical composition and their physical state. The chemical composition includes the atoms that make up the polymer molecules, as well as the number and arrangement of those atoms. It is determined by both the chemical composition of the monomers making up the polymer, and the polymerization conditions. Once determined, the chemical composition is fixed unless chemical reactions occur.

The physical state of the polymer includes such variables as the crystallinity of the material and the degree of orientation of the molecules. It is strongly dependent on the processing history of the material, and can be changed by changes in the environmental conditions to which the polymer is exposed, like heat and pressure, as will be discussed later.

The following properties are determined in large part by the chemical structure of the polymer:

- Density
- Thermal properties (enthalpy, thermal conductivity)
- Thermal expansion
- Chemical reactivity

- Melting and softening temperature
- Solubility, diffusion and permeability
- Friction

The long chain nature of the polymers is particularly important in determining:

- Strength
- Viscosity
- Elasticity
- Stress relaxation, creep, and other time-dependent properties
- Melting temperature

Note that for some properties, such as melting temperature, both the chemical structure and the long chain nature of polymers play important roles. As will be seen later, the stiffness and flexibility characteristics of polymers are largely determined by the degree of hindrance to free rotation about single bonds in the backbone chain.

2.5 Categorization of Plastics

The many types of plastics are often grouped into various categories. Commodity plastics are those used in high volumes, and are characterized by modest prices and reasonable performance. This group includes polyethylene, polypropylene, polystyrene, and polyvinyl chloride. Engineering polymers are sometimes defined as those that maintain their mechanical properties at temperatures above 100°C and that command a higher price than the commodity plastics. These include nylon, polyesters, and polycarbonate (although the most common polyester, PET, has moved into the commodity plastics category). Other categories sometimes used include intermediate, for those polymers that lie between the commodity and engineering resins (such as PET), and advanced, for those that have very high prices and unique properties. The term specialty resins is sometimes used to refer to packaging polymers that are relatively high in cost and therefore used for their unique properties, such as high barrier ethylene vinyl alcohol and polyvinylidene chloride.

2.6 References

[1] American Chemistry Council, U. S. Resin Production & Sales, 2019 vs 2018, March 2020

[2] Association of Plastics Manufacturers in Europe, Plastics – The Facts 2019, *https://www.plasticseurope.org/en/resources/market-data*, accessed 5/26/20

Study Questions

1. Cellulose, the major ingredient of paper, is a polymer. Is it a plastic? Why or why not?
2. What, if any, are the differences between the intermolecular forces in polymers and those in small molecules? How does this impact polymer properties?
3. What is the major difference between thermoplastics and thermosets? Which category is used more often in packaging? Why?
4. If we polymerized pentene, what would be the name of the resulting polymer? What if we copolymerized pentene and ethylene?
5. What monomer is used to produce polystyrene? Draw its chemical structure.
6. What monomer, or monomers, are used to produce ABS?
7. Why is chemical structure more important than physical structure in determining the density of a polymer?
8. Name a polymer that has a backbone chain made of: (1) only carbon atoms, (2) carbon, and oxygen, (3) silicon, carbon, and oxygen, and (4) nitrogen, carbon, and oxygen.
9. Define the following terms: macromolecule, polymer, and plastic. When are the constitutional unit and monomeric unit of a polymer the same?
10. What are the main similarities/differences between plastics, fibers, rubber, and adhesives?
11. Give an example of a polymer whose monomeric unit is different from its constitutional unit. Give an example where the monomeric and constitutional units are the same. Draw all the structures.
12. What are “intermolecular forces” in polymers? What are the main types of intermolecular forces? Which is the most common one? Why are intermolecular forces important? What is the typical range of intermolecular forces, in Å? How might we measure the intermolecular forces in a polymer?

13. Write the full names of the polymers represented by the following abbreviations: PVC, PAN, PVDC, PE, PP, EVA, PS, HDPE, PC, EVOH, LDPE, and PET.
14. Suggest an explanation for the behavior of polymers in Table 2.3. In other words, why do polymers with small, medium, or large intermolecular forces have the cohesive energy density and polymer characteristics listed?
15. Why is the cohesive energy density of a polymer related to its solubility?

3 Polymer Structure and Properties

3.1 Introduction

Polymers are produced by polymerization reactions that chemically bond large numbers of monomers together. Monomers, catalysts, solvents or fluid carriers, and other secondary chemicals are continually fed into polymerization reactors. The reaction process is maintained under controlled temperature and pressure. Common categories of polymerization reactions are bulk, in which monomers are fed as a pure gas or liquid; solution, in which monomers are dissolved in a solvent; suspension, in which monomers are suspended in an immiscible medium; and emulsion, in which monomers and growing polymer molecules are dispersed as very tiny droplets or particles in the carrier.

3.2 Molecular Architecture

Polymers are produced by chemically linking together a very large number of monomeric units in a chain-like or network structure. Because the monomers can react at different locations of the molecule, the monomers can be linked in the chain in different ways. Homopolymers can be linear, branched, or even cross-linked, while copolymers may have even more complex architectures such as block and graft. The molecular architecture of each polymer, in addition to the polymer's chemical composition and molecular weight, is an important determinant of the polymer properties. For example, a linear structure in general yields a more compact arrangement of atoms than a branched structure, which translates into higher density, and often into higher crystallinity, as well. If the polymer is more crystalline, it will have improved chemical resistance, increased tensile strength, and will be a better barrier to the permeation of gases.

3.2.1 Linear Polymers

In a linear polymer molecule, the monomers form a single long backbone chain. A linear polymer can be schematically represented as shown in Figure 3.1. As the figure illustrates, the polymer may not be totally linear, but branches, if any exist, are quite rare. Examples of linear polymers are HDPE, LLDPE, PET, nylons, PVC, and PP.

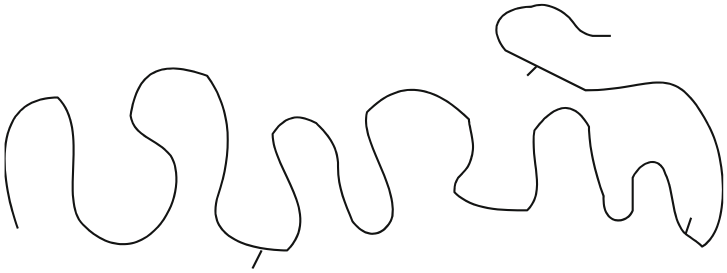


Figure 3.1 Representation of a linear polymer

One determinant of the polymer architecture is the functionality of the monomers from which it is formed. Functionality refers to the number of bonds that a monomer can form with other monomeric molecules during the polymerization process. If the monomer is bifunctional (has a functionality of two), it will generally form a linear polymer. A molecule with a functionality of one cannot form a polymer at all. It can react with one other molecule to form a dimer, but since each of the two molecules has "used up" its ability to react, it cannot grow further into a polymer. Trifunctional (or higher) monomeric units can produce either branched or crosslinked polymers, depending on the functionality of the monomer and the stoichiometry and conversion of the reaction.

Examples of bifunctional monomers are $H_2C{=}CH_2$, $HOOC{-}C_6H_4{-}COOH$, and $H_2C{=}CHCl$.

3.2.2 Branched Polymers

In a branched polymer, some monomers become part of side chains, branching off the main chain or off other branches. Monomers with a functionality of three or greater may form branched polymers, since three parts of the polymer molecule can extend from a single monomer wherever a trifunctional monomer is located. The degree of branching of the polymer will depend on the number of multifunctional monomers present during the reaction.

Branches can also arise during the polymerization reaction when reaction conditions convert what would normally be a stable structure into a reactive entity. This is very common with polyethylene. During the polymerization, a free radical can abstract (remove) a hydrogen atom from the backbone of the polymer and start a new growth point. From this growth point a whole new chain can grow. For LDPE, the branches (side chains) can be nearly as long as the backbone. (In fact, the backbone is defined as the longest pathway through the molecule, and parts of it may have originated as branches that grew longer than a portion of the molecule that used to be the backbone.) In polyethylene we talk about short chain branching (SCB) and long chain branching (LCB). LCB usually refers to side chains of 50 carbon atoms or more. Both long and short chain branches are illustrated in Figure 3.2.

Figure 3.2 Representation of a branched polymer

In polymers with side groups that are a part of the regular structure of one of the monomers, as in the case of polystyrene, polypropylene, poly(n-butyl methacrylate), etc., we generally do not consider these as branches or side chains. Instead, they are called side groups. An exception to this rule is for polyethylene/α-olefin copolymers, the LLDPE family, where the side group is referred to as a side chain. The reason for this exception is that the polymers look exactly like those that could be made by a side chain growth reaction. In fact, it is common for books to list LLDPE as a branched polymer, even though its name, linear low density polyethylene, clearly and correctly describes it as a linear polymer.

The effects of SCB and side groups are similar. They disrupt the ability of the polymer to crystallize. If the disruption is not complete, the added bulkiness will make the rate of crystallization slow down. SCB has little effect on the flow properties of a polymer, but LCB has a profound effect. We will discuss this more when we look at the differences in behavior between HDPE, LDPE, and LLDPE in Chapter 4. For now, we can illustrate the effects of branching by comparing LDPE with HDPE. The densities differ, the tensile properties differ, and the elastic character of the polymers differs greatly, even though both are made from the same monomer.

3.2.3 Cross-Linked Polymers

As indicated above, multifunctional monomers, instead of merely forming branches, can link main chains together to such an extent that the molecules are transformed into network type structures, known as cross-linked polymers, as shown in Figure 3.3. This is especially likely if one of the monomers has a functionality of four, such as divinylbenzene. These cross-linked networks can be two-dimensional, but most often are three-dimensional.

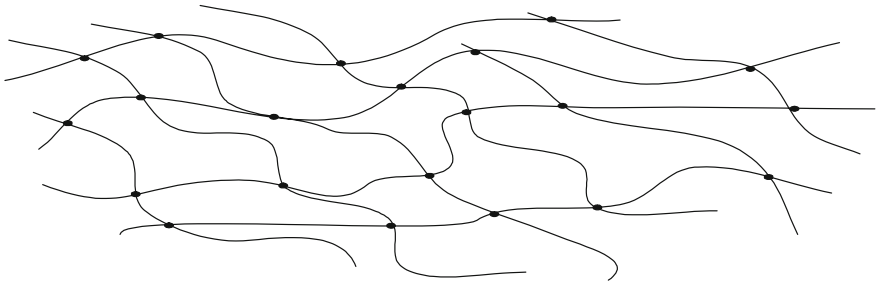


Figure 3.3 Representation of a cross-linked polymer

Cross-linked polymers, although not widely used in packaging, have important applications. In addition to cross-linking generated during the polymerization process, cross-linking can result from degradation reactions occurring during extrusion or other processing, or as a consequence of exposure to UV or gamma radiation. In film extrusion, if polymer with excessive exposure to high temperatures is used, it can result in cross-linked regions called *gels*, which cause film weakness and can create runnability problems in packaging equipment. Excessive use of regrind is one source of such problems.

The vast majority of polymers used in packaging are thermoplastics, and most have a linear or nearly linear structure. Important packaging polymers with a branched structure include low density polyethylene and ethylene vinyl acetate.

Cross-linking is characteristic of thermoset materials, and is important in some adhesives, many polymer coatings for cans, and very strong polymers for machine parts. In thermosets, linear or branched polymers react under the heat and pressure associated with the forming operation to produce a large number of cross-links that, once formed, no longer permit the polymer to flow. Thus, these materials are set into a permanent shape during processing and do not soften upon reapplication of heat and pressure. If only a very small number of cross-links are formed, a polymer may still exhibit typical plastic behavior, including the ability to be softened and reshaped.

3.3 Copolymer Structure

As indicated before, a copolymer is a polymer that is composed of two or more different types of monomers. For example, ethylene (E) and propylene (P) can be polymerized together in the same chemical reactor to produce polymeric chains containing units contributed by each of the two monomers. A common way of designating such a copolymer is E/P. Depending on the molar ratio of ethylene and propylene in the reacting gas mixture, the copolymer produced may have properties very similar to PE or to PP or properties intermediate between PE and PP. The goal of copolymerization is to control the properties of the resulting polymer through the ratio and type of co-reactants and the reactor conditions (temperature, pressure, and catalyst). This allows the processing temperature, permeability, glass transition temperature, thermoforming temperature, toughness, elastic modulus, and other properties to be varied in ways not possible with homopolymers. Copolymers can have linear, branched, or cross-linked structures just like homopolymers, and have additional variations related to the relative positioning of the monomer units within the structure. The monomers can be arranged to produce random, alternating, block, or graft architectures.

3.3.1 Random Copolymers

In a random copolymer, the monomers are randomly distributed along the chain, so there is no pattern to their arrangement (Figure 3.4). For example, random polypropylene copolymers are a type of polypropylene in which the basic structure of the polymer chain is modified by the incorporation of ethylene comonomer during the polymerization process. This results in changes in the physical properties compared to homopolymer PP such as increased clarity, improved impact resistance, increased flexibility, and a decrease in the melting point and heat-sealing temperature.

E…EEEEPEEEPPEEPPPPEPPPEEEEEEPPEEPP…EEE

Figure 3.4 Diagram of a random copolymer; capital letters represent different monomers

In general, the properties of random copolymers that are affected most strongly by chain flexibility and intermolecular forces tend to be a weighted average of those of the respective homopolymers. Properties affected primarily by crystallinity, however, such as melt temperature, tend to be decreased by copolymerization, due to the irregularity that copolymerization produces in the chemical structure of the polymer molecules. This will be discussed further in Section 3.10.