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Plastics Packaging

Properties, Processing, Applications, and Regulations

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Content

Preface

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

In this book we discuss the uses of plastics in packaging. Although this is not a course in chemistry nor in material science, we attempt to stress the relationship between chemical structure and packaging material properties. We expect the reader to have some knowledge of chemistry and physics. The major purpose of this book is to provide the students in the School of Packaging with reading material on plastics for packaging; however, we hope that it can also be useful to packaging professionals responsible for writing specifications, designing, fabricating, testing, and controlling the quality of plastic materials. We also hope to trigger the readers' curiosity to pursue further studies in the exciting world of packaging materials.

This third edition fixes some of the errors that, despite our best efforts, found their way into the previous editions. Unfortunately, we're sure that we have still not found them all! We have expanded and updated the discussion of biobased plastics such as PLA and PHA, plastics recycling, life cycle assessment, and a variety of other topics.

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

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 oldest of the purely 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
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
1942	Polyethylene, branched	1983	PEEK, PES
1943	Butyl rubber	1985	Liquid crystal polymers
1943	Nylon 6	1990	PHBV
1943	Fluoropolymers	1992	Metallocene polymers
1943	Silicones	1994	PEN
1947	Epoxies	2000	PLA (for packaging)
1948	ABS resins	2012	PEF

Today, dozens of different synthetic plastics are produced throughout the world by hundreds of companies. In 2012, world production of plastics totaled about 288 million metric tons [1]. U.S. resin production in 2013 was about 49 million metric tons (107 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 2013, packaging accounted for about 34% of the uses of the major thermoplastic resins in the U.S. (42% if exports were excluded) [3]. As shown in Fig. 1.1, packaging accounted for 39.4% of all plastics used in Europe in 2012 [4].

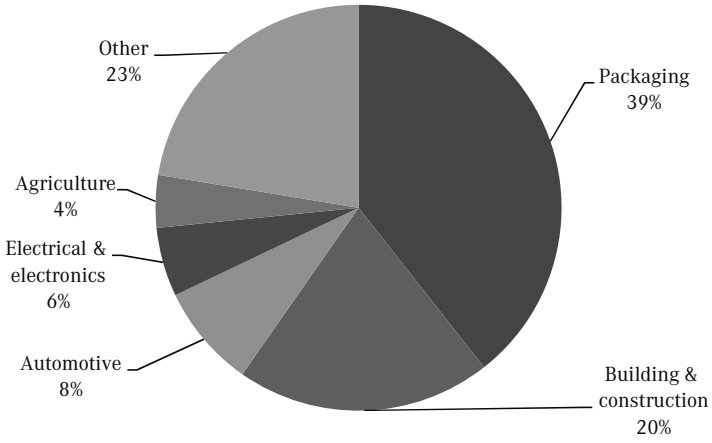

Figure 1.1 Major markets for plastics in Europe, 2012 [4]

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 introduced 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 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, although they have not disappeared altogether. Today, plastic packaging has earned its position as one of the choices of the package designer. Decisions about which material(s) should be used require consideration of (1) product protection requirements, (2) market image, (3) cost, and (4) environmental issues.

■ 1.3 Book Structure

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

Chapter 2 provides some introductory concepts and definitions. Chapter 3 looks at the relationship between the chemical and physical structure and the properties of

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

Throughout the book, long examples are placed in boxes. Most chapters end with a set of study questions. In many cases, the answers can be found (or calculated) from the material in the chapter. In other cases, answering the questions requires the reader to put together information from several previous chapters. Sometimes, the questions are intended to stimulate thinking in preparation for what will be discussed in subsequent chapters and cannot be answered completely with only the information that has already been presented. The correct solutions to quantitative questions are included.

1.4 References

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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, olefin is a common term that refers to the family of plastics based on ethylene and propylene. The term polyolefin strictly applies to polymers made of alkenes, whether homopolymers or copolymers. It includes the family of polyethylene, and the family of polypropylene.

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 other comonomer can be an alkene such as propene, butene, hexene, or 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, 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 Fig. 4.1.

Low density polyethylene has a branched structure. The family of branched polyethylenes includes homopolymers and copolymers of ethylene that are nonlinear, 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.

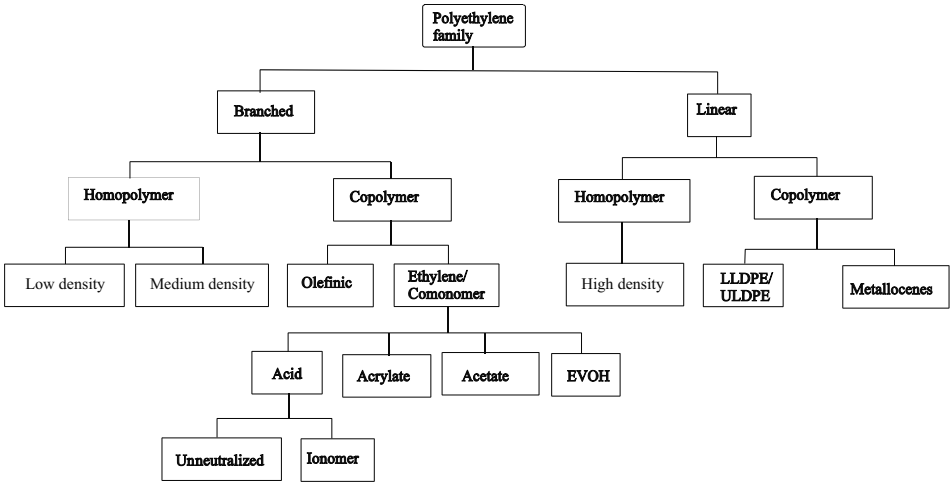


Figure 4.1 The polyethylene family

Linear PE has a high percent crystallinity, from 70 to 90%, because of its stereoregularity and the small size of its pendant groups. This is because the presence of branches in its backbone chain acts to limit the formation of polyethylene crystals by introducing irregularities in the structure. This high crystallinity results in relatively high density, so linear PE is known as high density polyethylene (HDPE). Branched PE has lower crystallinity and consequently lower density, so 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/cm^3; in contrast, HDPE has a density of about 0.940 to 0.970 g/cm^3. Comonomers such as propylene and hexene are commonly used in the 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 $1.60/kg). Its transparency is better than HDPE because of its lower percent crystallinity. For the same reason, 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_g	−120°C
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)
O_2 permeability, 25°C	163,000–213,000 cm^3 μm/m^2 d atm (400–540 cm^3 mil/100 in^2 d atm)
CO_2 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%

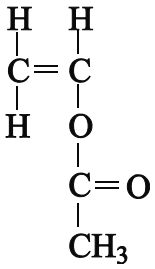
Medium density polyethylene (MDPE), 0.925–0.940 g/cm^3, is sometimes listed as a separate category, but usually is regarded as the high density end of LDPE. It is somewhat stronger, stiffer, and less permeable than lower density LDPE. MDPE processes similarly to LDPE, though usually at slightly higher temperatures.

The major competitor to LDPE is LLDPE (discussed in Section 4.2.1), which provides superior strength at equivalent densities. However, LDPE is still preferred in applications demanding high clarity or for extrusion coating a substrate.

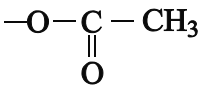
Ethylene can be copolymerized with alkene compounds or monomers containing polar functional groups, such as vinyl acetate and acrylic acid. Branched ethylene/alkene copolymers are essentially the same as LDPE, since in commercial practice a certain amount of propylene or hexene is always added to aid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

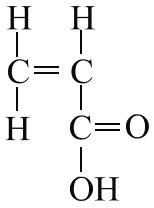
Vinyl acetate is a polar molecule. The inclusion of polar monomers in the main chain during production of branched ethylene copolymers will lower crystallinity, improve flexibility, yield a wider range of heat sealing temperature, and result in better barrier properties, as well as increasing density. 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 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. 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)



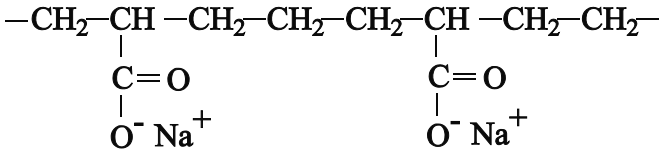
produces copolymers containing carboxyl groups (HO–C=O) in the side chains of the molecule. These copolymers are known as ethylene acrylic acid, EAA. They are flexible thermoplastics with chemical resistance and barrier properties similar to LDPE. EAA, however, is superior to LDPE in strength, toughness, 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^{++}, 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 caused by 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 excel-

tained from both materials, with LLDPE adding strength and LDPE adding heat seal and processability.

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 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 have the ability to provide more uniform incorporation of comonomers.

Metallocene catalysts (Fig. 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 (FINA) in 1986. However, 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.

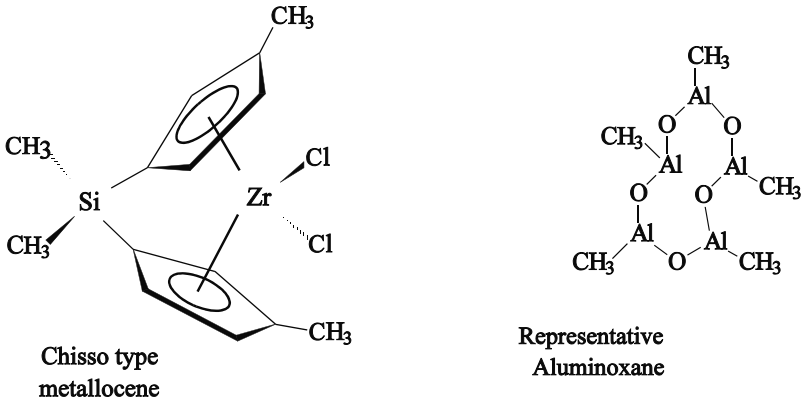


Figure 4.3 Single-site metallocene catalyst with aluminoxane co-catalyst

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 Fig. 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.

Metallocene catalysts, on the other hand, contain only one type of site geometry, so are often referred to as single site catalysts (Fig. 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.

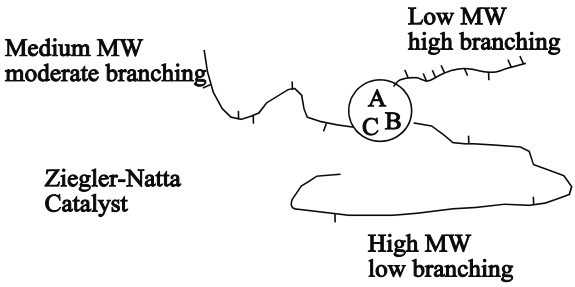


Figure 4.4 Ziegler-Natta catalyst sites (Note: "branching" stems from incorporation of comonomer, so the side groups are not true branches.)

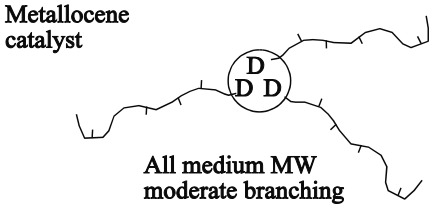


Figure 4.5 Metallocene catalyst; single site (Note: "branching" stems from incorporation of comonomer, so the side groups are not true branches.)

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.

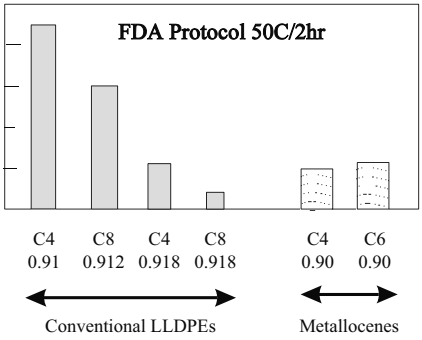


Figure 4.6
Hexane extractables, at densities indicated

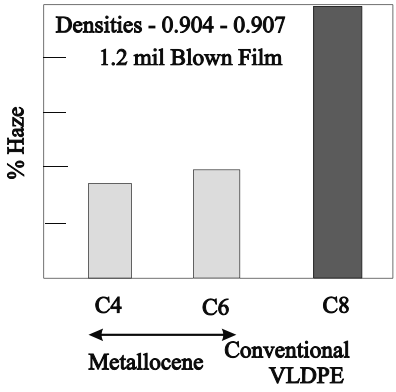


Figure 4.7
Haze

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 (Fig. 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.

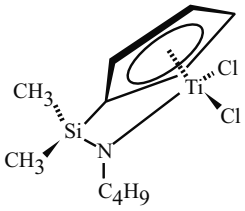


Figure 4.8 Constrained geometry catalyst

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. Polymer research with metallocene catalysts continues, so more advances can be expected for polyethylene, polypropylene, and other polyolefins.

4.2.4 Property Trends in the Polyethylene Family

The family of polyethylenes has many properties in common. Tables 4.4 and 4.5 show the relationship of these properties to molecular weight, MWD, and density.

Table 4.4 Effect of Density on the Permeability of Oxygen and Water in Polyethylene

Density of polyethylene g/cm³	WVTR g μm/m² day	Oxygen Permeability cm³ μm/m³ day atm
0.910	0.866	275
0.915	0.779	256
0.920	0.685	225
0.925	0.579	201

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 Barex™ 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.

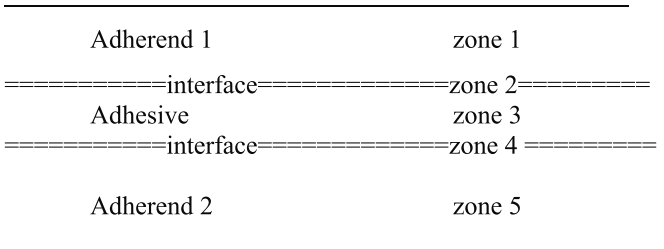


Figure 6.1 Structure of two bodies bonded by an adhesive

■ 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 Fig. 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 Fig. 6.2. (Of course, the overall strength is also limited by the cohesive strength of the substrates.)

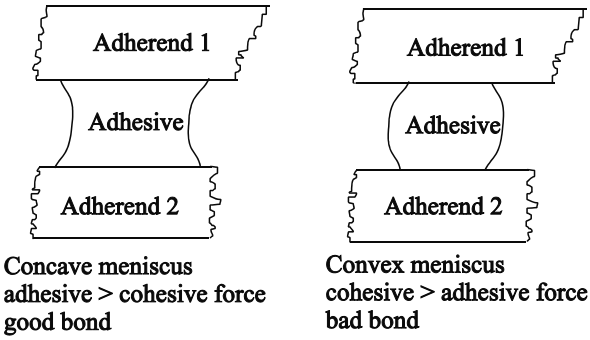


Figure 6.2 Cohesive and adhesive forces

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 moment 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

$$\gamma_{adh} < \gamma_c \tag{6.1}$$

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
PTFE	18
Water	73
Toluene	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 non-spreading, and the surface tension of the surface is related to the surface tension of the liquid and the contact angle.

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 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:

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

where ΔE is the energy of vaporization and V is the molar volume. A common unit for δ is $(\text{cal/cm}^3)^{1/2}$, 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.

$$\delta_1 \approx \delta_2 \tag{6.3}$$

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-pentadecafluoroctyl 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
Cellulose acetate	10.9	39
Cellulose nitrate	10.6–11.5	–

Table 6.2 Representative Solubility Parameters *(continued)*

Material	Solubility Parameter, δ (hildebrands)	Critical Surface Tension, γ_c (dyn cm^{-1})
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 word, the greater the chemical similarity between two materials, the larger will be the intermolecular forces between them.

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 Fig. 6.3.

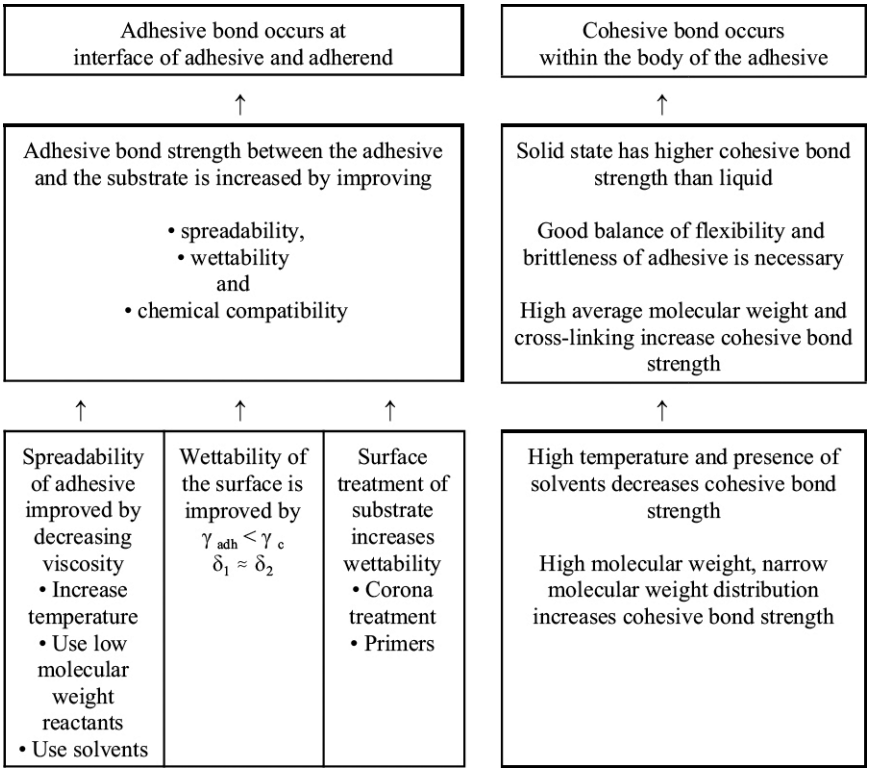


Figure 6.3 Variables affecting cohesive and adhesive forces

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:

$$S = \frac{\gamma_1 + \gamma_2 - \gamma_{12}}{d} \tag{6.4}$$

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 Å (5×10^{-8} cm).

Example:

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

$$\gamma_{l_1}(\text{PVC}) = 40\,\text{dynes/cm}, \gamma_{l_2}(\text{Epoxy}) = 41.7\,\text{dynes/cm},$$
$$\gamma_{l_{12}}(\text{PVC-Epoxy}) = 4.0\,\text{dynes/cm}; \text{d} = 5\,\text{x}\,10^{-8}\,\text{cm}.$$

$$\text{S} = \frac{\gamma_{l_1} + \gamma_{l_2} - \gamma_{l_{12}}}{\text{d}} = \frac{40 + 41.7 - 4.0}{5 \times 10^{-8}} = 1.55 \times 10^{9}\,\frac{\text{dyn}}{\text{cm}^2} = 2.24 \times 10^{4}\,\text{psi}$$

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:

$$\text{S} = \frac{2\gamma}{\text{d}} \tag{6.5}$$

where S is the shear stress of the cohesive bond of the adhesive, γ is the surface tension of the adhesive, and d is the distance of separation between the molecules at which failure occurs, approximately 5 Å.

6.8 Heat Sealing

Heat sealing is the process by which two structures containing at least one thermoplastic layer are sealed 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 (Fig. 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 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*.

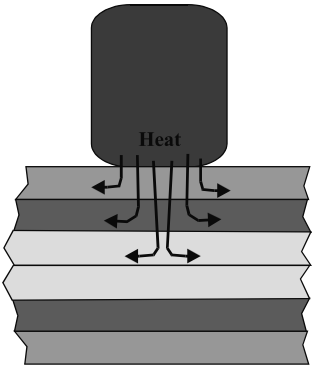


Figure 6.4
Heat conduction in heat sealing

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 (Fig. 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.

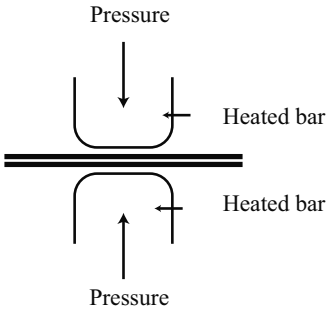


Figure 6.5
Bar sealing or thermal sealing (reprinted with permission from [6])

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 (Fig. 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.

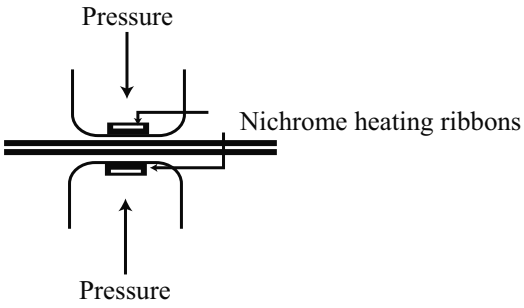


Figure 6.6
Impulse sealing (reprinted with permission from [6])

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 Fig. 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.

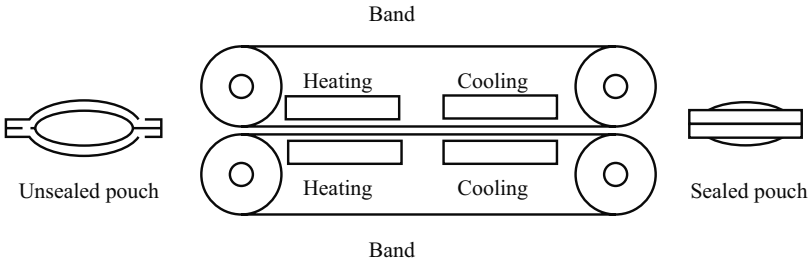


Figure 6.7 Band sealing (reprinted with permission from [6])

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. This appears to be a growth area.

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

packaging as the true driving force for the rapid growth in their use. The pouches are printed as rollstock, facilitating the use of high-quality multicolor images. The upright presentation makes the product readily visible to the consumer. Several shaped standup pouches have been introduced where the nonrectangular design is a significant advantage in catching the eye of the consumer and appealing to them, particularly in products designed for children.

Technological innovations in production of high barrier materials have also been important in the ability to use pouches for sensitive products. Many such pouches 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.

■ 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 (Figs. 9.3 and 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.

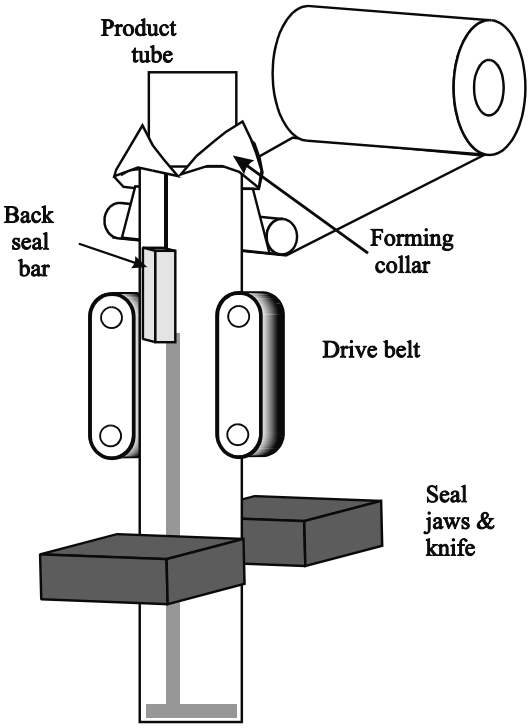


Figure 9.3
Vertical form-fill-seal machine

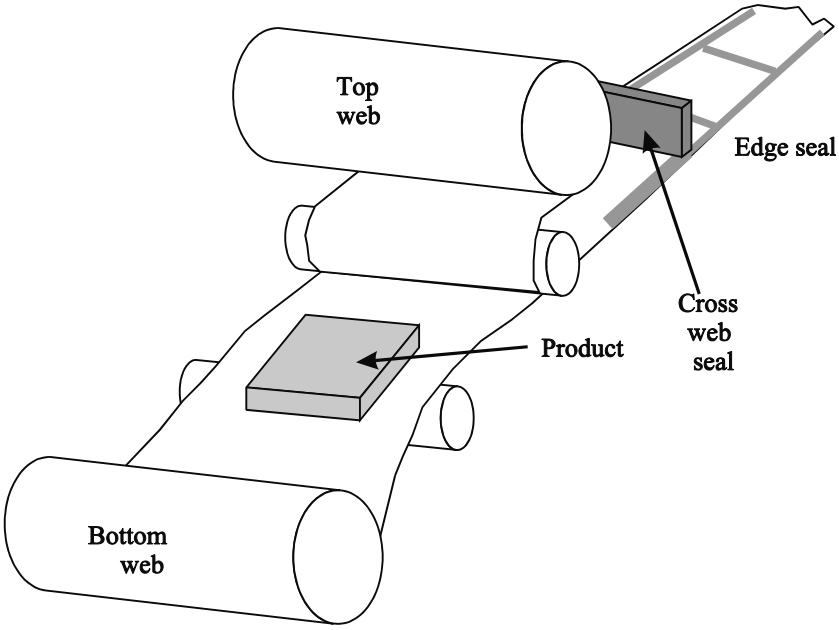


Figure 9.4 Horizontal form-fill-seal machine

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 are most often 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.

■ 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. Some time ago, retort packages 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 have, until fairly recently, been much less successful. They were introduced by a number of companies, and generally failed to win consumer acceptance. The major consumer packaging use for many years remained a small market for foods targeted at backpackers and other campers. However, this has changed significantly in the last five years.

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. It is estimated that about 45% of all stand-up pouches used in Europe are retorted [4]. 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].

■ 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 lbs) 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,

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 end-point 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 end-point 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. As shown in Fig. 14.14, moisture isotherms are usually sigmoid shaped curves. However, one can sometimes use only the linear portion of the curve for shelf life predictions.

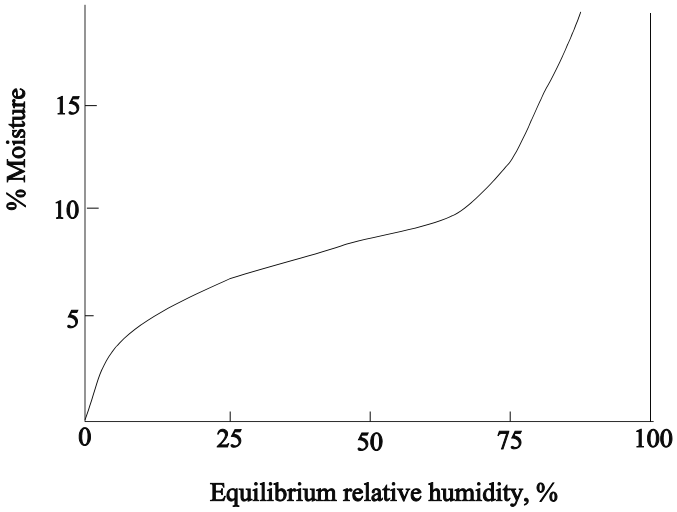


Figure 14.14 Moisture sorption isotherm

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 cm^2 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 14.13 by rearrangement,

$$\ell = \frac{P\, t\, A\, \Delta p}{q} \tag{14.35}$$

From the literature, PET at 25°C has an oxygen transmission rate (OTR) of 22 cm^3 (STP) μm/(m^2 d kPa)

t = 6 months = 180 d

A = 400 cm^2= 0.04 m^2

Δp = 0.21 atm = 21.27 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 flow:

$$q = 500\ \text{ml} \times \frac{0.005}{100} \times \frac{\text{mol}}{32\ \text{g}} \times 22{,}412 \frac{\text{cm}^3}{\text{mol}} = 17.5\ \text{cm}^3\ (\text{STP})$$

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.

$$q = \frac{P\,t\,A\,\Delta p}{\ell}$$

Assume that the for PET is 8.5 × 10^{-4}cm^3 (STP) μm/m^{2}d kPa. The Δp is the difference in the vapor pressure in the container (100% RH) and that outside (60% RH). From a steam table, saturation vapor pressure at 25°C = 0.4592 psi × 6.895 kPa/psi = 3.166 kPa.

$$\Delta p = 3.17 \times (100 - 60)/100\ \text{kPa} = 1.268\ \text{kPa}$$

$$q = \frac{8.5 \times 10^{-4}\ \text{cm}^3\ (\text{STP})\ \mu\text{m}}{\text{m}^2\ \text{d kPa}} \times 180\ \text{d} \times 0.04\ \text{m}^2 \times 1.268\ \text{kPa} \times \frac{1}{193\ \mu\text{m}}$$

$$= 4.0 \times 10^3\ \text{cm}^3\ (\text{STP}) = 3.22\ \text{cm}^3\ \text{liquid water}$$

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.

Let us consider an example where the external storage conditions are constant, and a product isotherm is known.

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