

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.

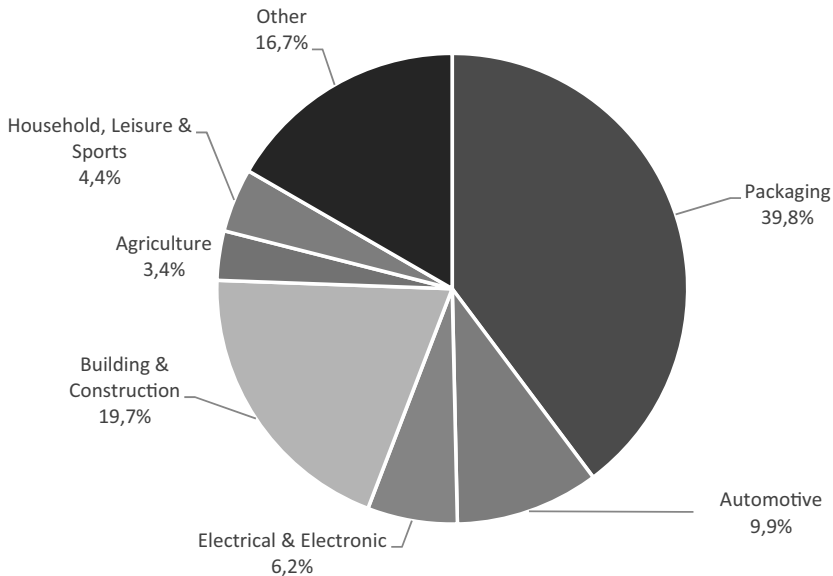


Figure 1.1 Major markets for plastics in Europe, 2018 [4]

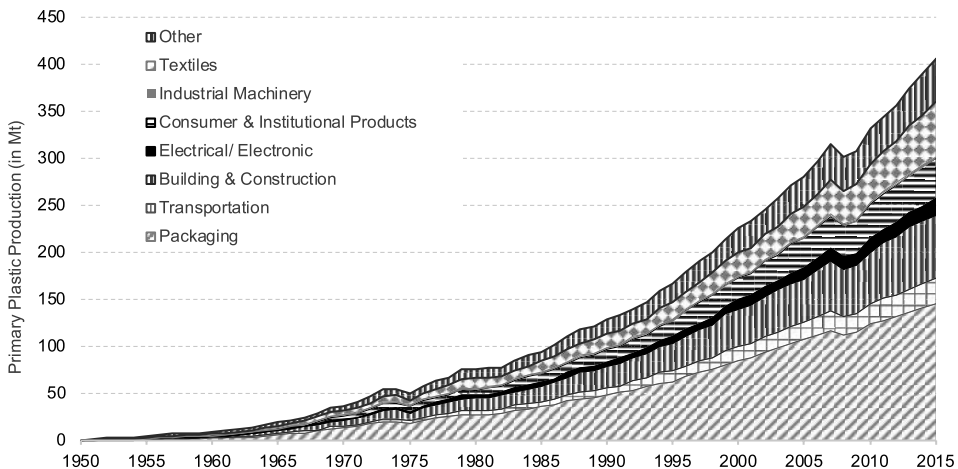


Figure 1.2 History of plastics use (adapted from [4])

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 spun-bonded 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,

4

Major Plastics in Packaging

■ 4.1 Branched Polyethylenes

Low density polyethylene is one of the most widely used packaging plastics. It is a member of the *polyolefin* family. Olefin, which means oil-forming, is an old synonym for alkene, and was, originally, the name given to ethylene. Alkenes are hydrocarbons containing carbon-carbon double bonds, such as ethylene and propylene. In the plastics industry, the term polyolefins refers to the family of plastics based on ethylene and propylene. Strictly speaking, it applies to polymers made of alkenes, whether homopolymers or copolymers. It includes both the polyethylene and polypropylene families.

Polyethylene (PE) is a family of addition polymers based on ethylene. Polyethylene can be linear or branched, homopolymer, or copolymer. In the case of a copolymer, the comonomer is commonly a terminal alkene such as propene, 1-butene, 1-hexene, or 1-octene; or a compound having a polar functional group such as vinyl acetate (VA), acrylic acid (AA), ethyl acrylate (EA), or methyl acrylate (MA). If the molar percent of the comonomer is less than 10%, the polymer can be classified as either a copolymer or homopolymer. Figure 4.1 presents a diagram of the family of polymers based on ethylene monomer.

Polyethylene was the first olefinic polymer to find use in food packaging. Introduced in the 1950s, it became a common material by 1960, used in film, molded containers, and closures. Since low density polyethylene was first introduced in 1940, its strength, toughness, thermal and heat sealing properties, optical transparency, and processing conditions have been much improved. Today there are a number of polyethylene grades of relevance to packaging, as shown in Figure 4.1.

Low density polyethylene (LDPE) has a branched structure. The family of branched polyethylenes includes homopolymers and copolymers of ethylene that are branched, thermoplastic, and partially crystalline. They are fabricated under high pressure and temperature conditions by a free radical polymerization process. The random polymerization of ethylene under these conditions produces a branched polymer that is actually a mixture of large molecules with different backbone

lengths, various side chain lengths, and with various degrees of side-chain branching. The presence of branches in its backbone chain acts to limit the formation of polyethylene crystals by introducing irregularities in the structure and impeding the regular packing of the polymer chains.

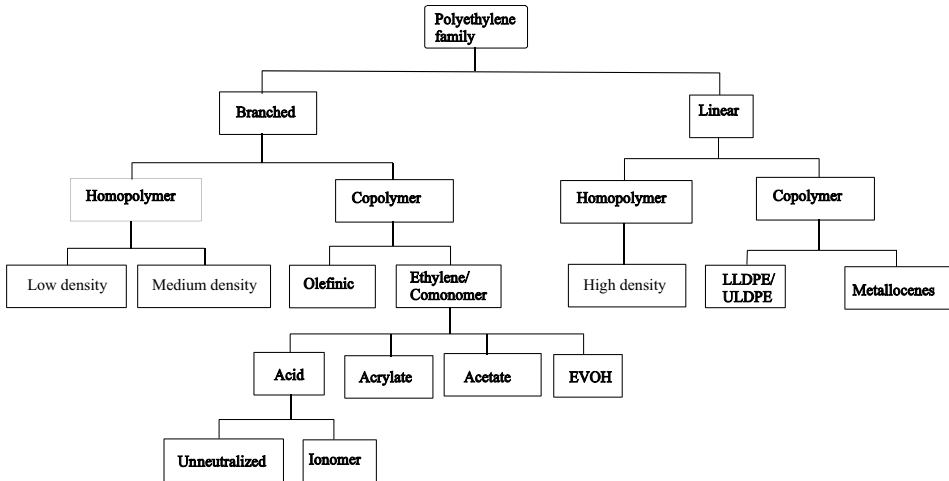


Figure 4.1 The polyethylene family

Linear PE has a high percent crystallinity, from 70 to 90%, because of its linear nature, stereoregularity, and the small size of its pendant groups. This high crystallinity results in relatively high density, so linear PE is known as high density polyethylene (HDPE). Branched PE with its lower crystallinity consequently has lower density, so it is known as low density PE (LDPE). LDPE typically has a crystallinity of 40 to 60%, with a density of 0.910 to 0.940 g/cm³; in contrast, HDPE has a density of about 0.940 to 0.970 g/cm³. Comonomers such as propylene and hexene are commonly used in the polymerization reaction to help control molecular weight. A wide variety of branched polyethylenes are commercially available, with properties dependent on the reaction conditions and on the type and amount of comonomer.

4.1.1 Low Density Polyethylene

The chain branching in homopolymer LDPE gives this polymer a number of desirable characteristics such as clarity, flexibility, heat sealability, and ease of processing. The actual values of these properties depend on the balance between the molecular weight, molecular weight distribution, and branching.

LDPE is also versatile with respect to processing mode, and is adaptable to blown film, cast film, extrusion coating, injection molding, and blow molding. Film is the single largest form of LDPE produced. In the U.S., more than half of total LDPE

production is made into films with thickness less than 300 microns (12 mils). Products made of LDPE include containers and bags for food and clothing, industrial liners, vapor barriers, agricultural films, household products, and shrink and stretch wrap films. LDPE can be used alone or in combination with other members of the PE resin family.

LDPE is characterized by its excellent flexibility, good impact strength, fair machinability, good oil resistance, fair chemical resistance, good heat sealing characteristics, and low cost (about \$1.40/kg). Its transparency is better than HDPE because of its lower percent crystallinity. For the same reason (lower crystallinity), while it is a good water vapor barrier, it is inferior to HDPE. Similarly, it is an even poorer gas barrier than HDPE. A summary of the properties of LDPE is presented in Table 4.1.

Table 4.1 LDPE Properties

Density	0.910 to 0.925 g/cm ³
T_m	105–115°C
Tensile strength	8.2–31.4 MPa (1200–4550 psi)
Tensile modulus	172–517 MPa (24,900–75,000 psi)
Elongation at break	100–965%
Tear strength	200–300 g/25 μm
WVTR (water vapor transmission rate)	375–500 g μm/m ² d at 37.8°C, 90% RH (0.95–1.3 g mil/100 in ² d at 95°F, 90% RH)
T_g	–120°C
O₂ permeability, 25°C	163,000–213,000 cm ³ μm/m ² d atm (400–540 cm ³ mil/100 in ² d atm)
CO₂ permeability, 25°C	750,000–1,060,000 cm ³ μm/m ² day atm (1900–2700 cm ³ mil/100 in ² d atm)
Water absorption	< 0.01%

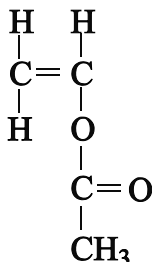
Medium density polyethylene (MDPE), 0.925–0.940 g/cm³, is sometimes listed as a separate category, but usually is regarded as the high-density end of LDPE. It is somewhat stronger, stiffer, and less permeable than lower density LDPE. MDPE processes similarly to LDPE, though usually at slightly higher temperatures.

The major competitor to LDPE is LLDPE (discussed in Section 4.2.2), which provides superior strength at equivalent densities. However, LDPE is still preferred in applications demanding high clarity or for extrusion coating of a substrate.

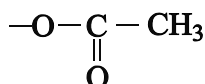
Ethylene can be copolymerized with alkene compounds or monomers containing polar functional groups, such as vinyl acetate and acrylic acid. Branched ethylene/alkene copolymers are essentially the same as LDPE, since in commercial practice a certain amount of propylene or hexene is always added to aid in the control of molecular weight.

4.1.2 Ethylene Vinyl Acetate (EVA)

Ethylene vinyl acetate copolymers (EVA) are produced by copolymerizing ethylene and vinyl acetate monomers.



The result is a random copolymer, where



groups appear as side groups at random locations on the carbon chain, replacing H atoms.

EVA copolymers with vinyl acetate (VA) contents ranging from 5 to 50% are commercially available. For most food applications, VA ranging from 5 to 20% is recommended. EVA resins are mainly recognized for their flexibility, toughness, and heat sealability.

Vinyl acetate is a polar molecule. The inclusion of polar monomers in the main chain during production of branched ethylene copolymers will decrease crystallinity, improve flexibility, yield a wider range of heat sealing temperature, and result in better barrier properties, as well as increasing density. These changes in properties result from the interference with crystallinity caused by the presence of random irregularities produced by the relatively bulky side groups from the comonomer, plus an increase in intermolecular forces resulting from the presence of polar groups in the comonomer. The increase in density is attributable to the presence of oxygen atoms with their higher mass, which more than compensates for the decreased crystallinity.

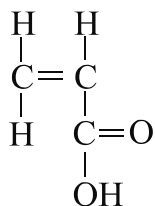
EVA, as stated above, is a random copolymer whose properties depend on the content of vinyl acetate and the molecular weight. As the VA content increases, the crystallinity decreases, but the density increases. This density increase corresponds to the presence of high atomic weight oxygen. Other properties are also affected, resulting in improvement in clarity, better flexibility at low temperature, and an increase in the impact strength. At 50% VA, EVA is totally amorphous. The increased polarity with increasing VA content results in an increase in adhesion

strength and hot tack. An increase in average molecular weight of the resin increases the viscosity, toughness, heat seal strength, hot tack, and flexibility.

Because of its excellent adhesion and ease of processing, EVA is often used in extrusion coating and as a coextruded heat seal layer. Examples include functioning as a heat sealing layer with PET, cellophane and biaxially oriented PP packaging films (20% VA) for cheese wrap, and medical films. Because EVA has limited thermal stability and low melting temperature, it has to be processed at relatively low temperatures. However, this also results in toughness at low temperatures, which is a significant asset for packages such as ice bags and stretch wrap for meat and poultry.

4.1.3 Ethylene Acrylic Acid (EAA)

The copolymerization of ethylene with acrylic acid (AA)



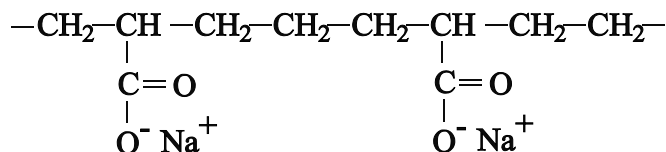
produces copolymers containing carboxyl groups (HO-C=O) in the side chains of the molecule. These copolymers are known as ethylene acrylic acid, EAA. They are flexible thermoplastics with chemical resistance and barrier properties similar to LDPE. EAA, however, is superior to LDPE in strength, toughness, hot tack, and adhesion, because of the increased intermolecular interactions provided by the hydrogen bonds. Major uses include blister packaging and as an extruded tie layer between aluminum foil and other polymers.

As the content of AA increases, the crystallinity decreases, which implies that clarity also increases. Similarly, adhesion strength increases because of the increase in polarity, and the heat seal temperature decreases due to the decrease in crystallinity.

Films of EAA are also used in flexible packaging of meat, cheese, snack foods, and medical products; in skin packaging; and in adhesive lamination. Extrusion coating applications include condiment and food packages, coated paperboard, aseptic cartons, composite cans, and toothpaste tubes. FDA regulations permit use of up to 25% acrylic acid for copolymers of ethylene in direct food contact.

4.1.4 Ionomers

Neutralization of EAA or a similar copolymer, for example EMAA (ethylene methacrylic acid), with cations such as Na⁺, Zn⁺⁺, or Li⁺, produces a material that has better transparency, toughness, and higher melt strength than the unneutralized copolymer. These materials are called ionomers because they combine covalent and ionic bonds in the polymer chain. The structure of an ionomer of the ethylene sodium acrylate type is:



Ionomers were developed in 1965 by R. W. Rees and D. Vaughan while working for DuPont, which uses the trade name Surlyn™ for these materials.

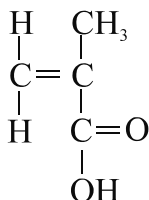
The ionic bonds produce random cross-link-like ionic bonds between the chains, yielding solid-state properties usually associated with very high molecular weight materials. However, ionomers behave as normal thermoplastic materials because the ionic bonds are much more readily disrupted than covalent bonds, allowing processing in conventional equipment. Normal processing temperatures are between 175 and 290°C. The presence of ionic bonds decreases the ability of the molecules to rearrange into spherulites, thus decreasing crystallinity. The high elongational viscosity resulting from the ionic bonds imparts excellent pinhole resistance.

Barrier properties of ionomers alone are relatively poor, but combined with PVDC, HDPE, or foil they produce composite materials that are excellent barriers.

Ionomers are frequently used in critical coating applications, films, and laminations. Applications include heat seal layers in a variety of multilayer and composite structures. They are used in combination with nylon, PET, LDPE, and PVDC. Coextrusion lamination and extrusion coating are the most common processing techniques.

Ionomers are used in packaging where formability, toughness, and visual appearance are important. Food packaging films are the largest single market. They are highly resistant to oils and aggressive products and provide reliable seals over a broad range of temperatures. Ionomers stick very well to aluminum foil. They are also used extensively as a heat-sealing layer in composite films for fresh and processed meats, such as hotdogs. Other applications of ionomers include frozen food (fish and poultry), cheese, snack foods, fruit juice (Tetra Pak™ type container), wine, water, oil, margarine, nuts, and pharmaceuticals. Heavy gauge ionomer films are used in skin packaging for hardware and electronic products due to their excellent adhesion to corrugated board and excellent puncture resistance. Ionomers can resist impacts at temperatures as low as -90°C (lower than LDPE).

Sodium can be replaced by other metals such as zinc, and other comonomers such as methacrylic acid

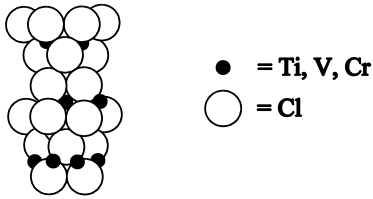


can be used. There are more than fifty commercial grades of ionomer with a wide range of properties. In general, sodium ion types have better optical properties, hot tack, and oil resistance. Zinc ionomers are more inert to water and have better adhesion properties in coextrusion and for extrusion coating of foil.

■ 4.2 Linear Polyethylenes

High density polyethylene is also one of the most widely used packaging plastics, along with LDPE and PET. As already discussed, it is produced by polymerization of ethylene, but it has a nearly totally linear structure, in contrast to the highly branched structure of low density polyethylene. This results in a greater ability to crystallize, producing a tighter packing of molecules and consequently a higher density.

Linear polyethylenes have traditionally been produced using a Ziegler-Natta stereospecific catalyst, named after the two chemists who invented them in the 1950s. These catalysts are made from a combination of a transition metal halide, such as titanium tetrachloride, with a reducing agent, such as an aluminum alkyl. An example of the catalyst structure is shown in Figure 4.2. The first application of these catalysts was production of HDPE. In a high pressure reactor, ethylene polymerization could not achieve densities much over 0.94 g/cm³. These new catalysts, which only allow the combination of free radicals in a specific orientation, allowed the density to be increased to 0.97 g/cm³. Later, in the 1970s, the use of Ziegler-Natta catalyst technology was extended by Dow and Union Carbide to the production of lower density polyethylenes by incorporating comonomers such as 1-butene, 1-hexene, and 1-octene into the polymer backbone. The resulting randomly placed side groups decreased the crystallinity of the material, consequently reducing the density. Ziegler-Natta catalyst technology allows control over the density through the percentage of comonomer incorporated into the backbone. Since the reactions are run at relatively low temperatures and pressures, the hydrogen abstraction reactions responsible for the branching in LDPE do not occur to any significant extent. The milder reaction conditions also facilitate improved control over the average molecular weight and the molecular weight distribution.

 **δ -form MX_3 catalyst crystal****Figure 4.2**

A typical Ziegler-Natta catalyst

Linear polyethylenes can be divided into the following groups, with density given in parentheses:

- ULDPE—ultra low density PE (0.89–0.915 g/cm³)
- LLDPE—linear low density PE (0.916–0.940 g/cm³)
- HDPE—high density PE (0.940–0.965 g/cm³)
- HMW-HDPE—high molecular weight HDPE (0.940–0.965 g/cm³)

The molecular weight of linear polyethylene ranges from medium to ultra high molecular weight, as shown in Table 4.2.

Table 4.2 Molecular Weight Range of Linear Polyethylene

Type	Relative Molecular Mass (Molecular Weight)
Medium Molecular Weight	< 110,000
High Molecular Weight	110,000–250,000
Very High Molecular Weight	250,000–3,500,000
Ultra High	>3,500,000

4.2.1 High Density Polyethylene (HDPE)

High density PE is a milky-white, nonpolar, linear thermoplastic. Its density ranges from 0.940 to 0.965 g/cm³, and it has a melting temperature of about 128 to 138°C. It is one of the most versatile polymers and its typical packaging applications include:

- Containers for milk, detergent, bleach, juice, shampoo, water, and industrial chemical drums made by extrusion blow molding;
- Buckets, thin walled dairy containers, and closures made by injection molding;
- Cosmetic containers, pharmaceutical bottles, and deodorant containers made by injection blow molding; and
- Blown and cast films utilized in flexible packaging applications such as cereal, cracker and snack food packaging, wraps for delicatessen products, and grocery sacks.

The molecular chains of HDPE homopolymers are long and straight with little branching. HDPE forms a large fraction of ordered, crystalline regions as it cools below its T_m . This close packing produces HDPE with a crystallinity of 65 to 90% and contributes to HDPE's good moisture-barrier properties and nontransparency. HDPE has excellent resistance to a wide range of chemical compounds such as water based products, medium molecular weight aliphatic hydrocarbons, alcohols, acetone, ketones, dilute acids and bases, but it is not acceptable for aromatic hydrocarbons such as benzene, toluene, etc. Tensile strength of HDPE can be as high as 45 MPa. Impact strength is primarily controlled by MW although it is affected by MWD. HDPE is also characterized by good moisture barrier properties, and poor oxygen and organic compound barrier characteristics. It has good machinability. Table 4.3 summarizes HDPE properties.

Table 4.3 Properties of HDPE

Density	0.94 to 0.965 g/cm ³
T_g	-120°C
T_m	128–138°C
Tensile strength	17.3–44.8 MPa (2500–6500 psi)
Tensile modulus	620–1089 MPa (89,900–158,000 psi)
Elongation at break	10–1200%
Tear strength	20–60 g/25 μm
WVTR	125 g μm/m ² d at 37.8°C, 90% RH (0.32 g mil/100 in ² d at 95°F, 90% RH)
O₂ permeability, 25°C	40,000–73,000 cm ³ μm/m ² d atm (100–185 cm ³ mil/100 in ² d atm)
CO₂ permeability, 25°C	200,000–250,000 cm ³ μm/m ² day atm (500–640 cm ³ mil/100 in ² d atm)
Water absorption	<0.01%

As is the case for other polymers, the properties are affected by the average molecular weight and molecular weight distribution. As relative molecular mass (or molecular weight) increases, tensile strength, impact strength and resistance to stress cracking increase.

Environmental stress cracking (ESC) is a common problem for high density polyethylene. ESC can be defined as the failure of a material that is under stress and exposed to a chemical substance, in conditions where exposure to either the stress alone or the chemical alone does not cause failure. Products such as laundry detergent are known stress-crack agents. In food products, fatty acids can also lead to stress cracking, but it is not as severe as with detergents. A high degree of crystallinity increases the tendency for environmental stress cracking. Therefore, copolymer HDPE is employed for applications such as detergent bottles. The comonomer

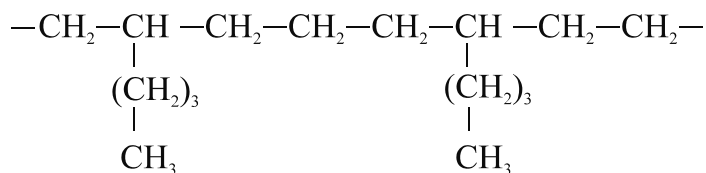
reduces crystallinity by disrupting the close packing of the linear molecular chains, and thereby gives greater resistance to crack propagation.

4.2.2 Linear Low Density Polyethylene (LLDPE)

As mentioned above, linear polyethylene can be produced as a homopolymer, resulting in high density polyethylene, HDPE, or as a copolymer having as comonomer alkenes such as 1-butene, 1-hexene, and 1-octene.

- 1-butene $\text{H}_2\text{C}=\text{CH CH}_2\text{CH}_3$
- 1-hexene $\text{H}_2\text{C}=\text{CH}(\text{CH}_2)_3\text{CH}_3$
- 1-octene $\text{H}_2\text{C}=\text{CH}(\text{CH}_2)_5\text{CH}_3$

The presence of a comonomer in the polymerization process, when a stereo-specific catalyst is used, results in the production of a rather linear polymer with very short branch-like pendant groups. This polymer is called linear low density polyethylene (LLDPE) or ultra low density polyethylene (ULDPE), depending on the density achieved by the addition of the comonomer. The larger the amount of comonomer added, the lower is the density of the copolymer. For example, if hexene is used, the pendant groups are as follows:



Normally the amount of comonomer ranges from 1 to 10% on a molar basis.

The physical properties of LLDPE are controlled primarily by its molecular weight (MW) and density (0.916–0.940 g/cm³). Due to the increased regularity of the structure and narrower molecular weight distribution, LLDPE tends to have improved mechanical properties, compared to LDPE at the same density. The greater stiffness results in an increase of 10 to 15°C in the melting point of LLDPE compared to LDPE. LLDPE has higher tensile strength, puncture resistance, tear properties, and elongation than LDPE. However, LDPE has better clarity and gloss than LLDPE. LDPE also has better heat seal properties.

Typical uses for LLDPE include stretch/cling film, grocery sacks, and heavy duty shipping sacks. LDPE and LLDPE are often blended to optimize the benefit obtained from both materials, with LLDPE adding strength and LDPE adding heat seal and processability. In fact, the term LDPE is commonly used, especially in statistics about resin use, to refer to both the branched type of LDPE and to LLDPE; sometimes the term LDPE/LLDPE is used to denote this explicitly.

It has been found that as the density is pushed below 0.91 g/cm^3 by the incorporation of higher levels of comonomer, the level of hexane extractables (low molecular weight compounds that can be removed through an extraction process with hexane) increases to a level beyond that sanctioned by the FDA. These extractables also can oxidize, resulting in off odors and off flavors.

Polyethylenes with larger amounts of comonomer and consequently density below the normal LLDPE range are called very low density polyethylene, VLDPE, or ultra low density polyethylene, ULDPE. While these can be produced using Ziegler-Natta catalysts, often they are made using metallocene catalysts, as described next.

4.2.3 Metallocene Polymers

In the 1990s, a new family of polyethylenes based on metallocene catalysts emerged. These catalysts offered significant new ability to tailor the properties of linear polyethylenes and other polyolefins. In particular, they had the ability to provide more uniform incorporation of comonomers.

Metallocene catalysts (Figure 4.3) were first discovered in the early 1950s by Natta and Breslow, and were first used to make polyethylene in 1957. These catalysts were used to produce syndiotactic polystyrene in 1984 and syndiotactic polypropylene (by FINA Technology, Inc.) in 1986. However, their commercialization for polyethylene did not come until the mid-1990s, since until that time the advantages the new catalyst systems offered were not fully appreciated. Metallocene catalysts employed today commonly contain a co-catalyst to increase the catalyst activity.

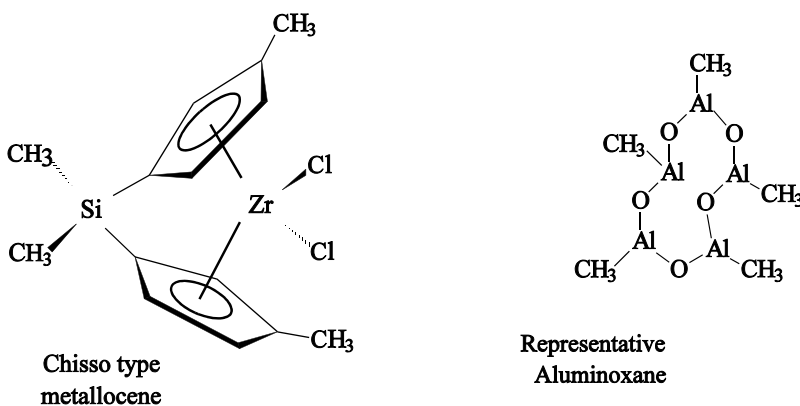


Figure 4.3 Single-site metallocene catalyst with aluminoxane co-catalyst

The first metallocene catalysts were biscyclopentadienyl titanium complexes and dialkylaluminum chloride. These catalysts were not stable and produced very low yields. However, they were the first catalyst systems to produce copolymers of polypropylene and 1-butene with very high comonomer uniformity, due to the fact that they had only one type of active site.

In the 1980s and 1990s, improved polymer characterization techniques were used to explain some of the characteristics, particularly higher haze and higher extractables, of LLDPE. Traditional Ziegler-Natta catalysts were found to have three different types of sites on the catalyst particles. As shown in Figure 4.4, one type of site produced a low MW species with a high proportion of comonomer. Another site produced a high MW species with very little comonomer, and the third type of site produced the predominant medium MW species with a medium amount of comonomer, which was the desired polymer. When the comonomer content was pushed up to produce densities below 0.91 g/cm^3 , the percentage of low molecular weight material with a high concentration of comonomer increased. The extractables and off odors are due to this low MW species. The haze in LLDPE is primarily due to the high MW, linear fraction, which develops a high degree of crystallinity.

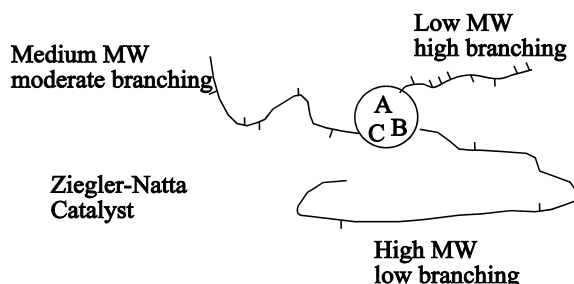


Figure 4.4 Ziegler-Natta catalyst sites (Note: “branching” stems from incorporation of comonomer, so the side groups are not true branches, which is why these are correctly categorized as linear polymers.)

Metallocene catalysts, on the other hand, contain only one type of site geometry, so are often referred to as single site catalysts (Figure 4.5). They produce the desired copolymer, incorporating the comonomer in proportion to the amount added to the reactor. This results in improved properties. Compared to Ziegler-Natta catalysts, metallocene catalysts, by providing greater control over comonomer content, produce more uniform incorporation and improved MWD control. This results in improved clarity and lower extractables, permitting a higher level of incorporation of comonomer. Tensile strength and tear strength are both improved, and the polymer has a softer feel.

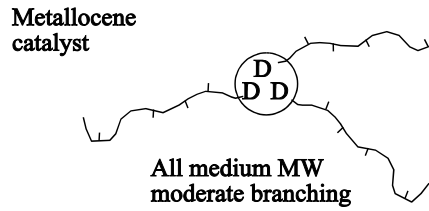


Figure 4.5 Metallocene catalyst; single site (Note: “branching” stems from incorporation of comonomer, so the side groups are not true branches.)

The main class of metallocene catalysts used today is Kaminsky-Sinn catalysts. They are based on titanium, zirconium, or hafnium, and use methylaluminoxane as a co-catalyst. These catalysts produce very uniform comonomer incorporation and very narrow molecular weight distributions.

Figure 4.6 shows the results for hexane extractables on conventional LLDPEs and on metallocene polymers of lower density, but similar comonomer content. Figure 4.7 shows the effect of the catalyst change on the haze in films.

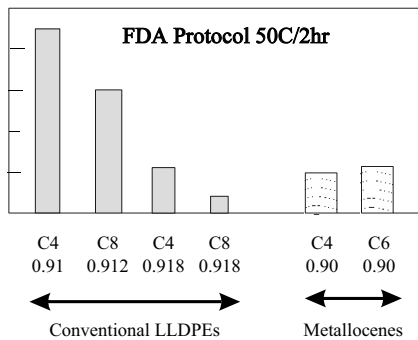


Figure 4.6
Hexane extractables, at densities indicated

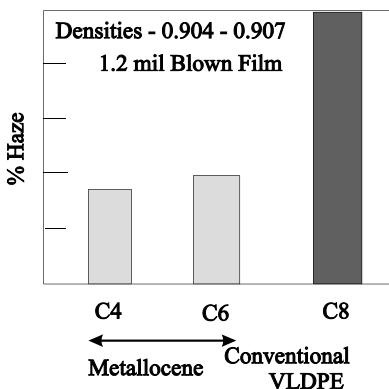


Figure 4.7
Haze

Metallocene catalysts also permit the incorporation of novel comonomers that cannot be used with older Ziegler-Natta catalysts. Long alpha olefins can be incorporated, giving the effect of controlled long-chain branching, and offering some of the benefits of LDPE, such as improved heat sealing, along with the benefits provided by control over MW and MWD. Constrained geometry catalysts (Figure 4.8) are used to produce LLDPE with controlled “long chain branching” (LCB). These so-called long chain branches arise from incorporation of higher α -olefins, which are long alkenes (longer than octene) with a double bond at one end.

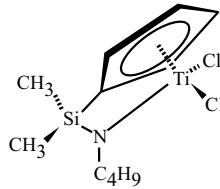


Figure 4.8 Constrained geometry catalyst

Processing is similar to LLDPE. The narrower MWD of the metallocenes results in higher viscosity at high shear rates, and therefore higher horsepower requirements for the extruder.

The improved control over the polymer structure offered by these catalysts offers the polymer producer a significantly greater ability to tailor the polymer to the end-user requirements. The result is a wide variety of resins produced using metallocene catalysts not only for polyethylene, but also for polypropylene and other polyolefins.

Figure 4.9 shows the major catalyst developments in the PE family.

■ Study Questions

1. How do high density, low density, and linear low density polyethylene differ in structure? How do these structural differences affect the properties of the polymers? Why?
2. Why is PP stiffer than HDPE? Why does it have a higher melt temperature? How does this affect packaging uses for these materials?
3. Ionomers are known for their excellent toughness and excellent heat seal characteristics. Relate these characteristics to the chemical structure of the polymer, to explain why they perform so well in these areas.
4. How is the dependence of permeability on density in polyethylene, as illustrated in Table 4.4, related to the structure (chemical or physical) of the polymer? What is the single factor most responsible for the difference in barrier ability?
5. What is the most significant reason that PVDC is a much better barrier than HDPE?
6. Draw the structures of the monomers used to form nylon 12 and nylon 6,10.
7. Explain why the oxygen barrier of EVOH is strongly affected by the amount of water present, but the oxygen barrier of PVDC is not much affected.
8. When we use PVDC and PAN, we commonly use copolymers, even though copolymerization reduces their barrier capability. Why?
9. Polyethylenes, especially low density PE, are referred to as soft and flexible, while nylons and PET are said to be stiff. What molecular feature(s) cause(s) a polymer chain to be stiff?
10. Why do we say that polyethylene is actually a family of polymers?
11. How would you design a copolymer containing ethylene that is more transparent, heat seals better, and is more permeable to water than LDPE?
12. What is the impact on polymer properties of catalysts like the Ziegler-Natta family and the newer single-site metallocenes?
13. Based on what you have learned in Chapters 2–4, explain the property trends of PE listed in Table 4.5.
14. Why are there three stereochemical configurations of PP? Explain why this affects the packaging applications of PP. What would be the effect of these configurations on the properties of a copolymer of PP?
15. Unplasticized PVC presents an important problem during processing. What is it, and why does it happen? What is the recommended solution? Explain.

16. In what aspect is PVC superior to HDPE as a packaging material? Why are the properties of PVC so different from those of PVDC?
17. Name a plastic that is completely transparent and brittle at room temperature. Give a list of uses for such a plastic. Explain.
18. Compare the properties of PVOH and EVOH. Explain the similarities and differences.
19. What family of polymers is very tough, has high melting temperatures, good impact strength, excellent temperature stability, and is moisture sensitive? Explain these properties based on the chemical structure of the polymers.
20. List the types of polyesters discussed in this chapter. Write their chemical structures and list their major characteristics.
21. List possible packaging applications for polytetrafluoroethylene.
22. How does BarexTM differ from SAN, ANS, and ABS? Explain.
23. Imagine that liquid crystal polymers are as inexpensive as PET. Suggest possible applications for LCP in packaging.
24. Do you think conductive polymers have a future in packaging? Explain.
25. What are thermoplastic elastomers, and how do they apply to packaging?
26. What are acrylic, epoxy, and phenolic thermosets?
27. Compare cellophane and polypropylene films.

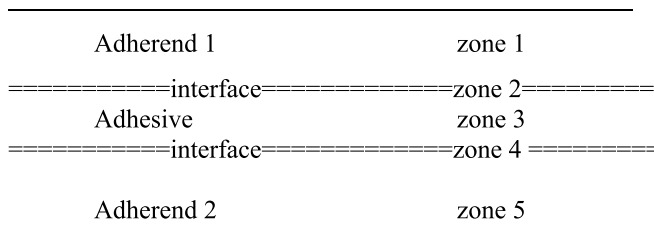


Figure 6.1 Structure of two bodies bonded by an adhesive

■ 6.3 Adhesive and Cohesive Bond Strength

As mentioned above, the adhesion forces develop at the interface between the adherend and the adhesive, and it is at this interface where interfacial forces play the important role of holding the two surfaces together. These are called the *adhesive forces*. If adhesives are used to join two materials as in Figure 6.1, besides the adhesive forces, the strength and integrity of the bonded structure depends on the strength of each material and of the bulk adhesive. The forces of intermolecular attraction acting within a material are termed *cohesive forces*. The cohesive forces in an adhesive depend on its own molecular and physical structure, and are not influenced by the interfacial forces. Therefore, adhesive forces determine the adhesive bond strength at the interfaces, and cohesive forces determine the cohesive strength both within the bulk of the adhesive, as well as in the substrates being joined. The survival and performance of the composite structure depends on all of these.

Adhesive forces are provided by attractions between neighboring molecules and include the same types of forces discussed in Section 2.2.2. Because these forces require a distance of no more than 3 to 5 Å to have reasonable strength, the neighboring molecules at the interface must be very close together for adhesion to occur. This has important practical implications for effective adhesion. The adhesive, at the time of application, must be able to completely “wet” the adherend surface, and must have a low enough viscosity to be able to flow into and fill any irregularities in the substrate surface, in order to bring the adhesive and substrate close together on a molecular scale.

To obtain maximum adhesion, the adhesive bond strength between the adhesive and adherend should be greater than the cohesive bond strength of the adhesive, as indicated in Figure 6.2. (Of course, the overall strength is also limited by the cohesive strength of the substrates.)

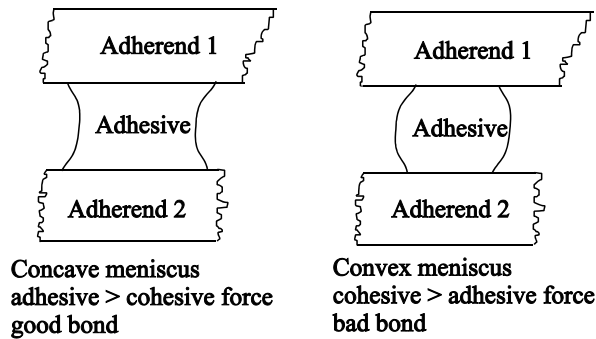


Figure 6.2 Cohesive and adhesive forces

6.3.1 Adhesive Bond Strength

There are several factors that can be used to match an appropriate adhesive to an adherend, including surface tension, solubility parameter, and viscosity.

6.3.1.1 Surface Tension

Solid surfaces have many irregularities, and since adhesion is a surface phenomenon, the adhesive must fill completely all pores and surface irregularities of the adherend at the time of application. To accomplish this, the adhesive must be applied in a liquid or semiliquid state. The liquid adhesive must penetrate all the pores and crevices, eliminating any air pockets, to obtain a homogeneous bond between the adherend and adhesive. The adhesive needs to “wet” the adherend surface, and the better the wettability of the adhesive/adherend pair, the better the chance of producing homogeneous spreading of the adhesive.

The wettability characteristics of an adhesive/adherend pair are determined by the relative values of surface tension of the adhesive and adherend. Surface tension of a liquid is a direct measurement of intermolecular forces and is half of the free energy of molecular cohesion. Surface tension is commonly represented by γ (gamma), and is measured in dynes/cm. The value of the surface tension of the solid substrate, or adherend, is called the critical surface tension, γ_c . To ensure that the surface of the adherend will be wetted by an adhesive, an adhesive whose surface tension is less than the critical surface tension should be selected, so that

$$\gamma_{\text{adh}} < \gamma_c \quad (6.1)$$

In practice, the surface tension of the adhesive should be at least 10 dynes/cm smaller than γ_c . Selected values of γ are listed in Table 6.1, and published in various handbooks.

Table 6.1 Selected Surface Tension Values

Material	Surface Tension, γ , dynes/cm
Nylon 6,6	42
PET	43
PLA	38–42
Polyethylene	36
PTFE	18
Water (solvent for adhesives)	73
Toluene (solvent for adhesives)	27

The surface tension of plastic surfaces can be measured using a calibrated set of solutions. A more sophisticated, and expensive, method is to measure the contact angle the liquid makes with the surface. This method was first described almost 200 years ago for evaluating the wettability of surfaces. The angle measured is the one formed by the tangent on the surface of a drop of liquid at the point of contact with the solid surface and the surface. If the angle is zero, the liquid is said to completely wet the surface. If the angle is not zero, the liquid is said to be nonspreading, and the surface tension of the surface is related to the surface tension of the liquid and the contact angle. In cases where the contact angle of water exceeds 150 degrees on a surface, the surface is referred to as superhydrophobic.

From the values in Table 6.1, one can conclude the following:

1. Water does not wet any of these polymers.
2. Toluene wets PET, polyethylene, PLA, and nylon 6,6 but not polytetrafluoroethylene (PTFE, Teflon).
3. The very low γ_c value of PTFE means it will not be wet by most substances, so adhering materials to it is difficult.

The critical surface tensions of polymeric materials such as polyolefins can be increased by surface treatment such as corona treatment, chemical etching, flame treatment, and mechanical abrasion, in order to facilitate adhesive bonding.

6.3.1.2 Solubility Parameter

An important criterion for determining the chemical compatibility between an adherend and an adhesive in a solvent is the solubility parameter, δ . The solubility parameter is the square root of the cohesive energy density, CED:

$$\delta = (\text{CED})^{1/2} = (\Delta E/V)^{1/2} \quad (6.2)$$

where ΔE is the energy of vaporization and V is the molar volume. A common unit for δ is $(\text{cal}/\text{cm}^3)^{1/2}$, which is called a hildebrand, equal to $\Delta H_v - RT$, where ΔH_v is the enthalpy of vaporization, R is the gas constant, and T is the absolute temperature.

When the adherend is an organic compound and is not too polar, the solubility parameter is useful in selecting an adhesive, allowing one to prescreen adhesives for a particular polymer application. According to the laws of thermodynamics, the greater the difference between the solubility parameters of two materials, the less compatible they are. Consequently, good compatibility is favored when the adhesive and adherend have similar solubility parameters.

$$\delta_1 \approx \delta_2 \quad (6.3)$$

where δ_1 and δ_2 are the solubility parameters of the adhesive and adherend. Representative solubility parameters for selected materials are listed in Table 6.2. Actual solubility parameters will vary somewhat, depending on the precise formulation of the materials.

Table 6.2 Representative Solubility Parameters

Material	Solubility Parameter, δ (hildebrands)	Critical Surface Tension, γ_c (dyn cm ⁻¹)
Poly(1H, 1H-pentadecafluorooctyl acrylate)	-	10.4
Polytetrafluoroethylene	6.2	18.5
Silicone, polydimethyl	7.6	24
Butyl rubber	7.7	27
Polyethylene	7.9	31
Natural rubber	7.9–8.3	-
Natural rubber-rosin adhesive	-	36
Polyisoprene, cis	7.9–8.3	31
Polybutadiene, cis	8.1–8.6	32
Butadiene-styrene rubbers	8.1–8.5	-
Polyisobutylene	8.0	-
Polysulfide rubber	9.0–9.4	-
Neoprene (chloroprene)	8.2–9.4	38
Butadiene-acrylonitrile rubbers	9.4–9.5	-
Poly(vinyl acetate)	9.4	-
Poly(methyl methacrylate)	9.3	39
Poly(vinyl chloride)	9.5–9.7	39
Urea-formaldehyde resin	9.5–12.7	61
Epoxy	9.7–10.9	-
Polyamide-epichlorohydrin resin	-	52
Ethyl cellulose	10.3	-
Poly(vinyl chloride-acetate)	10.4	-
Poly(ethylene terephthalate)	10.7	43

Table 6.2 Representative Solubility Parameters (*continued*)

Material	Solubility Parameter, δ (hildebrands)	Critical Surface Tension, γ_c (dyn cm ⁻¹)
Cellulose acetate	10.9	39
Cellulose nitrate	10.6–11.5	–
Phenolic resin	11.5	–
Resorcinol adhesives	–	51
Poly(vinylidene chloride)	12.2	40
Nylon 6,6	13.6	43
Polyacrylonitrile	15.4	44
Cellulose, from wood pulp	–	35.5, 42
Cellulose, from cotton liners	–	41.5
Cellulose, regenerated	–	44
Starch	–	39
Casein	–	43
Wool	–	45

For polar substances, the types of interactions, as well as their strength, becomes significant, and selection of a proper adhesive by solubility parameter alone does not always work well. A more general, simple rule for selection of adhesives is “like sticks to like.” In other words, the greater the chemical similarity between two materials, the larger will be the intermolecular forces between them.

Charles Hansen proposed an extension of the Hildebrand solubility parameter approach, dividing contributions to the total Hildebrand solubility parameter into three components representing nonpolar (δ_d), polar (δ_p), and hydrogen (δ_h) bonding contributions to the cohesive energy density. Thus, the now named Hansen solubility parameters have been combined as follows:

$$\delta_t^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (6.4)$$

The equivalent form of Equation 6.4 to estimate the enthalpy of mixing then becomes

$$\Delta H_M = \varphi_1 \varphi_2 \left[(\delta_{d1} - \delta_{d2})^2 + (\delta_{p1} - \delta_{p2})^2 + (\delta_{h1} - \delta_{h2})^2 \right] \quad (6.5)$$

The three components, δ_d , δ_p , and δ_h , lie as vectors along orthogonal axes. The end point of the radius vector represents the solubility parameter. This means that each solvent and each polymer can be located in a three-dimensional space. The distance $\Delta\delta$ between the end points of the vectors representing the polymer and solvent is given as:

$$\Delta\delta = \left[(\delta_{dp} - \delta_{ds})^2 + (\delta_{pp} - \delta_{ps})^2 + (\delta_{hp} - \delta_{hs})^2 \right]^{1/2} \quad (6.6)$$

where the subscripts p and s refer to polymer and solvent, respectively. A good solubility level is typically assigned when $\Delta\delta$ is smaller than $2.5 \text{ MPa}^{1/2}$ or $5 \text{ (J/cm}^3)^{1/2}$.

6.3.1.3 Viscosity

Once the condition of wettability of the adherend surface is settled, the viscosity of the adhesive has to be considered. Low viscosity of the adhesive facilitates the spread of the adhesive, while high viscosity makes it difficult to apply the adhesive homogeneously over the surface. Viscosity decreases with increasing temperature and increases with increasing values of average molecular weight (MW).

A summary of the main variables affecting adhesion is presented in Figure 6.3.

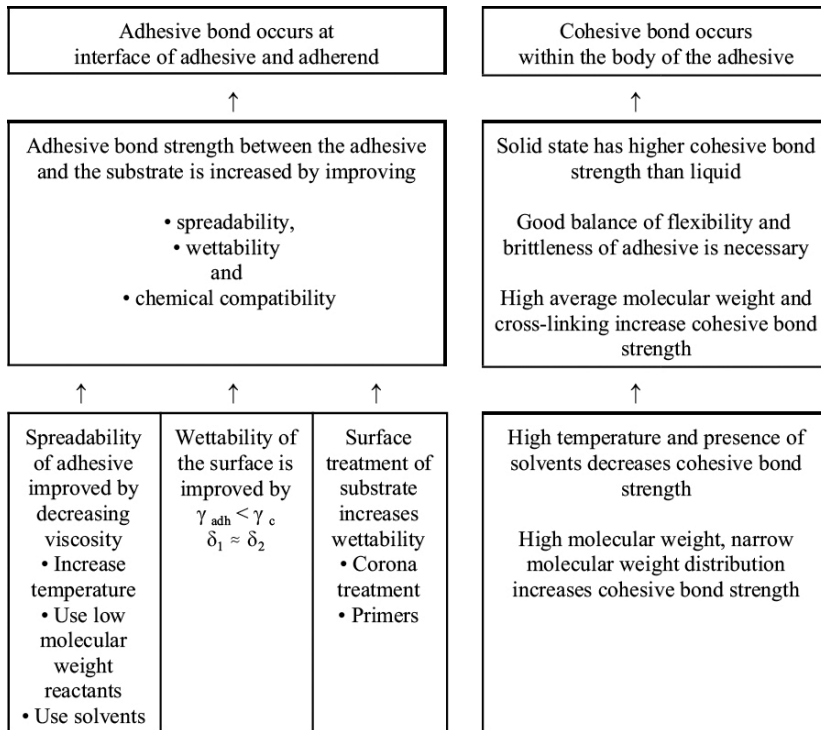


Figure 6.3 Variables affecting cohesive and adhesive forces

6.3.1.4 Estimation of Adhesive Bond Strength

The adhesive bond strength depends on the ability of the adhesive to wet the adherend surface and is quantitatively determined by the shear strength at the interface. It can be estimated from the following equation:

$$S = \frac{Y_1 + Y_2 - Y_{12}}{d} \quad (6.7)$$

where γ_1 and γ_2 are the surface tensions of the adhesive and adherend, γ_{12} is the interfacial surface tension, and d is the distance of separation between the molecules at which failure of the adhesive takes place. This corresponds approximately to an intermolecular distance of about 5 \AA ($5 \times 10^{-8} \text{ cm}$).



Example:

Estimate the strength of the adhesive bond produced on bonding PVC with an epoxy adhesive, given the following specific data:

γ_1 (PVC) = 40 dynes/cm, γ_2 (Epoxy) = 41.7 dynes/cm,

γ_{12} (PVC-Epoxy) = 4.0 dynes/cm; $d = 5 \times 10^{-8} \text{ cm}$.

$$S = \frac{\gamma_1 + \gamma_2 - \gamma_{12}}{d} = \frac{40 + 41.7 - 4.0}{5 \times 10^{-8}} = 1.55 \times 10^9 \frac{\text{dyn}}{\text{cm}^2} = 2.24 \times 10^4 \text{ psi}$$

6.3.2 Cohesive Bond Strength

Adhesives are applied in a liquid state to improve the wettability, as mentioned previously. In general, the liquid state is obtained by dissolving the adhesive in a solvent (organic solvent or liquid water), by dispersing or emulsifying the adhesive in water to produce a latex, by heating the adhesive, or by applying the adhesive in the form of liquid monomers that later react to form a solid. The adhesive, once applied between the two surfaces to be bonded, solidifies through eliminating the solvent, decreasing the temperature, or allowing time for reaction (curing).

Once it is solidified, the performance of the adhesive depends on its adhesive bond strength, as discussed, and on its cohesive bond strength. In many applications, the adhesive is selected so that the adhesive bond strength exceeds the cohesive bond strength. In that case, the overall strength of the adhesive joint will be the cohesive bond strength of the adhesive itself, or of the substrates, whichever is less.

Cohesive bond strength depends on both the chemical nature and the physical state of a material. Temperature and the molecular weight of the adhesive are two important factors. Increasing the molecular weight of an adhesive increases its cohesive strength, but also increases its viscosity and decreases wettability.

The cohesive bond strength of an adhesive can be estimated by the following equation:

$$S = \frac{2\gamma}{d} \quad (6.8)$$

■ 6.8 Heat Sealing

Heat sealing is the process by which two structures containing at least one thermoplastic layer are sealed together by the action of heat and pressure. This process can be applied to flexible, semirigid, and in some cases rigid packaging structures. The following discussion considers flexible structures, but the principles of heat sealing can be extended to other cases. Flexible structures can be classified in two groups, according to the type of material employed in their construction: supported and unsupported structures. Supported structures consist of laminations containing one or more nonthermoplastic layers (such as paper or foil), bonded to thermoplastic layers, at least one of which is used for sealing. Unsupported structures consist of one or more thermoplastic layers and do not contain a nonthermoplastic layer.

When sealing a flexible structure to make a package, the heat-sealing layer is located in the interface, typically contacting another heat-sealing layer. When heat and pressure are applied to the external surface to make the seal, the heat is transmitted by conduction or radiation to the packaging material, and then is transmitted through the material by conduction to the sealing layers (Figure 6.4). Conduction is used more frequently than radiation as the heat input. The heat at the interface must be sufficient to melt the interface materials in order to produce a seal. The external pressure is needed to bring the thermoplastic heat-sealing layers very close to each other, around a distance of 5 Å. A good seal is obtained when enough molecular entanglement has taken place within the polymer chains from the two thermoplastic heat-sealing layers to destroy the interface and produce a homogenous layer that remains homogeneous after cooling. *Dwell time* is the time during which the external pressure holds the two structures together to allow molecular entanglement to take place. The pressure is released at the end of the dwell time. Often, the heat-seal materials are still molten at this point, and the molecular interactions in the heat-seal polymer(s) must be able to keep the sealing surface together against the forces that may act to pull them apart. This strength during the cooling phase is called *hot tack*.

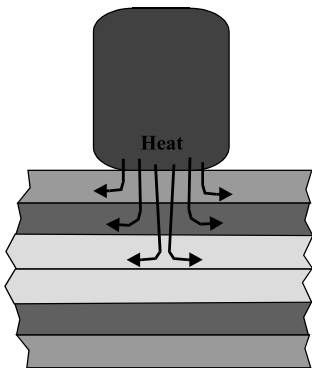


Figure 6.4
Heat conduction in heat sealing

6.8.1 Sealing Methods

The method for heat sealing a particular structure depends on the type and form of the structures being sealed, as well as the type of package and product. The following are the most important sealing methods used in packaging:

6.8.1.1 Bar or Thermal Sealing

Thermal sealing uses heated bars to press together the materials to be sealed, with heat from the bars conducted through the materials to the interface, melting the heat-seal layers and fusing them together (Figure 6.5). When sufficient time has elapsed, the bars release and the material is moved out of the seal area. At this point, the materials are still hot, and the seal does not have its full strength, but the materials must be able to adhere to each other well enough to insure the integrity of the seal (have sufficient hot tack). The full strength of the seal develops as it cools to ambient temperatures. Proper seal formation requires the correct combination of heat, dwell time (the time the material is held between the sealing bars), and pressure. Too little of any of these will prevent an adequate seal from forming. On the other hand, excessive heat, time, or pressure will result in too much flow in the heat-seal layers, weakening the material.

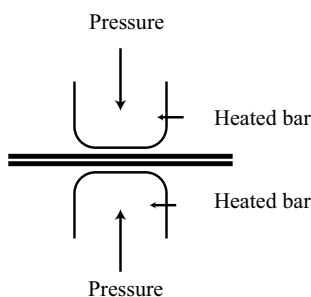


Figure 6.5
Bar sealing or thermal sealing
(reprinted with permission from [6])

The edges of the heat-seal bars are often rounded so that they do not puncture the packaging material. Often the contact surface of one of the bars contains a resilient material to aid in achieving uniform pressure in the seal area. Bar sealing is the most commonly used method of heat-sealing packaging materials and is often used in form-fill-seal operations.

A variation on bar sealing uses only one heated bar, with the other bar not heated, resulting in heat conduction occurring only in one direction. Another variation uses heated rollers instead of bars, with the materials sealed as they pass between the rollers. In this type of system, preheating, slow travel through the rollers, or both, are generally required due to the very short contact time between the rollers. A third variation uses shaped upper bars for sealing lids on cups and trays.

6.8.1.2 Impulse Sealing

Impulse sealing (Figure 6.6) is another common heat-seal method. Impulse sealing uses two jaws, like bar sealing, but instead of remaining hot, the bars are heated intermittently by an impulse (less than one second) of electric current passed through a nichrome wire ribbon contained in one or both jaws. The jaws apply pressure to the materials both before and after the current flow. The current causes the ribbon to heat, and this heat is conducted to the materials being sealed. After the pulse of current is passed through the wire ribbon, the materials remain between the jaws for a set length of time and begin to cool. Thus, impulse sealing provides for cooling while the materials are held together under pressure. This method allows materials with a low degree of hot tack to be successfully sealed, as well as permitting sealing of materials that are too weak at the sealing temperature to be moved without support. The sealing jaws can be water-cooled for faster cooling of the materials being sealed. Shaped impulse seals are used for sealing lids on cups and trays.

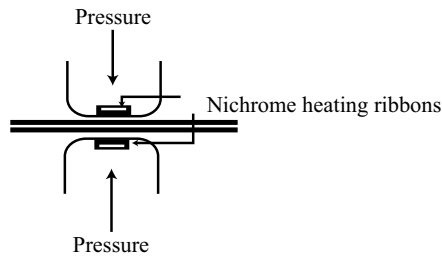


Figure 6.6 Impulse sealing (reprinted with permission from [6])

Impulse sealing produces a narrower seal than bar sealers, resulting in a better looking but weaker seal. Maintenance requirements tend to be heavy, since the nichrome wires often burn out and require replacement. A fluoropolymer tape on the jaws, covering the nichrome wire, is often used to keep the plastic from sticking to the jaws, and may also require frequent replacement.

6.8.1.3 Band Sealing

Band sealing, illustrated in Figure 6.7, like impulse sealing provides a cooling phase under pressure. This high-speed sealing system uses two moving bands to provide pressure and convey the materials past first a heating station and then a cooling station. The primary disadvantage of this method is the tendency for wrinkles in the finished seals. Preformed pouches that are filled with product are often sealed using this method.

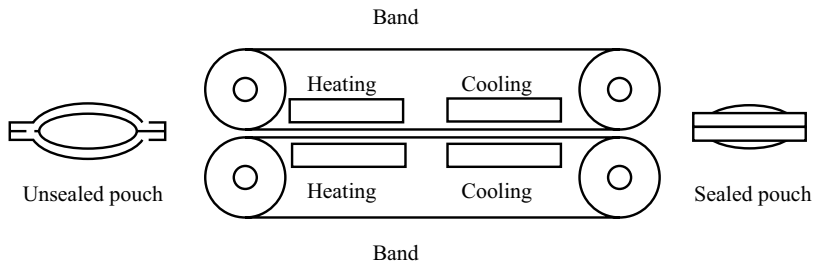


Figure 6.7 Band sealing (reprinted with permission from [6])

6.8.1.4 Hot Wire or Hot Knife Sealing

This method, as its name describes, uses a hot wire or knife to simultaneously seal and cut apart plastic films. The wire or knife causes the substrates to fuse as it is pushed through, cutting them off from the webstock. The seal produced is very narrow and often nearly invisible. It is also relatively weak and does not provide a sufficient barrier to microorganisms to be used when a hermetic seal is required. However, it is very economical due to its high speed, and is an excellent choice for relatively undemanding packaging applications with materials that seal readily, such as LDPE bags used in supermarket produce sections.

6.8.1.5 Ultrasonic Sealing

In ultrasonic sealing, two surfaces are rubbed together rapidly. The resulting friction generates heat at the interface, melting the surfaces of the substrates and producing a seal. Since the heat is generated only in the seal area, ultrasonic sealing is particularly useful for thick materials where conduction is inefficient. It is also useful when exposure to heat for a sufficient time to conduct heat to the seal can damage the substrates, such as in sealing highly oriented materials, which can lose their orientation and shrink when heated.

There has been considerable interest in recent years in ultrasonic sealing for food packaging applications. Systems are available for both continuous and intermittent ultrasonic sealing.

6.8.1.6 Friction Sealing

Friction sealing, often called spin welding, like ultrasonic sealing uses friction to produce heat. It is most often used for assembling two halves of a rigid or semirigid plastic object, such as a deodorant roller or a container, or sometimes for sealing caps to bottles. The two halves are most often circular in cross section, and one is rotated rapidly while the other is held in place. The halves are designed to fit together only with some interference, so there is considerable friction, generating heat that welds them together. The sealing mechanism usually has a sensor that measures the amount of resistance to rotation, and the object is released when the

fall into the dual category of stand-up retort pouches, and will be discussed in Section 9.4.

A remaining drawback to the use of pouches is their slow line speeds, which for beverage packaging is often only about half the speed used with bottles of the same capacity. Pouches have also been getting pushback on environmental grounds, as their complex flexible structure makes recycling difficult or impossible.

■ 9.3 Forming Pouches

The most common way to make pouches (and to package products in pouches) is to use a *form-fill-seal* (FFS) machine, in which preprinted roll stock is formed into a package and the package is filled and sealed with product, all in a continuous operation within one piece of equipment. Cutting the pouches apart is usually accomplished within the FFS machine, as well.

Two configurations, vertical and horizontal, are defined by the direction of travel of the package through the machine (Figure 9.3 and Figure 9.4). The pouches are always produced and filled vertically in a vertical FFS machine, and can be produced and filled either vertically or horizontally in a horizontal FFS machine. A variety of pouch types can be made on either type of equipment. The sealing and cutting apart can be done simultaneously, or the pouches can first be sealed, and then cut apart at a subsequent station.

An alternative to form-fill-seal equipment is to use preformed pouches. In this case, the preprinted pouch is supplied ready to be filled with product, and then after it is filled the top seal is made. In such cases, filling and sealing may be done on two separate pieces of equipment.

Both form-fill-seal and preformed pouches have advantages and disadvantages. For large operations using materials that seal readily, form-fill-seal operations are usually the most economical. However, use of preformed pouches requires less capital investment, since the equipment is simpler and less expensive. It also requires less quality control, since only one seal must be monitored. Therefore, for low volume operations or materials that are difficult to seal correctly, use of preformed pouches can be advantageous. Consequently, most moderate-to-high volume packaging pouch operations use form-fill-seal technology, but operations using retort pouches or stand-up pouches are an exception, most often using preformed pouches.

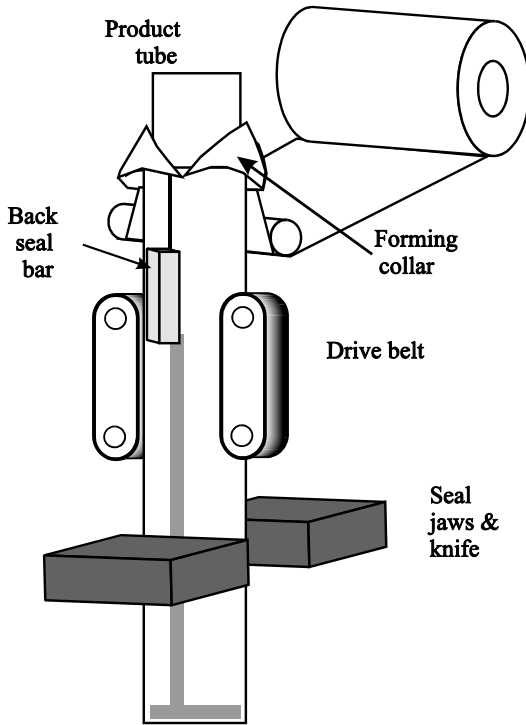


Figure 9.3
Vertical form-fill-seal machine

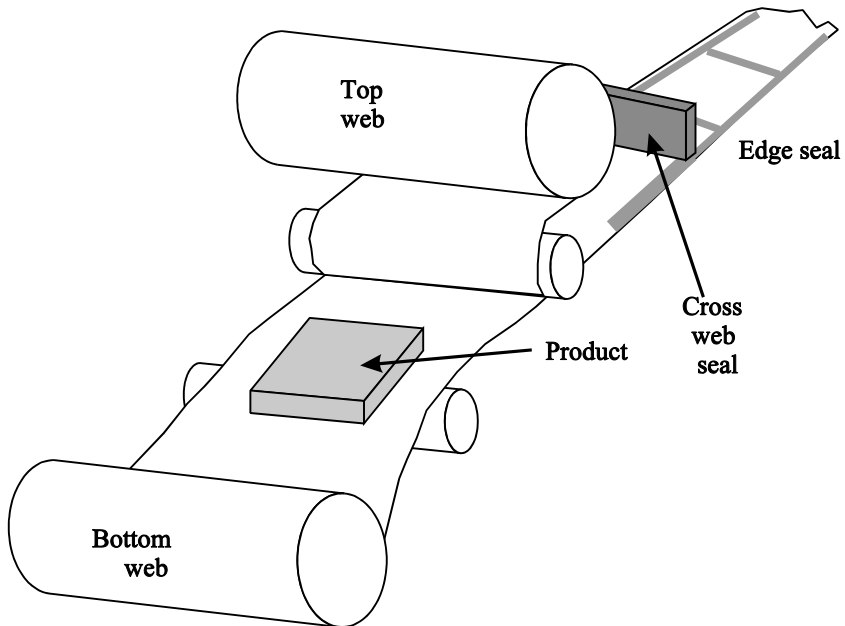


Figure 9.4 Horizontal form-fill-seal machine

■ 9.4 Retort Pouches

Retort pouches are pouches that are designed to be filled, usually with a food product, and then retorted (heat-sterilized in a procedure analogous to canning) to produce a shelf stable product, one that does not require refrigeration. Retort packages long ago replaced cans in the U.S. military MRE (meals ready to eat) program. Their flexibility, smaller volume, and much lighter weight than cans are a significant advantage. In the consumer segment of the market, retort pouches were, for a long time, much less successful. They were introduced by a number of companies, and generally failed to win consumer acceptance except in specialty markets for foods targeted at backpackers and other campers. However, this has now changed significantly. Retort pouches remain less common than cans but can be found in a number of markets. They tend to be less common in the U.S. than in other regions of the world.

The initial design for retort pouches, and the one still used by the military, was a multilayer lamination containing an outside layer of polyester, a layer of aluminum foil, and an inside layer of polypropylene. The polyester provides strength and puncture resistance, the aluminum provides barrier, and the polypropylene provides the sealant and product contact layer. A significant disadvantage of this structure is that the food cannot be heated within the pouch by microwaving.

There are obvious trade-offs between choosing a material that is easy to seal, and choosing a material whose seal will remain strong at the elevated temperatures reached during retorting. Consequently, the retort pouch is not easy to seal. In addition to the difficulty in working with polypropylene as the sealant layer, to ensure sterility, any wrinkling in the seal area must be eliminated. Therefore, efficient manufacture of these pouches is difficult. Nearly all operations using retort pouches buy preformed pouches rather than using form-fill-seal systems, letting the experts deal with producing all but the final seal.

After many false starts, the retort pouch, especially in its stand-up variations, has now taken off, replacing cans or bottles in a number of significant applications. In addition to the advantages associated with flexible packaging in general, retort pouches provide an additional advantage. Because of their thin profile and high ratio of surface area to volume, food products can be sterilized in less time, typically 30 to 50% less than is required for canning, and sometimes even more. This results in greater retention of product quality. Simply put, products in retort pouches taste better than equivalent products processed in cans. The products also look better, and have greater nutritional value.

Development of improved sealing layers has facilitated sealing of retort packages. Developments in filling equipment permit preheating of the package, injection of steam or nitrogen into the headspace to minimize the amount of oxygen in the

pouch in order to increase shelf life, and more rapid line speeds. Some retort pouches now incorporate zippers for reclosure. Others have spouts and caps. A variety of complex ultrahigh barrier laminate structures are now available as alternatives to the old aluminum foil structures. Retort pouches have been even more successful in a market few consumers see, replacing the large institutional size cans used by food service operations such as cafeterias and restaurants.

Retort pouches continue to be more successful in Asia and Europe than in the U.S. However, there are clear signs that U.S. consumers at long last are embracing the advantages that retort pouches can bring. The success of StarKist™ tuna in pouches was one of the early signs. Now it is increasingly common to find pet food, baby food, and a variety of other products appearing in pouches as an alternative to cans or glass bottles. Some have gone so far as to predict that cans would soon be on the “endangered species list” [7]. Experts cite the push for sustainability, cost reduction, and the 360-degree graphics as major influences in pouch growth [5]. However, their recovery at end of life is an increasing concern.

■ 9.5 Bulk and Heavy-Duty Bags

Bulk bags and heavy-duty bags are designed for packaging large quantities of solid or liquid product. They can contain as much as 5000 kg (11,000 lb) and, therefore, must have high tensile strength. Woven PP fabric is usually the material of choice, although HDPE, PVC, and polyester fabric are also used. Some bags, especially in smaller sizes, are made of film, usually LLDPE or HDPE, rather than fabric. Other bags include a plastic film layer in a construction that is mostly paper. An alternative is to use the plastic as a coating on the paper. HDPE, LDPE, PVDC, PP, and combinations are all used in such applications.

Bags made of woven fabric do not generally provide sufficient containment for liquid products, so such bags often incorporate a film liner. Polyethylene is used most often, but aluminum foil or PVDC copolymers can be used to provide improved barrier ability. The liner may be a single material or have a multilayer construction. Alternatively, the bags can be coated with PVC or latex to make them waterproof. Liners can also be used in bags for solid products. Often the liner is designed to be disposable to facilitate reuse of the bag.

The bag seams can be heat-sealed or sewn, depending on the material and the application. Some bags are made from tubular material, so sealing is required only at the top and bottom. Others have seams at the back, bottom, and top; or they can be made like three-side seal pouches, with a fold forming the bottom of the bag.

saleable condition under specific conditions of storage. The validity of the above equations is subject to the following conditions:

- a. There is a rapid equilibrium between the product and the package internal conditions.
- b. The delay in reaching the steady state condition of permeation through the package material is not considered.
- c. The temperature is constant through the shelf life period, t .
- d. P is not affected by concentration.

We now will consider the estimation of shelf life for moisture and oxygen sensitive products.

■ 14.11 Shelf Life Estimation

The first step in shelf life estimation is to determine the parameters controlling the loss of product quality. Shelf life may end for a product due to moisture uptake, oxidation, spoilage from microbial action, or a combination of these and other factors. Therefore, one must determine what is causing the endpoint to occur. Having done that, calculations to estimate when that will occur in a package can be made.

The first estimation of shelf life due to gain or loss of a volatile component is usually made using the assumption of a constant Δp across the package wall. The accuracy of this assumption will vary, depending on the product and the package. For instance, if the product was potato chips and the failure mechanism was oxidative rancidity, the assumption is fairly good. Oxygen pressure in the atmosphere is nearly constant at 0.21 atm. The oxygen concentration in the package will be nearly zero, since any headspace oxygen will quickly react with the oil in the product. If the product were a thick liquid where diffusion is slow, the assumption would not be so good. For moisture vapor over a long shelf life, the assumption is only a first approximation because the relative humidity of the atmosphere changes over time, and the relative humidity inside the package can change significantly as moisture is gained or lost in the product. For accurate estimates of shelf life, storage testing of real packages under nearly real-life conditions is often needed.

To determine the behavior of a product, it must be stored at known conditions for a period of time and its properties measured. In the case of oxidation, for example, some method must be available to determine the amount of reaction with oxygen that the product has undergone. This is often done by measuring peroxide values for oil-containing products, or hexanal values for products that have hexanal as the end degradation product for oxidation. For moisture sorption, the product can be stored over a saturated salt solution until moisture uptake is at equilibrium. Then

taste or texture is often the measured parameter to determine the endpoint of shelf life. For pharmaceuticals, the true end-point is determined by the bioavailability of the drug.

For any type of product that gains or loses water, one can measure the moisture content as a function of relative humidity, or water activity, and determine a moisture isotherm (often called moisture sorption isotherms). As shown in Figure 14.12, moisture isotherms are usually sigmoid shaped curves. However, one can sometimes use only the linear portion of the curve for shelf life predictions.

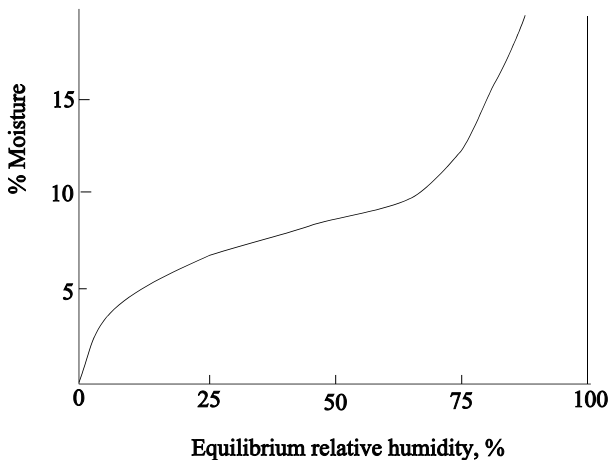


Figure 14.12
Moisture sorption isotherm

Let us look at an example of shelf life prediction where the Δp is constant throughout the storage.



Example:

Calculate the minimum thickness of PET for protection of a product that has an end of shelf life when it has reacted with 0.005% (wt/vol) of oxygen. The package design is a 500-mL container with 400 cm² area. The product is a water-based liquid. Storage conditions are 25°C and 60% RH. The desired shelf life is six months. Also, calculate the water loss at the end of six months in this package.

Solution:

From Equation 14.14 by rearrangement,

$$l = \frac{P_f A \Delta P}{q} \quad (14.36)$$

From the literature, PET at 25°C has an oxygen transmission rate (OTR) of 22 cm³ (STP) $\mu\text{m}/(\text{m}^2 \text{ d kPa})$

$t = 6 \text{ months} = 180 \text{ d}$

$$A = 400 \text{ cm}^2 = 0.04 \text{ m}^2$$

$\Delta p = 0.21 \text{ atm} = 21.27 \text{ kPa}$ (assuming $p_i = 0$) (p_i is oxygen partial pressure inside the package)

To determine q , we must convert the 0.005% gain over six months to a mass or volume:

$$q = 500 \text{ mL} \times \frac{0.005}{100} \times \frac{\text{mol}}{32 \text{ g}} \times 22,400 \frac{\text{cm}^3}{\text{mol}} = 17.5 \text{ cm}^3 \text{ (STP)}$$

Then

$$\ell = \frac{22 \text{ cm}^3 \text{ (STP)} \mu\text{m}}{\text{m}^2 \text{ d kPa}} \times 180 \text{ d} \times 0.04 \text{ m}^2 \times 21.27 \text{ kPa} \frac{1}{17.5 \text{ cm}^3 \text{ (STP)}} = 193 \mu\text{m} = 7.6 \text{ mil}$$

We can now use the same method to calculate the amount of water loss.

$$q = \frac{Pt \Delta p}{\ell}$$

Assume that the water vapor P for PET is as shown in Table 14.8, $850 \text{ cm}^3 \text{ (STP)} \text{ cm}/\text{m}^2 \text{ d atm}$. The Δp is the difference in the vapor pressure in the container (100% RH) and that outside (60% RH). The saturation water vapor pressure at $25^\circ\text{C} = 23.756 \text{ mm Hg} \times \text{atm}/760 \text{ mm Hg} = 0.0312 \text{ atm}$.

$$\Delta p = 0.0312 \text{ atm} \times \frac{(100 - 60)}{100} = 0.01875 \text{ atm}$$

$$q = \frac{850 \text{ cm}^3 \text{ (STP)} \text{ cm}}{\text{m}^2 \text{ d kPa}} \times 180 \text{ d} \times 0.04 \text{ m}^2 \times 0.01875 \text{ atm} \times$$

$$\frac{1}{193 \mu\text{m}} \times \frac{10000 \mu\text{m}}{\text{cm}} = 5946 \text{ cm}^3 \text{ (STP)}$$

We need to convert this volume of water vapor at STP (assuming ideal gas behavior) to an amount of liquid water lost.

We use the volume of 1 mol of ideal gas of $22,400 \text{ cm}^3$ and the mass of water vapor of 18 g/mol , along with the density of liquid water of 1.0 g/mL :

$$5946 \text{ cm}^3 \text{ (STP)} \times \frac{\text{mol}}{22,400 \text{ cm}^3 \text{ (STP)}} \times \frac{18 \text{ g}}{\text{mol}} \times \frac{1 \text{ mL}}{\text{g}} = 4.77 \text{ mL}$$

Now suppose that a product is stored in a real-world situation where the moisture on the inside or the outside of the package changes over time. Then one needs the external environmental conditions and a moisture isotherm for the product. The moisture on the inside of the package may change over time even if the external conditions are constant because the product is reaching equilibrium with the internal moisture content. If the external conditions vary over too wide a range of temperatures, then multiple isotherms may be needed.

Index

Symbols

δ 195

ϵ 83

A

abrasion resistance 91

absorbance 100, 277

accelerated testing 403

acceptable daily intake
409

acetaldehyde 328

acrylate 204

acrylic 125, 157, 203

acrylonitrile/butadiene/
styrene (ABS) 3, 33,
125, 143

acrylonitrile copolymer 3

acrylonitrile-styrene 143

Actis™ coating 261, 341

activation energy 379

addition polymer 33, 34

additives 165, 407

adherend 191

adhesion 18, 109, 132, 191,
198, 248, 316, 342

adhesive 3, 9, 32, 62, 157,
191, 203, 204, 262, 358,
406

adhesive bond strength
94, 198

adhesive forces 193

ADI (accepted daily intake)
409

adipate plasticizer 184

adipic acid 181

adjuvant 405

advanced polymers 21

air gap 255

air knife 229

air ring 239

alkene 105

alkyds 157

alkyl acids 182

alkyl salts 182

alpha-olefin 118

alpha-tocopherol (Vitamin
E) 171

aluminum 179, 182, 259,
271, 291, 301, 338, 441

– foil 253, 260, 271, 272,
303, 307

– hydrate 179

– oxides 261

– silicate 179

American Plastics Council
437

amide 157

amine; also see hindered
amine light stabilizers
(HALS) 157

amorphous 32, 58,
60–62, 70, 74, 86, 128,
139, 276, 280, 362, 384

amorphous carbon 261,
341

anisotropic behavior 67

annealing 243

ANS, see acrylonitrile-
styrene

anthraquinone 177

antiblock 174

antifog 180

antimicrobial 187

antioxidant 169

antislip 176

antistat 180, 182, 359

APET 136

architecture (of polymers)
25, 42

aromatic polymer 17

Arrhenius equation 379

arylamine 170

aseptic packaging; also
see blow molding,
aseptic 292

ash, incinerator 418

aspect ratio 297

atactic 46, 61, 70, 122, 128

autoclave (stirred tank)
38, 122

axial ratio 324

azo compound 37

B

backbone 9

bag-in-box 265, 273

bags 6, 68, 266, 272, 439

Bakelite 1

barefoot resin 166

barrel 219

- barrier 92, 127, 131, 136, 141, 142, 235, 310, 323, 324, 332, 341, 361, 372
- barrier screw 223
- beer 336
- bentonite 179
- benzimidazole 178
- benzoic acid 181
- benzotriazole 170
- BHT 171, 365
- biobased PET 155
- biobased plastics 147, 155
- biobased polyethylene 154
- biocides 187
- biodegradable 146, 150, 154
- biodegradable plastics 149, 451
- BIRP 436
- bisphenol-A 157, 183, 425
- black body radiation 276
- blends 32, 138, 139, 142, 159, 165
- blister packaging 144, 275, 286
- blocking 95, 174, 206, 250
- bloom(ing) 95
- blowing agent 129, 189, 348
- blow molding 38, 60, 68, 307, 309, 338
- aseptic 340
 - coextrusion 335
 - coinjection 335
 - extrusion 136, 309, 310, 322
 - injection 137, 300, 309, 322
 - rotary blow molding 313
 - shuttle blow molding 313
 - simulation 320, 322, 336
 - stretch 68, 137, 307, 310, 319, 324
- blown film 234, 238, 241
- blow-up ratio 235, 325
- boil-in-bag 268
- bottle dimensions 343
- bottle(s) 6, 112, 113, 132, 136, 138, 142, 143, 160, 184, 192, 202, 211, 213, 219, 268, 293, 309, 341, 439
- boxes 358
- branching 27, 40, 61, 62, 105
- long chain 27, 38, 65, 118
 - short chain 27, 38
- breaker plate 225
- break point 85
- bridging 221
- brittleness 87
- bubble 234
- bubble wrap 352
- bursting strength 91
- bushing 315
- butene 114
- ## C
- cadmium compounds; also see heavy metals 172, 419
- calcium compounds 172, 179, 385
- calendering 230
- can linings 157
- carbonated soft drink (CSD) 323
- carbon black 173, 178
- carbon nanotubes 188
- carboxyl (-COOH) groups 254
- casein 202
- cast film, sheet 229, 233
- catalyst 2, 12
- chromium 41
 - Kaminsky-Sinn 117
 - metallocene 115, 118, 366
- single-site 2, 115
 - Ziegler-Natta 2, 40, 41, 111, 121
- CB-A 170
- CB-D 170
- cellophane 3, 147
- celluloid 1
- cellulose 1, 147
- acetate 3, 149
 - butyrate 149
 - esters 149
 - nitrate 149
 - propionate 149
- cellulosic plastics 147, 150
- chain scission 169
- channel depth ratio 224
- Charpy impact test 91
- chemical activity 362, 367
- chemical blowing agents (CBA) 189
- chemical composition 20
- chemical plasma deposition 261
- chemical potential 366
- chemical recycling 444
- child-resistant packaging 304
- chill roll 229
- chiral 45
- chlorinated polyethylene 125
- chlorofluorocarbons (CFCs) 189
- clamp 295
- clay 174, 188, 207
- clay nanocomposites 262
- cling 244
- closures 300, 301, 304
- CT 302
 - dispensing 304
 - friction 301
 - linerless 303
 - snap-on 301, 302
 - threaded 301, 302
- coadhesive 204

- Coalition of Northeastern Governors (CONEG) 418
coat-hanger die 233
coating(s) 9, 127, 148, 246, 253, 262, 341
– extrusion 253
cobalt compounds; also see heavy metals 178, 185, 337
Code of Federal Regulations (CFR) 402
coefficient of friction 95
coefficients, thermal expansion 80
coextrusion; also see blow molding, coextrusion 236, 237, 246, 253, 256, 262, 316
cohesive bond strength 94, 199
cohesive energy density, CED 18, 159, 195
cohesive forces 193
cold cast; also see cast film, sheet 229
cold-seal adhesive 204
collapsing core 299
collapsing frame 240
collection, recyclables 437
colligative properties 53
colorants 176, 405
commingled 438, 450
commodity plastics 21
compatibilizer 450
compostable 152
composting 451
compounding 166
compression cutting 287
compression molding 306, 307
compression section 219, 222
condensation polymer 14, 33, 47, 50, 133, 136
conductive polymer 145, 182
configuration 42, 44
conformation 42, 45, 63
constitutional unit 13
consumption factor 409
containers 347
contaminants 415
converting 253
cooling 318
copolymer 13, 25, 29, 33, 42, 61, 63, 108, 109, 116, 123, 138, 139
– alternating 14, 30, 50
– block 14, 30, 63, 142
– graft 14, 32, 63, 142
– random 14, 29, 108
copolymerization 158, 159
copper 207, 338
core 309
core rod 318
cork 301
corona discharge 248
corona treatment 195, 307
corrugated plastic 358
cosmetic packaging 417
coupling agents 189, 385
covalent bond 16, 17, 32
CPET 136, 280
CPSC 424
crates 358
creep 21, 87, 303
critical point 38
cross-linking 28, 62, 76, 86, 157, 169, 245
cross-machine direction 68
crystalline, crystallinity 20, 25, 29, 40, 42, 58, 61, 74, 80, 86, 91, 106, 108, 110, 113, 127, 130, 134, 136, 138, 141, 147, 233, 235, 276, 280, 333, 362, 384
crystallites 31, 181, 235, 324
crystallization 63, 64, 331
cure, curing 157, 204
curtain 255
cushion curves 353
cushioning 6, 352
cyanoacrylate 200
cyclic olefin copolymers (COC) 143
- D**
dalton 9
dancing mandrel 316
dart drop impact test 90
dead spots 236
deformation 85, 89, 280
degradable plastic 417
degradation 17, 28, 44, 329
– oxidative 122, 169
degree of polymerization, *n* 51
dehydrochlorination 172
density 20, 40, 69
density gradient 69
deposit legislation 433, 436, 445
desiccant 185
design 286
dextrin 202
diatomaceous earth 174, 179
diazo 177, 178
dibutyl phthalate 183
dibutyltin 172
dichloromethane 191
die 219, 225, 233, 236, 312
die gap 237, 238
dielectric constant 98
die shaping 309, 315
die swell 312
diethylhexyl phthalate (DEHP or DOP) 183, 425

- differential scanning calorimetry (DSC) 69
 diffusion 21, 69, 92, 361, 363, 370
 diffusion coefficient 92, 372, 387
 dimensional stability 81
 dimer 26
 dioctyl sebacate 183
 dioxazines 178
 dioxin 126
 dipole forces 18, 19
 dispersion 166
 dispersion forces 18, 19
 dispersity (dispersion index) 54
 dissolution 368
 distribution 166
 doctor blade 258
 double bubble 235, 243
 draft angle 289
 drawdown 237
 draw ratio 287
 drive mechanism 225
 drum 6, 311, 358
 dry bonding 257
 DSD system 433
 dual lip air ring 239
 ductility 87
 Dulmage mixer 224
 dwell time 208
 dye 177
- E**
- easy-peel heat seal layer 161
 ebonite 1
 E/EA 15
 ejection system 298
 elastic elongation 85
 elasticity 21, 53
 elastic limit 85
 elastic modulus 74
 elastomer 3, 146
- electrical properties 98
 electron affinity 17
 electron beam 140, 261
 electronegative 18
 electropositive 17
 electrostatic 150
 electrostatic attraction 18
 electrostatic discharge (ESD) 359
 elongation 85, 169, 244
 emissivity 278
 emulsion 206
 endocrine disruptors 424, 453
 energy 6, 17, 42, 44, 60, 65, 76, 80, 100, 452
 engineering polymer 21
 entanglement 58, 192
 enthalpy 20
 environment 429
 environmental issues 6
 environmental stress cracking 113
 E/P 15, 29
 EPA, Environmental Protection Agency 188, 430, 452
 epoxide 172
 epoxidized oil 184
 epoxy 3, 62, 157, 200
 EPS Industry Alliance 449
 erucamide 175
 estimated daily intake (EDI) 409
 ethylene 105, 107
 ethylene acrylic acid (EAA) 109
 ethylene chloride 207
 ethylene/maleic anhydride 176
 ethylene methacrylic acid 110
 ethylene vinyl acetate (EVA) 28, 108, 201, 203, 244
- ethylene vinyl alcohol (EVOH) 3, 20, 21, 131, 144, 160, 186, 248, 316, 337
 expanded polystyrene foam (EPS) 348, 349
 extended producer responsibility (EPR) 433
 extenders 187
 extruder 219, 238, 293
 extrusion 28, 307
- F**
- family of hindered amine light stabilizers 173
 fatigue 121, 244
 fatty acid 176, 180, 182
 fatty alcohol 180
 FDA 115, 125, 139, 143, 149, 172, 179, 182, 338, 341, 365, 402–404, 412, 413, 416, 417
 Federal Food, Drug, and Cosmetic Act 402
 Federal Register 402, 411
 feed block 246
 feed port 221
 feed section 221
 feedstock recycling 444
 fiber 187, 207
 Fick's law 92, 363, 370, 371
 filler 187, 207, 385
 - conductive 182
 film 39, 106, 123, 127, 134, 262, 448
 finish 309, 312, 318, 323, 324, 333, 334, 343
 - crystallized 334
 finite element analysis (FEA) 320
 fin seal 266
 fitments 305

- flair swell (mandrel swell) 312
- flame resistance 165, 188
- flame retardants 189
- flame treatment 195, 248, 341
- flash 310, 311, 313, 317
- flex-cracking 260
- flexibility 76
- flexible packaging 5, 214, 265
- flexural modulus 85
- Flory-Huggins (FH) model 369
- flow 57, 58, 74, 79, 122, 167, 176, 193, 217, 224, 225, 280, 296, 305, 306
- fluorescent pigments 179
- fluorination 342
- fluoropolymers 3, 141
- foam 79, 129, 337, 338, 347
- closed cell 347
 - foam-in place 351
 - open cell 347
 - starch-based 352
- fogging 180
- folding endurance 91
- food additive 404
- food packaging 5, 404
- formaldehyde 157
- form-fill-seal (FFS) machine 269
- Fourier's law 79, 355
- fragility 353
- fragrance enhancer 186
- free radical 37, 43, 44, 169
- primary 44
 - secondary 44
 - tertiary 44
- free volume 362, 377
- friction 18, 21, 221, 250
- frostline 235, 240
- F-style bottle 314
- functional barrier 413, 416
- functional groups 47
- functionality 26, 48
- ## G
- gas constant 379
- gas transmission rate (GTR) 373
- gate 296, 318
- gauge 231, 236
- gel 28, 250
- gel permeation chromatography 57
- generally recognized as safe (GRAS) 413
- glass transition temperature (T_g) 32, 65, 71, 75, 89, 147, 276, 362
- glassy state 73
- global warming (climate change) 453
- gloss 97, 250
- glue, animal 202
- glycol 185
- glycolysis 444
- gravure roll 258
- Green Dot system 433
- grid melters 205
- gusset 267, 268
- ## H
- handles 309, 323
- haze 97
- HCFC 349
- head 307
- head-to-head 43, 61
- head-to-tail 43, 124
- heat capacity 78, 214
- heat conduction 214, 355
- heat(ing) 276
- radiative 276
- heat of fusion 70, 78
- heat sealing 96, 109, 110, 191, 208
- heat-setting 324, 330, 333
- heat stabilizers 171
- heavy metals 177, 419
- helix angle 222, 224
- Henry's law 93, 368, 372
- hermetic 217, 301
- heteroatoms 47
- hexene 114
- high density polyethylene (HDPE) 27, 40, 63, 106, 111, 112, 171, 237, 240, 301, 338, 436, 446
- spunbonded 212
- hildebrand 195
- hindered amine light stabilizers (HALS) 173
- HIPS (high impact PS) 14, 32, 142, 161, 171
- HMW-HDPE 112, 240
- HNR 142
- homopolymer 13, 25
- hoop ratio 320, 325
- hopper 220
- hormones 424, 453
- hot-fill 324, 330, 332
- hot melt 201, 203
- hot runner molding 299, 318
- hot tack 96, 208, 215
- humidity 81, 95, 133, 145, 186, 352, 382, 397
- hydrobenzophenone 173
- hydrofluorocarbons (HFCs) 189
- hydrogen bond 20, 77, 130, 134, 147, 149, 382
- hydroperoxide 37, 169
- hydrophilic polymers 98
- ## I
- ideal gas law 367
- impact modifiers 189
- impact strength 90

- incineration 430, 432, 452
- indirect food additives 404
- induction forces 18, 19
- inflatable bags 353
- inherently dissipative polymers (IDPs) 145
- initiation 37
- initiator 37
- injection mold(ing) 60, 64, 106, 112, 122, 123, 127, 219, 275, 293, 294, 298, 300, 306, 307, 309, 318, 324, 326, 339, 357
- inner seals 213
- insulation 348, 355, 356
- interactions 361
- interatomic forces 16
- interfacial energy 94
- intermediate polymer 21
- intermolecular forces 16, 18, 75, 130, 134, 142, 192
- internal bubble cooling (IBC) 239
- intramolecular forces 18
- intrinsic viscosity (IV) 328
- ionic bond 17, 110
- ionomer 3, 18, 110, 255
- iridescent 317
- iron compounds 178, 184, 212
- IR spectrophotometry 99
- isomorphous 62, 63
- isostatic 386
- isotactic 46, 61, 64, 121
- Izod impact strength; also see impact strength 91
- J**
- jaws, heat-seal 215
- K**
- KURARISTER™ 262
- L**
- labels, labeling 339
- in-mold 339
- lacquer 157
- lactic acid 151
- lake pigment 179
- lamella(e) 63
- laminar flow 167
- lamination 192, 246, 253, 257, 262
- adhesive 257
- dry 257
- extrusion 253, 262
- hot melt 256
- thermal 259
- wet 257
- land 233, 238
- landfill 430
- land length 312
- Langmuir-Henry's law 369, 376
- Langmuir's law 93
- lap seal 266
- latex 199, 202, 204
- lead; also see heavy metals 177
- letter of no objection 415
- letting down 166
- lidstock 185, 201, 291
- lifecycle assessment 454
- lifecycle impact analysis (LCIA) 455
- lifecycle inventory analysis (LCI) 454
- light-weighting 300
- linear line 235
- linear low density polyethylene (LLDPE) 3, 27, 41, 107, 112, 114, 144, 159, 171, 237, 256
- liner 303
- liquid crystal polymers (LCP) 3, 144
- load-deformation curve 81
- lock-up seals 216
- London forces 19
- long chain branching (LCB) 41
- loosefill 347
- low density polyethylene (LDPE) 3, 38, 39, 62, 85, 106, 171, 182, 191, 248, 287, 301, 304, 448
- lubricants 176
- M**
- machine 293
- machine direction 68
- macromolecules 1, 9
- macrosorting 442
- Maddock mixer 224
- magnesium oxide 179
- mandrel 307, 351
- manifold 233
- market, for plastics 4
- mass transfer 363
- master batch 166
- Mayer rod 258
- MBS 124
- mechanical properties 81
- medical devices 403
- medical packaging 6, 212, 402
- medium density polyethylene (MDPE) 107
- MEK 207
- melt 219
- melt flow 298
- melt fracture 238
- melt(ing) temperature 4, 21, 63, 65, 71, 75, 112, 120, 201, 204, 226, 233, 254, 255, 276, 298, 345
- melt strength 255, 309
- mesogenic monomer 144
- metal deactivator 171

- metallic pigment 179, 317
metallized film, metallizing 259, 273
metallocene polymers 3
metering section 219, 223
methacrylate-butadiene-styrene (MBS) 124
methanolysis 444
methyl-ethyl ketone (MEK) 207
methyl isobutyl ketone (MIBK) 207
methyl methacrylate 191
MIBK 207
mica 179
microbubbles 338
microcellular foam 338
microcrystalline cellulose 188
microsorting 442
migrants 364
migration 165, 363, 364, 407, 412, 414
miscibility 18
Mocon Oxtran 386
Model Toxics Law 419
modified atmosphere 140, 291, 364
modulus of elasticity 84
mold 219, 278, 288, 291, 306, 310, 348
– block 296
– cooling 291, 295
– female 279
– male 278
– negative 279
– parting line 295, 300, 339
– positive 278, 283
– release agent 176
molding 278
molecular architecture 25
molecular mass 9, 51, 57
molecular sieves 378
molecular weight 1, 9, 51, 52, 63, 122, 148, 159
– average 53
– critical 58
– distribution 41, 51, 52, 60, 366
– number average 53
– viscosity average 57
molecular weight distribution 366
monomer 1, 10, 12, 13, 25, 365
– bifunctional 26
– trifunctional 26
morphology 61, 63, 66, 80
multichannel die 246
multimanifold die 246
municipal solid waste (MSW) 430, 437
MXD6 nylon 135, 185
- N**
nanoclay 188
nanocomposites 262
nanoscale additives 188
naphthalate dicarboxylate (NDC) 138
natural 207
NDA 403
neck-in 255
negative migration 366
Newtonian behavior 59
nipple height 290
nip roll 231
nips 242
nitrocellulose plastics 149
nonpolar bonds 17
norbornene 143
notched Izod impact strength 91
NPRC 449
nucleating agents 136, 180
nylon; also see polyamide 2, 3, 9, 20, 21, 49, 62, 133, 160, 181, 195, 260, 280, 406, 444
- O**
octene 114
olefin 105
oleic acid amide 175
opacity, opaque 70, 96, 98, 177, 180
open time 206
optical properties 96
– absorption 96
– reflection 96
– refraction 96
– scattering 96
oriented, orientation 20, 66, 67, 80, 86, 123, 134, 136, 137, 232, 235, 240, 310, 323, 324, 331, 384
– balanced 68, 232
– biaxial 68
– unbalanced 68, 232
– uniaxial 68, 384
OSHA 177
overcaps 305
oxidation 248, 254
oxygen scavenger 184, 337
ozone 248
- P**
packing, mold 293
pails 358
pallets 357
paneling 314, 333, 334
paracrystalline 70
parison 60, 309–311, 314, 316, 318, 319, 324, 330, 335
– programmed 309
partition coefficient, K 365, 370, 413

- pearlescent 179
PEF 3
pelletizing 443
pendulum impact test 91
permeability coefficient, P 93, 372, 387
permeability, determination of 386
– isostatic method 386
– quasi-isostatic method 386
permeability, permeation 21, 66, 361, 364, 371, 377, 390
permeance (R) 373
permeant 364, 413
peroxide 37, 169
pesticide 188
PET, biobased 155
PETG 138
PHBV 3
phenol-formaldehyde 3
phenol, hindered 170, 173
phenolics 157, 207
phosphite 170, 172, 173
photodegradable 418
photooxidation 172
phthalate plasticizers 424
phthalocyanines 178
physical blowing agents (PBA) 189
pigment 177, 178
– lake 179
– metallic 179
pinch 312
pinch rollers 235
pineapple mixing section 224
pinhole flex resistance 91
pin mixing section 224
plasma 261
plastic 343
plasticizer 124, 127, 148, 183, 382
plastic properties 161
plastics 3, 12
plastics coding system 421
plastics identification 99
plastomer 146
platelet 179
platen 294
– fixed 295
– floating 295
– moving 295
plug flow 223
Poisson's ratio 87, 320
polar atoms 19
polar bond 17
polar groups, polymers 76, 108, 124, 131, 142, 159, 183, 197, 212, 382
polyacrylonitrile (PAN) 70, 142, 181, 323, 410
polyamide; also see nylon 9, 47, 133, 261
polyarylate 138
poly(bisphenol-A carbonate) 139
polybutadiene 32, 76, 142, 161, 196
polybutene 161
polybutyl acrylate 15
poly(butylene succinate) (PBS) 155
polybutylene succinate (PBS) 156
polybutylene terephthalate 307
polycarbonate (PC) 3, 14, 21, 49, 62, 139
polychlorotrifluoroethylene (PCTFE) 141
polyester; also see PETG, polyethylene terephthalate, polyethylene naphthalate 3, 9, 14, 21, 135, 200, 280
polyether 145
polyethylene acrylic acid 255
polyethylene furanoate (PEF) 156
polyethylene imine (PEI) 255
polyethylene naphthalate (PEN) 3, 138, 337
polyethylene (PE); also see high density polyethylene, linear low density polyethylene, low density polyethylene 2, 4, 10, 13, 18, 21, 27, 34, 61, 77, 99, 105, 165, 171, 176, 181, 196, 201, 222, 230, 254, 272, 287, 312, 347, 376
– biobased 154, 155
polyethylene terephthalate (PET) 10, 15, 21, 49, 62, 68, 126, 136, 181, 184, 195, 260, 261, 307, 309, 323, 326, 336, 422, 436, 444, 445
– biobased 155
polyhydroxyalkanoates (PHAs) 147, 153
polyhydroxybutyrate (PHB) 153
polyhydroxybutyrate-valerate (PHBV) 153
polyimide 3
polyisobutylene 244
polylactides (PLA) 3, 147, 151
polymer 1, 9, 10, 25
– branched 26, 42
– cross-linked 26, 28, 42, 351
– linear 26, 42, 106
– nomenclature 14
polymerization 20, 25, 30, 38, 39, 43
– addition 33

- bulk 25
 - chain-polymerization 33
 - condensation 33
 - degree of 69
 - emulsion 25
 - fluidized bed 41
 - gas phase 41
 - ring-opening 152
 - slurry 41
 - solution 25, 41
 - step-polymerization 34
 - step-reaction 62
 - suspension 25
 - polymethyl acrylate (PMA) 15, 377
 - polymethyl methacrylate (PMMA) 3, 280
 - polyolefin 2, 10, 105, 171-173, 195, 212, 234, 237, 248, 280, 299, 332, 341, 342, 350, 405, 441
 - polyphenol 171
 - polypropylene (PP) 10, 21, 44, 61, 63, 64, 121, 149, 171, 181, 230, 232, 235, 260, 261, 301, 304, 307, 316, 449
 - atactic 45
 - isotactic 45
 - syndiotactic 45
 - polysaccharide 202
 - polystyrene
 - foam 348
 - polystyrene (PS) 3, 10, 14, 21, 128, 172, 181, 261, 280, 301, 347, 425, 439, 449
 - crystal 129
 - high impact 129
 - polyterpenes 207
 - polytetrafluoroethylene (PTFE, Teflon) 3, 35, 141, 195
 - poly(trimethylene terephthalate) (PTT) 156
 - polyurethane 62, 157, 200, 201, 203, 349, 351, 444
 - polyvinyl acetate (PVA) 3, 130, 203
 - polyvinyl alcohol (PVOH) 62, 130, 214
 - polyvinyl chloride (PVC) 3, 10, 12, 19, 21, 68, 70, 124, 172, 176, 181-183, 188, 301, 424, 449
 - polyvinyl fluoride 62
 - polyvinylidene chloride (PVDC) 3, 15, 21, 35, 61, 126, 172
 - pot life 206
 - pouches 68, 265, 266
 - four-side seal 267
 - pillow 266
 - retort 271
 - stand-up 265, 268
 - three-side seal 266
 - power law 59
 - preform 320, 324-326, 330
 - prepolymer 157
 - pressure 228
 - pressure-sensitive adhesive 203
 - primary bonds 18
 - primers 207, 255
 - printing 94, 243, 248, 258, 307, 406, 420
 - prior-sanctioned 413
 - processing 10, 12, 20, 28, 66, 80, 105, 106, 109, 145, 170, 179, 183
 - processing aids 405
 - processing, recyclables 441
 - propagation 37, 43
 - proportional limit 84
 - PVOH/EVOH copolymer 262
 - pyrazolone 177
 - pyrolysis 444
- ## Q
- quartz 174
 - quasi-isostatic 386
 - quencher, excited state 170
 - quench(ing) 123, 134, 173, 235
 - quench tank 230
 - quiniphtalone 177
 - quinoline 177
 - quinone 185
- ## R
- radiation 28, 37, 276
 - infrared 99, 277
 - sterilization 6
 - range, adhesive 206
 - reactive adhesives 200
 - reactive extrusion 167
 - reciprocating screw 293
 - recovery rate 436
 - recycled plastics 414
 - recycling 420, 436
 - curbside 438
 - drop off 439
 - rates 423, 437
 - recycled content 423, 430
 - regrind 28, 160, 219, 317
 - regulations 401
 - reinforcements 187
 - relaxation 66, 145, 231, 236
 - relaxation temperature 77
 - renewable 146
 - reseal 265, 268, 300
 - resilience 86, 125, 209, 300, 302, 303, 352
 - resistivity 98
 - retorting 132
 - reuse 435
 - RIM 357
 - rising mold 313

roll stack 230
 rotational molding 305,
 357
 rubber 1, 3, 12, 202, 204
 runner 296

S

sacks 6
 scalping 366
 scavenger 173
 Scotch tape 203
 screen pack 225
 screw 219
 sealing 209
 – band 210
 – bar 209
 – contact 212
 – dielectric 212
 – friction 211
 – heat 60
 – hot gas 212
 – hot wire, knife 211
 – impulse 210
 – magnetic 212
 – peel 216, 265
 – radiant 212
 – solvent 213
 – strength 217
 – thermal 209
 – ultrasonic 211
 secondary bonds 18
 secondary carbon 171
 secondary forces 18
 segmental mobility 72, 76
 self-seal adhesive 202
 semicrystalline 70
 separation for recycling
 437
 serum leaker 216
 setting time 206
 shear 59
 shear cutting 287
 shear stress 200
 sheet 229, 275, 352

shelf life 361
 shelf life estimation 391
 shipping containers 358
 shooting pot 294
 shortness 206
 short shot 297, 306
 shrinkage 80, 250, 332
 shrink bands 305
 shrink film, wrap 245, 266
 side chain 27
 side entry dies 236
 side groups 27
 sienna 179
 sigma blade mixer 167
 silica 174, 179, 181, 262
 silicone 3, 9
 silicon oxide coating 136,
 260, 341
 siloxanes 261
 single-screw extruder 222
 sink mark 296
 skin packaging 110, 285,
 286
 skirt, tube 307
 sleeve 307
 slip agent 175, 249
 slitting, film 242
 soap, metallic 176
 sodium bicarbonate 189,
 349
 sodium silicate 203
 solids content 206
 solid-state properties 60
 solid-stating 136
 solubility 18, 21, 92, 98,
 130, 368
 solubility coefficient, S
 93, 363, 368, 372
 solution 206
 solvent 122, 127, 139, 189,
 191, 207, 257, 443
 solvent-borne adhesives
 201
 solventless adhesive lami-
 nation 257

sonic velocity 290
 sorbates 366
 sorption 92, 361, 363,
 366, 377
 sorption isotherm 382,
 392
 sorting 441
 source reduction 423,
 435
 source separation 437
 specialty resin 21
 specular reflectance 97
 spherulites 63
 SPI 422
 spider dies 236
 spin welding 307
 spiral channel dies 236
 sprue 296, 307
 sputtering 261
 squeeze 338
 stabilizer; also see heat
 stabilizer, UV stabilizer,
 antioxidant 124, 201,
 420
 stalk 240
 starch 202
 starch-based plastics 150
 static electricity 181
 stearate 176
 Stefan-Boltzmann constant
 277
 stereochemistry 44, 61
 stereoregularity 44, 64
 sterilization 6, 79, 172
 – ethylene oxide 142, 143
 stiffness 76, 85
 strain 60, 64
 strain hardening 159, 256,
 331
 strength 60, 187, 310,
 324
 – melt 136
 – tensile 60, 68
 stress 83
 stress cracking 92

- stress-induced crystallization (SIC) 323
stress relaxation 21, 87, 303, 326
stress-strain curve 82
stretch film, wrap 125, 244, 266, 439, 448
stretch ratio 68
stretch rod 324
stripper rings 298
styrene-acrylonitrile (SAN) 143, 350
styrene-butadiene 3, 32, 142
styrene-methyl methacrylate 33
Styrofoam™ 348
substrate 191
sulfonation 342
surface tension 18, 94, 180, 194, 199, 200
surface treatment 195, 248, 253, 340
Surlyn™ 255
sustainability 146
swell 312
symmetry configurations 44
syndiotactic 46, 61, 64, 70, 115, 124
- T**
- tack 206
tackifier 201, 207, 244
tactic, tacticity 44
take-off speed 232
talc 174, 175, 179, 207, 349, 385
tamper-evident packaging 213, 305
tandem coating 256
tandem extrusion 350
tank melters 205
tear strength 90
Temperature Rising Elution Fractionation (TREF) 41
tensile modulus 85
tensile strength 53, 85
tensile testing 217
tentering 232
termination 38
tertiary recycling 444
thermal conductivity 20, 79, 355
thermal expansion 20, 79, 362
thermal properties, polymers 71
thermodynamic equilibrium 366
thermoform-fill-seal 291
thermoform(ing) 6, 134, 212, 275, 281, 300, 357
– bubble (billow) 282
– drape 278
– foam 283
– in-line 285
– matched mold 283
– melt-to-mold 285
– plug-assist 281
– pressure 279
– scrapless 284
– SPPF 282
– twin sheet 285, 357
– vacuum 279
– vacuum snap-back 283
thermomechanical analysis (TMA) 80
thermoplastic 4, 12, 28, 301
thermoset 12, 28, 62, 157, 187
thickness normalized flow, N 373
threads 302
three-side seal 267
threshold of regulation 410, 415
tie layer 132, 248, 317
tin 172
titanium oxide 178, 179, 207, 262, 338, 385
torpedo 294
torque 302
toughness 29, 68, 70, 87
Toxics in Packaging Clearinghouse (TPCH) 420
TPE 146
TPO 146
TPU 146
transesterification 139
transmittance 98, 100
transparency, transparent 63
triboelectric series 98
trimming 313
triple bubble process 244
T-shaped die 233
tube(s) 307
tube wall swell 312
tubular reactor 39
twin-screw extruder 167, 226
two stage screw 226
Tyvek™ 212
- U**
- ultimate elongation 85
ultimate strength 85
ultra low density polyethylene (ULDPE) 114
ultramarine pigment 179
undercut 291, 299
unsaturated, unsaturation 34
urea 301, 307
urea formaldehyde 196
USP 403
UV absorbers 173
UV stabilizer 173, 273

V

vacuum panels 333
van der Waals forces 18,
19
vapor pressure 378
VC/E 15
VC/E/MA 15
VCM 126
VC/VA 15
VC/VDC 15
vented extruder 226
vent holes 289, 300
venting 289, 300, 339
vibration 353
vinyl acetate (VA) 108
vinyl chloride 126
vinylidene chloride (VDC)
35, 126
vinyl polymers 14, 35, 43
viscoelastic 87
viscose 148

viscosity 18, 21, 53, 57, 58,
60, 110, 193, 198, 247,
256, 298, 318
viscous instability 247

W

warping 298
water bath process 230
water-borne adhesives
202
– natural 202
– synthetic 202
water vapor transmission
rate (WVTR) 107, 129,
140, 154, 373, 374, 385,
389
wavelength 99
wave number 99
wax 201, 213
web(stock) 265
weld line 297

wet bonding 257
wetting, wettability 94,
180, 193, 199
winding film, winder 231,
242
work hardening 281
wraps 266

Y

yield 249
yield point 60, 85
yield strength 86
Young's modulus 84

Z

zeolite 174
zinc compounds 172, 179,
207