8 Food Packaging Materials, Barrier Properties, and Selection

Ruben J. Hernandez

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8.1 INTRODUCTION

The share of plastics in the packaging market has been growing at remarkable pace, partially replacing paper, glass, and metal. Because of their unique combination of properties, plastics have expanded the packaging industry to sophisticated levels. Plastic containers are light weight, breakage resistant, transparent, flexible, squeezable, moldable in complex shapes, easily colored and printed, retortable, sterilizable, reusable, and recyclable. Plastics have many positive tradeoffs within their array of versatile properties, including easy processing, good mechanical properties, large range of processing temperatures, lowest density among packaging materials, and (for better or worse) they are pemeable materials. In addition, plastics are economically competitive in cost with paper, glass, steel, and aluminum. A brief cost analysis of plastic packaging is now presented.

Comparative costs of resins between 1980 and 1996 are presented in Table 8.1. Although the price of resins fluctuates up to 40% within a short period of time, compared with 1980 prices they have remained quite stable. Demand for resins between 1993 and 1988 is presented in Table 8.2.

8.1.1 Main Economic Factors of Plastic Packages

The prices of packaging containers depend on the type of material and desired shape of container. Complex conversion processes (e.g., blow molding, coating, and laminations) add to the cost of the finished package. Price of packaging products are affected by the costs of raw materials, technology competition, vertical integration, and opportunities in material substitution. Prices are affected by domestic economic conditions, recessions result in over-supply, and growth cycles strain production capacity. The international demand for goods and packaging materials also affects prices. Packages can be produced in house, or purchased directly from molders and converters or from independent distributors. While a container may be obtained from any of these sources, one is rarely able to obtain all packaging components from a single source. Normally, bottles, caps, films, labels, pallets, and stretch-wrap are produced by independent sources.

TABLE 8.1
Comparative Price of General Purpose Resins (Truckload Quantities) in 1980 and 1996

		$/lb	
Plastic	**Density (g/ml)**	**1980**	**1996**
Acrylic		0.65	0.92
Nylon 6,	1.120–1.140	1.30	1.42
Polycarbonate		1.30	1.90
HDPE, blow molding	0.940–0.965	0.47	0.52
LDPE, extrusion	0.915–0.942	0.47	0.55
LLDPE, extrusion	0.918–0.940		0.46
Polypropylene	0.895–0.910	0.45	0.46
HIPS		0.55	0.57
Polystyrene	1.05–1.06	0.54	0.55
PET	1.35–1.41		0.64
PVC homopolymer	1.220–1.400	0.33	0.55
PVC compounds		0.50	0.41

Note: Resin prices can fluctuate as much as ± 40% of the given price. HDPE = high density polyethylene; LDPE = low density polyethylene; LLDPE = linear LDPE; HIPS = high impact polystyrene; PET = polyethylene terephthalate; PVC = polyvinyl chloride.

8.1.1.1 Development Costs

According to Leonard (1980), the main factors determining the cost of a package can be classified as follows.

1. Identification of package characteristics that takes into account the nature of the product, FDA requirements, and customer's needs.
2. Concept search; when several types of packaging material can equally serve the same goal, at least two different packages must be considered.
3. Design to provide the best combination of material, shape, size, appearance, color, special features, and product's shelf-life.
4. Preparation of package models to provide a basis for evaluation and even customer research.
5. Fabrication of samples to test the package in real situations.
6. A sample evaluation program may be necessary to assess extreme processes and market conditions, i.e., rough handling or high temperatures.
7. Preparation of cost analysis and specifications taking into account results of the sampling program.
8. Test marketing to evaluate on a small-scale the whole development plan from package production to logistics and consumer satisfaction.
9. Design and specification refinements that may be necessary to improve the original concept.
10. Tooling for production including, but not limited to, molds, litho plates for caps, and containers.

TABLE 8.2
Plastics Demands in Flexible and Rigid Containers

	Flexible Packaging		Rigid Packaging	
Resin	**Demand (%)[a]**	**Growth (%)[b]**	**Demand (%)[a]**	**Growth (%)[b]**
LDPE	38.3	0.5	0.6	–2.6
LLDPE	25.7	9.9	3.3	8.4
PP	8.7	2.9	10.7	4.3
HDPE	12.2	6.7	43.9	3.6
PVC	2.3	–2.1	1.4	–3.6
PS	3.2	4.7	15.5	2.7
TP polyesters	4.1	9.8	19.3	9.0
EVA	0.9	2.4	—	—
Nylon	0.9	3.3	—	—
PVA	0.7	5.4	—	—
Polyurethanes	—	—	1.2	3.9
Other	3.0	3.5	4.1	3.9
Total	100.0	4.0	100.0	4.4
Total resin demand, in Mkg	4426 [c]		5707 [c]	

Note: LDPE = low density polyethylene; LLDPE = linear LDPE; PP = polypropylene; HDPE = high density polyethylene; PVC = polyvinyl chloride; PS = polystyrene; EVA = ethylene vinyl acetate; PVA = polyvinyl acetate.

[a] Demand percent between 1993 and 1988.
[b] Expected annual average growth rate between 1993 and 1988.
[c] Expected total demand in 1988.

Adapted from Shroeder, G. O., *Modern Plastic Encyclopedia*, McGraw-Hill, NY, 1995, A-35.

11. A quality control program to regulate quality requirements, attributes, and allowable limits.
12. Startup costs that will occur at the starting of production.

8.1.1.2 One-Time Costs

One-time costs are the expenditures that are made only once during the expected time of the package.

1. Machines to make the containers, which may include, e.g., a bag former or blow molder.
2. Supplier molds or dies for the packages, caps, secondary packages.
3. Printing plates, dies, or cylinders.
4. Packaging line equipment or replacement parts.
5. Equipment installation.

8.1.1.3 Package Material Costs

1. Resins or films to make the container.
   The cost of resin is, in many cases, the main package cost component, and its price can be used as an estimation of the container's price. Numerical factors relating the price of resin to the cost of containers may be useful guides to the food engineer in estimating packaging costs.

2. Packaging for inbound shipment
3. Inbound freight
4. Storage and handling the package material from the supplier to the packer's filling lines
5. Waste factor from damage and loss during container production, filling, or printing
6. Sampling and inspection

8.1.1.4 Packaging Machinery Costs Other Than One-Time

1. Rental or lease of equipment and machines
2. Services and maintenance
3. Amortization of purchased machines, auxiliary equipment
4. Energy and utilities

8.1.1.5 Packaging Process Costs

1. Direct labor
2. Indirect labor
3. Overhead
4. Incidental materials

8.1.1.6 Distribution Costs

1. Storage handling and warehousing.
2. Outbound freight.

8.1.2 Cost Analysis of Plastic Rigid Containers

Food-grade resins are more expensive than the general-purpose grade since they require sanitary process conditions, US Food and Drug Administration (FDA) additives, and limitations in the use of scrap and reworked conditions. In the case of polyvinyl chloride (PVC), the addition of heat stabilizer, color, and plasticizer almost double the price of the raw resin.

Resin density directly affects the cost of a plastic container. For a given container, the cost of the material in a container, C_m, is

$$Cm = A \cdot \ell \cdot d \cdot r = W \cdot r$$

where A is the package area, l is its average thickness, d is the resin density, and r is the resin cost per unit of mass.

If the container can be made of two different resins having prices r_1 and r_2 when the container's thickness is kept constant, the cost of container 1 is related to container 2 by their densities values

$$Cm_1 = X \cdot Cm_2$$

where $X = d_1r_1/d_2r_2$, and d_1 and d_2 are the respective density of the resins. Example: if d_2 = 0.953 g/cm^3, r_2 = \$0.385, d_1 = 1.257, and r_1 = \$0.63, then X = 2.157, that is, the container made of resin 1 will cost 2.157 as much as resin 2.

8.1.2.1 Injection Molding (IM)

IM is used for producing containers and parts, i.e., closures, that require high precision in their dimensions. A rule of thumb for large production runs and simple product geometry is that the cost of a container or part is twice as much the cost of the resin — the resin is 50% of the container cost — (Leonard, 1980). For example, 1000 closures of polypropylene (PP) costing \$0.46/lb. and weighing 10 g each will have a producing cost of approximately C = $2 \times 1000 \times 10 \times 0.46/454$ = \$20.2/1000 pieces. Main cost components of injection molded pieces are

1. Plastic resin(s)
2. Mold and cavities; the mold cost is amortized over a million pieces
3. Molding processes (labor, energy, and overhead)
4. Scrap discarded or grounded for re-use
5. Assembling, finishing, and/or decorating

Therefore, the simpler the molded piece, the lower its cost.

For example, simple injection-molded closures, i.e., snap-ons, are made on two-piece molds and follow the 50% rule.

More complex molding operations are required for the linerless threaded screw cap used for glass bottles. In this case, the thread prevents the cap from being removed from the mold by a simple push, like the snap-ons. This requires a mold that costs twice as much as the snap-on mold. The actual impact in the cost of the cap is hard to estimate since there are many variables, i.e., number of frames, cavities, tooling, and cycling time, that affect the design and operation of the mold. The linerless thread cap may cost about 3.4 times the cost of the resin. If a liner made of fiberboard and plastic layer is incorporated into the cap, it may increase the cost by 25 to 30% over the unlined cap.

Dispenser caps for detergent bottles and aerosol push-up button caps are made of several parts. This requires the combination of multi molding and assembly making the cost of these pieces much higher than indicated by the 50% rule. Some factors increasing the cost include:

1. Complexity of the molded piece
2. Multipart pieces requiring additional manual assembling
3. The inventory practice of the proprietary molder (A custom molder that manufactures based on existing purchase orders has lower costs than a molder that stocks an inventory, and maintains a warehouse.)
4. Lot size of several million pieces will be more cost-effective than smaller runs of several ten thousands
5. Mold ownership (If the container maker is the owner of the mold, the injection-molder sells the pieces as stock items rather than using a customer's mold.)

8.1.2.2 Blow Molding

As indicated in Table 8.2 the most common resins for blow-molded containers are: high density polyethylene (HDPE), thermoplastic polyesters, polystyrene, and PP. They make up 90% of the market. Rigid blow-molded containers, primarily bottles, are widely used in beverages, food, medicinal products, cleaning products, and many other applications.

Compared to glass containers, the cost ratio of polyolefin resins to glass is 1.4 to 1. But plastic containers' lower weight reduces transportation costs, and can more than equalize the raw material cost between polyolefins and glass containers. As a rule of thumb, the price of bulk shipment in large boxes of blow-molded bottles of natural HDPE is about 3.2 times the

price of the resin at the molder's plant. Smaller containers, 12 oz (360 ml) have a slightly higher factor while larger containers of 1 gal (3.75 l) are lower. Colored containers cost more depending on the formulation and number of pieces produced.

Major manufacturers of blow molded containers in North America are: Constar International, Inc. (Atlanta, GA); Johnson Controls, Inc., Plastic Containers Division (Manchester, MI), Owens-Brockway Plastic Products (Toledo, OH); Graham Packaging, Co., (York, PA); Plastipak Packaging, Inc. (Plymouth, MI); Continental PET Technologies, Inc. (Florence, KY); Continental Plastic Containers, Inc. (Norwalk, CT); Silgan Plastic Corp. (Chesterfield, MO); Wheaton Plastic Products (Millville, NJ); and Southeastern Container, Inc. (Enka, NC).

Table 8.3 illustrates a cost analysis for producing injection blow molded polyethylene terephthalate (PET) containers (Albrant, 1996).

8.1.2.3 Thermoforming

Thermoformed packages are made from sheets of thermoplastic materials. Polyethylene, PVC, Ionomers, PETG, polystyrene, and cellulose acetate are common plastics used for thermoformed packages. The sheets are prepared by extrusion-casting or calendering.

Many variations of thermoforming processes are available, among the most important are (Gruenwald, 1987) billow, cavity vacuum, drape vacuum forming, plug-assisted forming, billow drape forming, snap-back forming, reverse draw, trapped sheet pressure forming, twin sheet forming, mechanically thermoformed, matched-mold forming, and rubber pad and fluid pressure. The cost of thermoformed packages includes:

1. Cost of resin
2. Cost of fabricating the sheet
3. Alternatively, price of purchasing the sheet
4. Thermoforming equipment, mold, and trimming tools (Thermoforming molds are less expensive than blow molding and injection molds.)
5. Thermoforming operations that include heating of sheet, forming the container, and trimming it off
6. In the case of a blister package, heat sealing the blister to a paperboard, normally 0.015 in thick (380 μm)
7. Other costs associated with waste handling, e.g., regrinding and re-extrusion (Laminated structures are eliminated or included as reground layer; scrapless thermoforming substantially reduces the waste.)
8. Post-forming costs including stacking, packing, and shipment

8.1.2.4 Flexible Packaging

Versatile flexible, or nonrigid, containers, are made from plastic films and multilayer structures combining plastic, paper, foil, and aluminum-oxide, silica-coated or metallized films. A structure can be transparent, opaque, colored, or metallized in appearance. These materials are formed into bags, stand-up pouches, liners, and wrappers. Almost any requirement can be achieved by combining the appropriate material in a flexible web. Flexible packaging can be used for many products, a variety of filling methods are available, and diverse delivery methods exist to remove the product from the bag. Solids, liquids, powders, food, chemicals, and drugs can be packaged under vacuum, or special atmosphere conditions. Flexible packages can be frozen, retorted, boiled, heated or irradiated. With the new polyolefin plastomers (POP), higher values in O_2 and CO_2 permeability can be achieved facilitating the packaging of fresh-cut produce (Young, 1996). On the other hand, ultra-high oxygen barrier structures are manufactured for oxygen-sensitive products. Flexible packaging can be presented with high quality surfaces printed by flexo, gravure, offset, or letterpress processes. Since there

TABLE 8.3
Cost Analysis of PET Bottles

Container type		**0.5 l**	**1.0 l**
Net weight	Gram	24	30
Type of resin		PET	PET
Resin cost[a]	$/lb	1.10	1.10
Scrap loss	Percent	1.0	1.0
Machine type		RBU-225[b]	RBU-225[b]
Number of cavities		2	4
Cycle time	Seconds	3	3.3
Blow molder efficiency	Percent	59	95
Container per hour		2280	4145
Depreciation term	Years	7	7
Blow molder	Cost	$511,250.00	$511,250.00
Mold/tool	Cost	$30,000.00	$30,000.00
Auxiliary equipment	Cost	$163,620.00	$ 163,620.00
Installation	Cost	$ 5,000.00	$ 5,000.00
Misc. fixed costs	Cost	$0.00	$0.00
Interest terms	Month	84	84
Interest annual	Rate %	8.0	8.0
Direct labor cost	$/h	$7.50	$7.50
Operators (0.5)	$/h	$5.00	$5.00
Inspectors/Pack (0.5)	$/h	$2.50	$2.50
Utilities	$/h	$0.00	$0.00
Paletize (0.5)	$/h	$0.00	$0.00
Indirect Labor Cost	$/h	$0.00	$0.00
Overhead cost	$/h	$5.00	$5.00
Miscellaneous hourly cost	$/h	$0.00	$0.00
Energy cost auxiliary		$0.07	$0.07
Energy consumption	kW/h	85	85
Energy cost		$0.07	$0.07
Operating hours/year		6000	6000
Production per year		**13,680,000**	**13,680,000**
Fixed Costs	Total	$188,060.75	$188,060.75
Depr. blow molder		$73,035.71	$73,035.71
Depr. mold tool		$4,285.71	$4,285.71
Depr. auxilliary equip.		$714.29	$714.29
Depr. miscellaneous fixed cost		$0.00	$0.00
Annual interest		$71,313.25	$71,313.25
Prevent maintenance/parts		$15,337.50	$15,337.50
Hourly Costs	**Total**	**$75,000.00**	**$75,000.00**
Direct labor		$45,000.00	$45,000.00
Indirect labor		$0.00	$0.00
Overhead		$30,000.00	$30,000.00
Miscellaneous hourly cost		$0.00	$0.00
Energy cost	Total	$35,700.00	$35,700.00
Resin cost	Total	$804,152.38	$804,152.38
Total mfg costs		**$1,102,913.13**	**$1,102.913.13**
Cost per 1000 containers		$80.62	$95.38

Note: PET = polyethylene terephthalate.

[a] Resin cost = cost of purchasing preforms.

[b] Supplier is Bekum American Corporation (Williamston, MI)

are several plastic materials that can be combined with foil, paper, and a variety of surface treatments, the number of flexible structures is very large.

Total investment for manufacturing the web of material including the printing is very high. From the standpoint of using a flexible structure, the material cost is related to the flexible structure composition, which in turn is determined by the product characteristics, storage and transportation conditions, and shelf-life requirements. The cost of flexible packaging materials is usually expressed per area of structure, m^2 or 1000 in^2. The cost can be expressed by unit of package or "repeat."

One of the less expensive flexible packages is an unprinted polyethylene bag. The cost of the material for a bag made of a simple polymer is given by

$$Cm = A \cdot \ell \cdot d \cdot r / 454$$

where A is the area, l thickness, d density, and r price of resin per pound. For instance, an unprinted 50 cm × 30 cm heavy-duty bag made of HDPE (density = 0.95 g/cm^3) with total area of 3000 cm^2 (465 in^2) and 125 μm (5 mils) thick has a material cost of

$$Cm = 3{,}000 \times 125 \times 10^{-4} \times 0.95 \times 0.47/454 = \$0.004.8138$$

with an estimated 60% increase for blowing into film and 50% for converting it into a bag, the final cost is approximately $0.14 per bag.

In the converting operation, the cost of a multilayer structure is built up from the elements combined in it. Consider the fabrication of a laminate for ground coffee bag. As an illustration of cost analysis, a possible structure can be made by combining a 100% reverse-printed 0.6-mil Mylar laminated to 0.0003 in aluminum foil and extrusion-coated to a blend of 50% low-density polyethylene (LDPE) and 50% metallocene. Table 8.4 shows the main cost components of this structure.

Major manufacturers of film and sheet in North America are: DuPont Co. (Wilmington, DE); Mobile Chemical Co. (Pittsford, NY); Bemis Co. (Minneapolis, MN); First Brand Co. (Danbury, CT); Cryovac Division (Duncan, SC); American National Can Co. (Chicago, IL); Printpack, Inc. (Atlanta, GA); Huntsman Packaging Co. (Salt Lake City, UT); ICI Americas, Inc. (Wilmington, DE); and James River Co., Packaging Business (Milford, OH).

8.2 PLASTICS IN FOOD PACKAGING

Synthetic or natural polymers are macromolecules made from the repetition of one or more species or group of atoms called mer and linked to each other by covalent bonds. The smaller chemical unit that completely describes the main polymer structure is called the constitutional unit. For instance, the constitutional unit of polyethylene is CH_2. The peculiar properties of polymers are determined by the large number of constitutional units in the molecule. The effect of the large number of mer are such that the polymer's properties do not vary markedly with the addition or removal of a few hundred constitutional units. In the field of engineering and related areas thermoplastic polymers are referred to as plastics. We will briefly review the most important properties that characterize a plastic material commonly used in the design, evaluation, specification, and fabrication of food plastic containers.

8.2.1 Properties of Plastic Resins

Composition — The final composition of a plastic resin includes the macromolecules made of a particular monomer (or monomers) as well as additives that are incorporated during processing. For example, PP is based on propylene and PVC results from the polymerization

TABLE 8.4
Cost Analysis of a High Barrier Lamination for Coffee

Foil lined coffee pouch			Cost ($/m²)
Material costs			
0.6-mil Mylar film, 20 g/m²	$3.00/lb	$0.00661/g	0.130
Ink, 1.5 g/m² (30% solid)[a]	$2.50/lb	$0.00551/g	0.030
Adhesive acrylic, 5 g/m² (50% solid)	$2.00/lb	$0.00441/g	0.040
0.3-mil Aluminum foil, 21 g/m²	$2.25/lb	$0.00496/g	0.100
Extrusion coating 16 g/m² of	$0.63/lb	$0.00138/g	0.020
50% LDPE	$0.40/lb	$0.00088/g	
50% Metallocene	$0.85/lb	$0.00187/g	
Subtotal material cost			0.330
Waste 10%			0.030
Total material cost			**0.360**
Conversion costs			
Hourly printing[b] rate	$200.00	96,000 m²/h	0.022
Hourly laminate rate	$600.00	96,000 m²/h	0.066
Total converting cost			**0.088**
Flexible material cost			0.448
Gross margin 18%			0.081
Total flexible material cost			0.529

Note: LDPE = low density polyethylene.

[a] White ink @ 100% coverage.

[b] Reverse printed with 8 color press.

vinylchloride monomer. PP resins contain antioxidants, and plasticizers are added to PVC as processing aids.

Molecular Weight — Unlike low-molecular-weight compounds made of the same type of molecules, a polymer is made of macromolecules having different lengths. For this reason the molecular weight of a polymer is actually a distribution of molecular weights. The molecular weight distribution of polymers is defined by the average molecular weight and its broadness. Two average molecular weights are commonly employed: number average molecular weight, $\overline{M}n$; and weight average molecular weight, $\overline{M}w$. The broadness of the molecular weight distribution (MWD) is given by the ratio $\overline{M}w/\overline{M}n$. This is called the dispersity index (DI). For most commercial polymers DI falls between 2 and 8. A low DI value indicates narrow distribution of the polymer, while large DI indicates a broad distribution, (Progelhof and Throne, 1993). $\overline{M}n$, $\overline{M}w$, and MWD determine properties such as strength, melting temperature, and heat sealing temperatures. A popular method to determine Mn, Mw, and MWD, is gel permeation chromatography which is described in the standard ASTM (American Society for Testing and Materials) D 3593.

Melting Temperature, T_m — The melting temperature marks the maximum temperature at which a plastic can be heated before it becomes a melt. Most crystalline and semicrystalline polymers have their melting temperature given as a temperature range which depends on their MWD and composition. Plastics show T_m as low as 275 K for polyisobutylene, and as high as 728 K in the case of PET (Van Krevelen, 1990). Semicrystalline plastics become soft

before reaching their melting temperature. Most noticeable, amorphous plastic such as polystyrene do not show a melting temperature range but rather they soften as temperature increases, especially above the glass transition temperature. Methods for measuring T_m are described in ASTM D 2117 and ASTM D 3418.

Glass Transition Temperature T_g — T_g is associated with the onset of the rotation and mobility of chain segments involving a small number of monomers. The concept of glass transition is important because below T_g a polymer is stiff and glassy and above T_g it has a plastic and rubbery behavior (Progelhof and Throne, 1993). In food packaging, T_m and T_g determine the temperature range of application of a container. For instance, a PP container may become brittle at a freezing temperature if its T_g is near 0°C, and polystyrene is brittle at room temperature because it has a T_g about 80°C and does not contain plasticizer. On the other hand, a polymer with low T_m value such as polyethylene cannot be steam sterilized. Differential thermal analysis (DTA) and differential scanning calorimetry (DSC) are used to determine T_m and T_g. These methods are described in ASTM D 3418.

Melt Flow INdex, MFI — MFI gives information about the extrusion characteristics of a resin and is used primarily in quality control. MFI is expressed in grams of extrudate per 10 min according to ASTM D 1238.

Mechanical Properties — These properties of plastics measure the strength, elongation, stiffness, tensile strength at break, elongation at break, tensile yield strength, tensile modulus, force/area, which are described in ASTM D 638. Other properties of interest are listed below. The respective ASTM standard methods are in parentheses.

- Methods for conditioning plastics (D 618)
- Coefficient of linear thermal expansion (D 696)
- Thermoforming heat deflection temperature (D 648)
- Thermal conductivity (C 177)
- Flammability (D 1433)

8.2.2 Properties of Sheets and Films for Flexible Packaging

Thickness — The unit in the SI system is the micrometer, μm (10^{-6} m). The customary unit used in the U.S. is mil (equals to 0.001 inch), gauge is 0.01 mil (TAPPI [Technical Association of the Pulp and Paper Industry] 411).

Area Factor — Also referred to as yield, this gives the area of the film per unit of mass, m^2/kg. Area factor is calculated as the inverse of density times thickness in coherent units (ASTM D 4321).

Tensile Characteristics — Stress-strain tensile characteristics of a flexible structure include ultimate tensile strength to determine the maximum tensile stress the material can sustain, elongation, and modulus of elasticity to determine the force required to deform the structure. Modulus of elasticity or Young's modulus, is a measure of the material stiffness in N/m^2 (ASTM D 882). The area under the stress-strain curve also gives the toughness of a material.

Density — The density of a plastic is proportional to its crystallinity. The standard ASTM D 1505 describes the "density gradient" method to evaluate the density of films and resins; the units are kg/m^3.

Bursting Strength — This is the hydrostatic pressure required to produce rupture of the material when the pressure is applied at a controlled increased rate through a rubber diaphragm to a circular area of 30.48 mm (1.2 in) in diameter. "Points bursting strength" is the pressure in pounds per square inch. This is the same test used for the bursting strength of paper and paper products, ASTM D 774. Free falling dart method is described in ASTM D 1709.

Impact Strength — Impact strength is the energy required to puncture a flexible structure to shock loading. This gives a measure of the toughness. The test is described in the ASTM D 3420 and ASTM D1709.

Tear Strength — The measurement of tear strength takes into account the energy absorbed by the film sample in propagating a tear. Two standard methods are available: ASTM standard D 1004 describes the measurement for initial tear resistance, and ASTM D 1922 refers to the energy absorbed by a test specimen in propagating the tear that has already been initiated by cutting a small hole in the sample. The value of tear strength in one film may vary widely depending on the degree of orientation such as oriented PP, and whether the measurement is performed in the machine direction or cross machine direction. This is described by ASTM D 1938.

Pinhole Flex Test — Pinhole flex resistance is the ability of a film to avoid the formation of pinholes during repeated folding. A film that has a low value of pinhole flex resistance will generate pinholes, at the folding line, following repeated flexing (ASTM F 456). A related test is the folding endurance.

Folding Endurance — This test measures the resistance of the material to flexure or creasing. The ASTM recommended procedure is described in the standard D 2176 which is used to determine the number of folds necessary to break a sample film.

Heat sealing Temperature — Important properties for wrapping, bag making, or sealing a flexible structure is the heat sealability characteristic of the material. To evaluate the seal, two values are normally measured: the peel strength (ASTM F 88), and the hot tack strength. As previously indicated, the absolute temperature and range of temperature must be considered. The polymer's average molecular weight determines the temperature level and the MWD determines its range.

Coefficient of Friction — The coefficient of friction (COF) is a measurement of the friction force between two surfaces. Cases in which friction is important include films passing over free-running rolls, bag forming, wrapping film around a product, and bag stacking. Speed, temperature, static, humidity, blocking, and surface smoothness affect the COF (TAPPI T 503 and ASTM D 1894).

Blocking — This is the tendency of two films to stick together when they are contacting each other. This effect is enhanced by a smooth surface and when the films are left under pressure, as is the case of stacked sheets or compacted rolls of film. Blocking can be measured by the force needed to separate two sheets when force is applied perpendicular to them, (ASTM D 1893 and D 3354, or Packaging Institute Procedure T 3629).

Haze — Haze is the percentage of transmitted light that, in passing through the sample, deviates by more than 2.5° from an incident parallel beam. The appearance of haze is caused by light being scattered by surface imperfections and nonhomogenous materials, (ASTM D 1003).

Gloss — Gloss is the percentage of incident light that is reflected at an angle equal to the angle of incidence (normally 45°). It is a measure of the ability of a surface to reflect the incident light. High gloss produces a sharp image of any light source and gives a pleasing sparkle, (ASTM D 2457).

Transparency and Opacity — A transparent material has a transmittance above 90%. Transmittance is the percent of incident light that passes through a material sample and is determined by the effectiveness of the absorption and scattering of light by the material. In most polymers light absorption is insignificant, therefore, scattering controls the light transmission. The scattering of power of a polymer results from morphological inhomogeneities and/or the presence of crystal and fillers. The less crystalline a polymer is, the more transparent it is. Amorphous homogeneous polymer, such as "crystal" polystyrene, showing little or no scattering power, is transparent. A highly crystalline polymer as HDPE will be mostly opaque. Transmittance is measured according to ASTM D 1003.

Dimensional Stability — Dimensional stability refers to the capability of a structure to maintain its dimensions under changing conditions of temperature and humidity. Machine and transverse directions may produce different changes in dimensional stability. Dimensional stability is important in any flexible material converting process particularly in printing, since even small changes in dimensions during printing may lead to serious problems in holding a print pattern (ASTM D 1204).

Permeability — The barrier properties of a plastic material is commonly expressed by its permeability coefficient value P. As the permeability increases, the barrier value decreases. But the permeability coefficient actually depends on the combined effect of the diffusion and solubility process. The well known relationship P = DS where D is the diffusion coefficient and S is the Henry's law solubility applies well to relatively low concentration values of permeant, which is the case found in many food systems. Several factors affect D, S, and P of polymers: (1) chemical composition of polymer and permeant; (2) polymer crystallinity; the diffusion and sorption occur mainly through the polymer's amorphous phase; (3) temperature, as temperature increases permeation increases; and (4) presence of plasticizers and fillers in the polymer. In food systems, the values of permeability of water, gases as well as aromas and flavor components. ASTM 1434 describes the standard method for measuring gas permeability of plastic film and sheeting. The oxygen permeability of films using a coulometric sensor is described in ASTM D 3985, and for packages in ASTM F 1307. Water vapor permeability method for flexible barrier materials is describe in ASTM 372, for film/sheeting using infrared sensor in F 1249, and for packages in ASTM D 895, D 1251, and D 3079. Water vapor transmission rate (WVTR) for pressure sensitive tapes is in ASMT D 3833. Permeability of organic compounds, flavors, and aroma are described by Hernandez et al. (1986).

Chemical Resistance — The evaluation of plastics resistance to chemicals is as follows: for acids, ASTM D 543; for alkalis, ASTM D 543; greases and oils, ASTM D 722; solvents, ASTM D 543; and sunlight, ASTM D 1435.

Wettability — Adhesion and printing operations to a plastic surface depend on the value of the plastic surface tension. A measure of a material's surface tension is given by the wettability (ASTM D2578).

8.2.3 Plastics and the FDA

Food packaging manufacturers are concerned with components that, originally contained in the packaging material, may come in contact with food by a migration process. When these

components are found in the food they are called indirect additives. Therefore, all plastic packaging for indirect contact with foods are required to be FDA-sanctioned. It is worth noting that the use of components are made in compliance or in accordance with "sanctioned" or "certified" ingredients rather than "FDA-approved."

Title 21 of the Code of Federal Regulations (CFR) covers all indirect additives as well as direct additives. Part 174 considers general aspects of indirect additives in food in relation with good manufacturing practice. Part 175 includes a long list of sanctioned indirect additives in adhesives and components of coatings, Part 176 is for paper and paperboard components, Part 177 covers polymers, and Part 178, adjuvants, production aids, and sanitizers. Since all ingredients in the packaging material must comply with the CFR, the packaging manufacturer should inform the food packer of that. For instance, a heat induction foil innerseal for rigid containers is a lamination containing Aluminum foil, PP film, paperboard, and adhesive as main components. The FDA status for all the components, in reference to 21CFR, is as follows: 175.105 for the adhesives, 175.300 for resinous and polymeric coatings, 175.320 for coatings of polyolefin films, 176.170 for paper and paperboard components in contact with aqueous and fatty foods, 176.180 for paper and paperboard components in contact with dry foods, 176.300 for fungicides, 177.1210 for closures with sealing gaskets, 177.1520 polyolefins. Aluminum foil is regulated in Section 409 of the Food Additives amendment of the Federal Food, Drug and Cosmetic Act.

8.3 MAJOR PLASTICS

8.3.1 POLYOLEFINS

Olefin, which means oil-forming, is an old synonym for alkenes. Originally, the term olefin was the name given to ethylene. Alkenes are hydrocarbons containing a carbon-carbon double bond, i.e., ethylene and propylene. In the plastic industry, olefin is a common term that refers to the family of plastics based on ethylene and propylene. The term polyolefin should strictly apply to polymers made of alkenes, whether a homopolymer or copolymer. This includes the family of polyethylene, and the family of polypropylene.

Polyethylene, the first useful olefinic polymer in food packaging, was introduced in the 1940s. Low-density polyethylene was first produced by free-radical polymerization at extremely high pressures and temperatures. The structure of this polymer was quite randomly branched. Better polyolefins, linear polymer chains (e.g., HDPE), became possible by the development of low-pressure polymerization process based on multi-sited Ziegler-Natta catalysts in the 1960s. Multi-sited catalysts procedure polymers having short, medium, and long molecules, and wide range of comonomer branches. These resins then, are characterized by wide MWD and wide composition distributions. An improvement in chain linearity came in 1970s with the solution- and gas-phase technology to produce linear low density polymer. Today, new and sophisticated polyolefins are being produced by the process based on the single-site metallocene catalysts known as metallocene catalyzed polymers. Unlike the multi-site catalyzed resins, metallocene polyolefins have a much narrower MWD and composition distribution.

Branched and linear polyethylenes are described in Section 8.3.1.1 and metallocenes are described in Section 8.3.1.3.

8.3.1.1 Polyethylene

General information — Polyethylene (PE) is a family of addition polymers based on ethylene ($CH_2{=}CH_2$). PE can be linear or branched, homopolymer or copolymer. In the case of a copolymer, the other comonomer can be an alkene, i.e., propene, butene, hexene, or octene, or a compound having a polar functional group, i.e., vinyl acetate (VA), acrylic acid (AA),

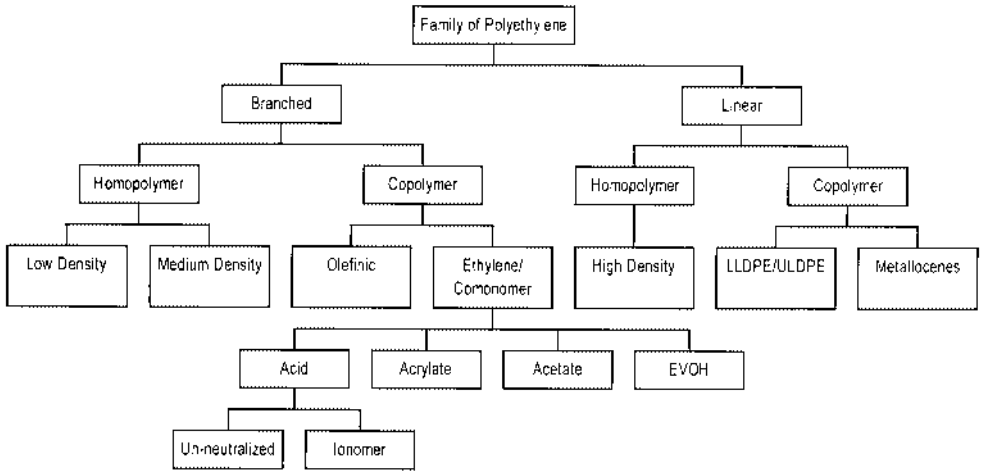


FIGURE 8.1 Family of polyethylene. EVOH = ethylene vinyl alcohol; LLDPE = linear low density polyethylene; ULDPE = ultra low density polyethylene.

ethyl acrylate (EA), methyl acrylate (MA), or vinyl alcohol (VOH). If the molar percent or the comonomer is less than 10% the polymer can be classified as either a copolymer or homopolymer. Figure 8.1 illustrates a diagram of the family of PE. PE resins are used as films, molded containers, closures, and in multilayer laminations. They are available in a large range of composition and MWD that determine a wide range of values in strength; toughness; thermal, heat-sealing, and barrier properties; and processing conditions.

Linear and branched polyethylene — Linear PE implies long chains of the ethylene monomer linked without major branching. The long range stereo-regularity of the linear molecule tends to yield highly crystalline PE. For this reason, linear PE has a crystallinity between 70 to 90%. On the other hand, the major effect of branches in the backbone chain is to limit the formation of PE crystals and produce amorphous or "loosely packed" PE. Since crystalline regions are denser than amorphous regions, linear PE is more dense than the branched PE. Linear low density PE combines the main features of both HDPE and LDPE.

Branched PE typically has a crystallinity of 40 to 60% and the density ranges from 0.910 to 0.950 g/cm^3. In contrast, HDPE will have a density of about 0.950 to 0.970 g/cm^3.

By the addition of comonomers, such as propylene and hexene, the number and the length of the branches in PE can be controlled. A wide variety of branched PE are commercially available depending on the reaction conditions and on the type and amount of comonomer.

Linear PE can be produced as a homopolymer HDPE, or copolymer linear low density polyethylene (LLDPE) and ultra low density polyethylene (ULDPE). Copolymers are produced with butene, hexene, or octene. The controlled placement of the comonomer in the polymer chain during the polymerization process, produces a rather linear polymer with very short strands and low density. LLDPE is characterized by a relatively narrow molecular weight and MWD, and a linear structure with very short branches due to the presence of butene, hexene, or octene.

The FDA has cleared the use of polyolefin resins for direct food contact as specified in 21 CFR, Section 177.1520.

8.3.1.1.1 Low density polyethylene

Properties — LDPE is a branched homopolymer. The branching of the chains yields a polymer with low percent of crystallinity on properties such as clarity, flexibility, sealability, and ease of processing. The actual values of these properties depend on the balance of the molecular weight, MWD, and branching.

TABLE 8.5
LDPE Branched Film and Resin Properties

Melting temperature	98–115°C	208–239°F
Glass transition temperature	–25°C	–13°F
Specific gravity	0.917–0.942	—
Tensile strength at break	8.3–31.8 kPa	1.2–4.6 kpsi
Tensile modules, stiffness	172–283 kPa	25–41 kpsi
Flexural modulus, 23°C	242–331 kPa	35–48 kpsi
Bursting strength, mil (Mullen)	10–12	10–12
Initial tearing strength	25.1–222 kN/m	65–575 g/mil
Propagating tearing strength	87.5–52.5 kN/m	50–300 lb/in
Permeability		
Water, at 37.8°C	66–99[a]	17–25.5[c]
Oxygen, at 25°C	1940[b]	500[d]
CO_2, at 25°C	10490[b]	2700[d]
N_2, at 25°C	700[b]	180[d]
Resistance to		
Acids	Good	
Alkali	Good	
Grease and Oil	Poor	
Water	Good	

Note: LDPE = low density polyethylene.

[a] Units in g·µm/m²·d·kPa.
[b] Units in cc(STP)·µm/m²·d·kpa.
[c] Units in g·mil/100 in²·d·atm.
[d] Units in cc(STP)·mil/100 in²·d·atm.

Adapted from *Modern Plastic, Guide to Plastics*, 1987, McGraw-Hill, New York.

Applications — LDPE is very versatile with respect to processing mode. Diverse processing techniques common to thermoplastic materials, i.e., blown film, cast film, extrusion coating, extrusion molding and blow molding, are available to LDPE.

Compared with other plastics, LDPE is one of the higher barriers to water but one of the lower to oxygen, CO_2, organic vapors, and flavors.

Film is the single largest production form of LDPE. In the U.S., 55% of the total volume is made into films with thickness less than 300 µm (12 mils). Products made of LDPE include containers and bags for food (i.e., packaging bakery items, snacks, and produce), clothing, industrial liners, agricultural films, household products, shrink- and stretch-wrap films. Selected properties of LDPE are presented in Table 8.5.

Medium density polyethylene (MDPE), 0.925 to 0.950, is more crystalline and therefore somewhat stronger, stiffer, and less permeable than LDPE. MDPE processes similarly to LDPE, though usually at a slightly higher temperature.

A major competitor material of LDPE is LLDPE which provides superior strength at equivalent densities. However, LDPE is still preferred in applications demanding high clarity or for coating a substrate. Table 8.6 presents trends in properties of PE resins.

Branched copolymers of PE — Other branched PEs are produced by copolymerizing ethylene with either alkene compounds or monomers containing polar functional groups, i.e., VA, AA, and VOH. The inclusion of polar monomers in the main chain produces branched ethylene copolymers with lower crystallinity, more flexibility, wider range of heat sealing

TABLE 8.6
Properties Trends in Polyethylene

As average molecular weight increases	
Tensile strength,	Increases
Impact strength	Increases
Clarity	Increases
Ultimate elongation,	Increases
Melt strength,	Increases
Tear resistance,	Decreases
Melting temperature	Increases
As molecular weight distribution broadens	
Ultimate elongation,	Decreases
Tear impact,	Decreases
Impact strength,	Decreases
Melt pressure,	Decreases
Melt strength,	Increases
Heat seal range	Increases
As density increases	
Tensile strength,	Increases
Melting temperature,	Increases
Clarity,	Decreases
Ultimate elongation,	Decreases
Tear resistance,	Decreases
Impact strength,	Decreases
Blocking,	Decreases
Gas permeability,	Decreases

temperatures, and denser materials. Some of these copolymers, like EVOH, have substantially different barrier properties than the original homopolymer.

The content of VA in the copolymer ranges from 5 to 50% and are commercially available, although for optimal food applications primary copolymers with ranges from 5 to 20% are recommended. Ethylene vinyl acetate (EVA) resins are mainly recognized by their flexibility, toughness, and heat sealability in extruded coatings. The physical properties of available LDPE vary widely by the choice of reaction conditions and by the type and amount of comonomer.

8.3.1.1.2 Ethylene vinyl acetate

Properties — EVA is a random copolymer whose properties depend on the content of VA (CH_2=CHOCOCH$_3$) and the molecular weight. As the content of the VA increases, the crystallinity decreases; however, in contrast with LDPE, the density increases at the same time. As the VA content increases, clarity improves, flexibility is better at low temperatures, an increase in the impact strength is expected, and the material is tougher. EVA is totally amorphous (transparent) when the content of VA reaches 50%. Since the acetate group is polar, as the VA content increases so does the polarity of the resin. As polarity increases there is an increase in adhesion strength and tackiness. As the molecular weight increases, the viscosity, toughness, heat seal strength, hot tack, and flexibility all increase.

Applications — Because of its excellent adhesion and ease in processing, EVA is available as film, useful as heat sealing layer in coextrusion, and it blends well with homopolymer PE. As a heat sealing layer, EVA is used in extrusion coating with PET, cellophane, and biaxially oriented PP packaging films for applications such as cheese wrap and medical films. EVA is a good choice when toughness is required at low temperatures such as in the case of ice bags

and stretch wrap for meat and poultry (Landvatter; 1994). FDA has cleared the use of EVA copolymers for direct food contact as specified in 21 CFR, Section 177.1350.

8.3.1.1.3 Ethylene acrylic acid

The copolymerization of ethylene with acrylic acid (CH_2=CHCOOH) produces copolymers containing carboxyl groups along the main and side chains of the molecule. These copolymers are known as EAA.

Properties — 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 of crystallinity. EAA copolymers are flexible thermoplastics having chemical resistance, and barrier properties similar to LDPE. EAA is superior to LDPE in strength, toughness, hot tack, and adhesion, with two major uses as blister packaging and as an extrusion-coating tie layer between aluminum foil and other polymers.

Applications — Films of EAA are used in flexible packaging of meat, cheese, snack foods, medical products, in skin packaging and adhesive lamination. Extrusion coating applications include condiment and food packages, coated paperboard, aseptic cartons, composite cans and toothpaste tubes. The FDA has cleared the use of EAA copolymers for direct food contact as specified in 21 CFR, Section 177.1320. Up to 25% of AA for copolymers of ethylene in food direct contact is permitted by FDA (Mergenhagen; 1992).

Suppliers of branched PE — American Polymers (Worcester, MA); Bamberger Polymers, Inc. (Lake Success, NY); Chevron Chemical Co. (Houston, TX): Down Plastics (Midland, MI); DuPont Co. (Wilmington, DE); Eastman Chemical Co. (Kingsport, TN); Exxon Chemical Americas (Houston, TX); Mobil Polymers (Norwalk, CT); Monmouth Plastics, Inc. (Asbury Park, NJ); Novacor Chemicals, Ltd. (Calgary, AB, Canada); Quantum Chemical Corp. (Cincinnati, OH): Rexene (Dallas, TX); Union Carbide Corp. (Danbury, CT); Washington Penn Plastic Co. (Washington, PA); and Westlake Plastics PVC Corp. (Houston, TX).

8.3.1.1.4 Ionomers

Neutralization of EAA or EMAA (ethylene methyl acrylate), with a cation such as Na^+, Zn^{++}, of Li^+, produces a material that shows even better transparency, toughness, and higher melt strength than the un-neutralized copolymer. These materials are called ionomers because they combine covalent and ionic bonds in the polymer chain. Surlyn® is the DuPont's trade name for ionomers.

Properties — Ionomers are used in packaging where formability, toughness, and visual appearance are important. They are used in combination with nylon, PET, LDPE, polyvinylidene chloride (PVDC), paperboard, and aluminum foil to form a heat seal layer in films and multilayer structures. Ionomers improve the pinhole and flexing resistance of the structure. Coextrusion lamination and extrusion coating are the most common techniques for processing ionomers. With normal processing temperatures in the range of 175 to 290°C, ionomers can resist the impact at temperatures as low as –90°C (lower than for LDPE) (Reed and Vaughan; 1965). Barrier properties of Ionomers are rather poor, but when combined with PVDC produce a composed material that is an excellent barrier. There are more than 50 commercial grades of ionomer with a wide range of properties. In general, sodium ion types are better in optical, hot tack, and oil resistance. Zinc ionomers are more inert to water, have better adhesion properties in coextrusion and for extrusion in coating foil (Statz; 1994).

Applications — Ionomers are used in composite films for fresh and processed meats such as hotdogs. Other applications of ionomers include frozen foods (fish and poultry), cheese, snack foods, fruit juice, wine, water, oil, margarine, nuts, and pharmaceuticals. Ionomers are highly resistant to oils and aggressive products, and provide reliable seals over a broad range

TABLE 8.7
LLDPE Film and Resin Properties

Melting temperature	122–124°C	252–255°F
Glass transition temperature	°C	°F
Specific gravity	0.910–0.940	
Tensile strength at break	13–27.6 MPa	1.9–4.0 kpsi
Tensile modules, stiffness	262–518 MPa	38–75 kpsi
Flexural strength	–kPa	–kpsi
Flexural modulus, 23°C	276–725 MPa	40–105 kpsi

Note: LLDPE = linear low density polyethylene.

Adapted from *Modern Plastic, Guide to Plastics*, 1987, McGraw-Hill, New York.

of temperatures. FDA has cleared the use of ionomeric resins for direct food contact as specified in 21 CFR, Section 177.1330.

Producers of Ionomer — DuPont and Exxon.

8.3.1.1.5 Ultra low density polyethylene

ULDPE is a copolymer of both ethylene and octene. It has density between 0.880 and 0.915 g/cm^3. ULDPE copolymers show a good combination strength, sealability, flexibility, and optical properties. They are superior to LLDPE in tear strength, puncture resistance, impact strength, and transparency. Their oxygen permeability is higher than other PEs, yet similar to that of EVAs. However, the WVTR values of ULDPE are similar to those of PEs.

8.3.1.1.6 Linear low density polyethylene

Properties — Physical properties of LLDPE are controlled by its molecular weight and density (0.916 to 0.940). Due to the linearity of its molecules, LLDPE is more crystalline and therefore stiffer than LDPE. This results in an increase of 10 to 15°C in the melting point of LLDPE as compared to LDPE. LLDPE has higher tensile strength, puncture resistance, tear properties, and elongation than LDPE. However, LDPE has better clarity than LLDPE. The haze and gloss of LLDPE is worse than LDPE due to its higher crystallinity.

Applications — Common uses of LLDPE include stretch/cling film, grocery sacks and heavy duty shipping sacks. A summary of LLDPE is presented in Table 8.7.

8.3.1.1.7 High density polyethylene

Properties — HDPE is a milky-white nonpolar, linear thermoplastic. The molecular chains of HDPE homopolymers are long and straight with little branching. HDPE forms large fractions of ordered, crystalline regions as it cools below its T_m. This close molecular packing produces HDPE with a crystallinity of 65 to 90% and contributes to HDPE's good moisture-barrier properties, its chemical resistance, and its opacity. Its density ranges from 0.940 to 0.965. It is a versatile polymer, and, together with LDPE, is one of the most common plastics in the packaging industry. Table 8.8 presents HDPE film and resin properties. Table 8.9 shows the relation between PE density, and oxygen and water permeability.

Applications — Containers for milk, detergent, bleach, juice, water, and industrial chemical drums are made by blow molding. Buckets, thin walled dairy containers and closures are made by injection mold, while cosmetic containers, pharmaceutical bottles, and shampoo and deodorant containers are made by injection blow molding. Blown and cast films are utilized in feasible packaging applications. HDPE replaces glassine for cereal, crackers, and snack

TABLE 8.8
HDPE Film and Resin Properties

Melting temperature	130–137°C	266–276°F
Glass transition temperature	–100°C	–148°F
Specific gravity	0.940–0.965	—
Tensile strength at break	22–31 kPa	3.2–4.5 kpsi
Tensile modules, stiffness	1070–1090 kPa	155–158 kpsi
Flexural modulus, 23°C	1000–1550 kPa	145–225 kpsi
Propagating tearing strength	2.6–52.5 kN/m	15–300 lb/in
Permeability		
Water, at 37.8°C	16–94[a]	4–23.5[c]
Oxygen, at 25°C	390–1750[b]	100–450[d]
CO2, at 25°C	2300[b]	590[d]
N_2, at 25°C	160[b]	42[d]
Resistance to		
Acids	Good	—
Alkali	Good	—
Grease and oil	Good	—
Water	Good	—

Note: HDPE = high density polyethylene.

[a] Units in g·µm/m²·d·kPa.
[b] Units in cc(STP) ·µm/m²·d·kPa.
[c] Units in g·mil/100 in²·d·atm.
[d] Units in cc(STP) ·mil/100 in²·d·atm.

Adapted from *Modern Plastic, Guide to Plastics,* 1987, McGraw-Hill, New York.

TABLE 8.9
Effect of Density on the Permeability of Oxygen and Water in Polyethylene

Density of polyethylene	Water permeability (g·µm/m²·d·kPa)	Oxygen permeability (g·µm/m²·d·kPa)
0.910	94	1750
0.915	84	1630
0.920	74	1440
0.925	63	1280
0.930	50	1050
0.935	40	880
0.940	30	660
0.945	26	580
0.950	23	490
0.955	20	450
0.960	16	390

Adapted from Smith, M. A., 1986, in *Wiley Encyclopedia of Packaging Technology,* Bakker, M., Ed., John Wiley & Sons, New York.

food packaging. It is used for wrapping delicatessen products and to produce bags. FDA has cleared the use of PE for direct food contact as specified in 21 CFR Section 177.1520.

Producers of linear PE and HDPE — In addition to the ones listed as producers of branched PE, the following companies are also manufacturers: Federal Plastics Co. (Cranford, NJ); Hoechst Celanese Corp. (Chatham, NJ); Novacor Chemicals Ltd. (Calgary, AB, Canada); Paxon Polymers Co. (Baton Rouge, LA); Shulman, Inc. (Akron, OH); and Solvay Polymers, Inc. (Houston, TX).

8.3.1.2 Polypropylene

PP is a group of thermoplastic polymers based on the polymerization of propylene monomer (CH_2=$CHCH_3$). PP is commercially available as a PP homopolymer, and PP random copolymer. The latter is produced by the addition of a small amount of ethylene (2 to 5%) during the polymerization process. Thermoplastic PP polymers are characterized by their low density (0.89 to 0.92 g/cc) and good resistance to chemical and mechanical fatigue. Applications of PP in packaging include film, cups, trays, closures, and other containers. Manufacturers of PP continuously are offering PP grades with improved or modified properties. FDA has cleared the use PP resins for direct food contact as specified in 21 CFR, Section 177.1520.

8.3.1.2.1 PP homopolymer

General — Depending on the type of catalyst and polymerization conditions, the molecular structure of the resulting polymer consists of the three different types of stereo-configurations for vinyl polymers: isostatic (stereo-regular), syndiotactic (alternating stereo-regular) and atactic (random configuration) (McCrum et al.; 1988). Industrial processes are designed to minimize the production of the atactic PP, a lower-value, noncrystalline, tacking byproduct that is used mainly in adhesives. Metallocene polypropylene (mPP) is a new generation of PP for which a controlled balance between isotacticity and atacticity, type of comonomer, mean molecular weight, molecular distribution, are truly controlled. Containers with a PP have much thinner walls but keeping the same stiffness with very high melt flow index values.

The isostatic PP (iso-PP) is the most common commercial form of a PP homopolymer. The placement of the methyl groups all on the same side of polymer backbone provides a structure which readily yields a highly crystalline material. The crystalline nature of the iso-PP gives its good chemical and heat resistance, but is not transparent. Compared with LDPE and HDPE, PP has a lower density, higher melting point temperature and higher stiffness (higher tensile modulus). These properties determine the different types of application for PP homopolymer. For example, higher value of stiffness and ease of orientation make PP homopolymers suitable for stretched application, while their higher heat resistance allow a container made of this material to be autoclavable.

Properties — Compared with PE, iso-PP is more sensitive to oxidative degradation due to heat and light. Oxidative degradation may produce chain scission which reduces the average molecular weight and chemically degrades the polymer. To control this process, antioxidants are added during processing. Other processing additives for PP include antistatic agents, commonly used in packaging to dissipate static charge (see section 8.4). Properties of PP are summarized in Table 8.10.

Orientation of PP films improves strength, clarity, and gloss over the nonoriented PP films, see Table 8.11. Oriented PP (OPP) film is a very versatile material. It can be metallized, coextruded, laminated, coated, and even silica- and aluminum-oxide coated to meet specific applications.

Applications — Acrylic-coated OPP is available for candy, cookie, and snack packaging, where good machinability, low coefficients of friction (0.2 to 0.3), attractive appearance, and

TABLE 8.10
Polypropylene, Biaxially Oriented (BOPP) Film and Resin Properties

Melting temperature	160–175°C	194–347°F
Glass transition temperature	–20°C	–4°F
Specific gravity	0.895–0.910	
Tensile strength at break	31–42 MPa	4.5–6.0 kpsi
Tensile modules, stiffness	1140–1550 MPa	165–225 kpsi
Flexural strength	42–55 MPa	6.0–8.0 kpsi
Flexural modulus, 23°C	1170–1725 MPa	170–250 kpsi
Initial tearing strength	386–579 kN/m	1000–1500 g/mil
Propagating tearing strength	0.53–1.75 kN/m	3–10 lb/in
Permeability		
Water, at 37.8°C	16.5–26[a]	4.3–6.8[c]
Oxygen, at 25°C	622[b]	160[d]
CO_2, at 25°C	2100[b]	540[d]
N_2, at 25°C	78[b]	20[d]
Resistance to		
Acids	Good	
Alkali	Good	
Grease and oil	Good	
Water	Excellent	

[a] Units in g·µm/m²·d·kPa.
[b] Units in cc(STP)·µm/m²·d·kPa.
[c] Units in g·mil/100 in²·d·atm.
[d] Units in cc(STP).mil/100 in²·d·atm.

Adapted from *Modern Plastic Encyclopedia* (1987).

TABLE 8.11
Effect of Chain Orientation on PP Film Properties

	Nonoriented PP	Oriented PP
Water permeability, g·µm/m²·d·kPa, 37°C	60	25
Stiffness	Very low	High, similar to cellophane
Propagated tear strength	High	Very low CD; very high MD
Heat sealability	Yes, 350–450°F	No, film distorts
Density	0.902	No change
Optics	Good	Excellent
Surface adhesivity to inks, etc.	Low	Low
Oxygen permeability, cc(STP)·µm/m²·d·kPa at 25°C	930	620

Note: PP = polypropylene; CD = cross direction ; MD = machine direction.

cost-effectiveness are essential. For flavor protection and odor sensitive products, e.g., chocolate bars, a PVDC coated OPP can be selected. A higher barrier metallized OPP will extend the shelf-life of oxygen-sensitive products, e.g., low fat chips, nuts, and dried fruits. For applications in bag-in-box, e.g., cereal, crackers, soup mix packaging, stand up pouches, OPP

TABLE 8.12
Values of Heat Sealing Temperature, T_g, and Heat Deflection Temperature in PP-Containing Ethylene

Weight percent ethylene	Maximum heat sealing temperature[a] (°C)	T_g (°C)	Heat deflection temperature[b] (°C)
0	163	6	115
2	152	2.5	95
4	143	–2	80
6	138	–6	64
8	125	–9	46
9	120	–11	40

[a] Melting temperature.
[b] AT 66 psi.

Adapted from Davis, D. S., 1992, *J. Plastic Film Sheeting* 8(4):101–108.

is a well-suited material (Rice; 1995). PP has a melting point of 163°C (325°F), therefore, microwave applications are limited to reheating. PP is also an excellent material for injection-molded closures for HDPE, PET, and glass beverage bottles. Plastic-lug®, Double-lok®, and Drip-lok® from Alcoa are examples of closure application so for PP, (Alcoa, 1993). Two-sided acrylic coated biaxially oriented PP (BOPP) films are heat sealable, highly transparent, highly glossy, and flavor barrier. Heat sealing temperature ranges from 93°C (200°F) to 145°C (293°F) with high hot-tack values. The films also show low COF and enhanced stiffness. OPP uses include shrink wrap for records, toys, games, hardware items, frozen foods, and cigarettes (Mobil, 1994).

8.3.1.2.2 PP random copolymer

Properties — PP copolymers show markedly different thermal properties as compared to PP homopolymer. As indicated in Table 8.12, the copolymers have lower heat sealing temperature, lower heat deflection temperature for thermoforming, and resist better subzero storage conditions. Random copolymer PP typically contains 1.5 to 7% ethylene, by weight, as comonomer. The addition of ethylene placed randomly in the chain backbone decreases the high crystallinity of iso-PP. Low crystallinity results in improved clarity and flexibility, and lower melting point (up to 152°F with 7% ethylene). The density is also lower 0.89 to 0.90 g/cc, showing that random copolymer is slightly lighter than homopolymer. Random PP has good toughness and lower temperature impact than homopolymer PP. These copolymers show good chemical resistance to acids, alkalies, alcohols, and to low-boiling hydrocarbons (no aromatic hydrocarbons).

Applications — PP random copolymers are used as films, blow, and injected parts. Applications include medical and food packaging, bakery products, and produce. The 7% ethylene copolymer is used as heat-seal layer in food packaging. Unoriented films are soft and are easy to heat seal.

Coextruded thermoformed containers — Thermoformed containers from multilayer cast sheet are used for shelf-stable and retortable single food packaging, e.g., microwaveable meals, prepared puddings, microwaveable baby foods, single-service apple sauce, nutritional supplements for the elderly, and even high-end pet foods. Other applications include modified atmosphere packaging (MAP) for meat, medical, and pharmaceutical products.

Typically, the coextruded structures are made of 5, 7, or 9 layers. They contain a symmetrical arrangement of polyolefin/regrind/tie layer/barrier layer/tie layer/regrind/polyolefin. The barrier layer is normally EVOH, PVDC, of Nylon. For MAP structures, it may include formed PS/tie layer/EVOH/PE or EVA with one regrind layer.

Suppliers of PP — American Polymers (Worcester, MA); Amoco Chemicals (Chicago, IL); Aristech Chem Corp. (Pittsburgh, PA); Bamberger Polymer, Inc. (Success, NY); ComAlloy International Co. (Nashville, TN); Exxon Chemical (Houston, TX); Federal Plastics Co. (Cranford, NJ); Fina Oil & Chemical Co. (Dallas, TX); Monmouth Plastics, Inc. (Asbury Park, NJ); Montell Polyolefins (Wilmington, DE); Phillips Chemical Co. (Bartlesville, TX); Quantum Chemical Corp. (Cincinnati, OH); Rexene (Dallas, TX); A. Shulman, Inc. (Akron, OH); Shell Chemical (Houston, TX); Solvay Polymers, Inc. (Houston, TX); and Washington Penn Plastic Co. (Washington, PA).

8.3.1.3 Metallocenes

As indicated in Section 8.2.1, single-site catalyst (SSC) polymers are characterized by narrow MWD and composition distributions. This means that the polymers molecules all have a similar number of side branches of comonomers at the same place along the polymer chain. In 1992, Exxon introduced metallocene plastomers (under the name EXACT®) with a range of density of 0.860 to 0.915 and a molecular weight ranging from 40,000 to 120,000. Polyolefin plastomers are being produced by Dow Chemical using SSC under the name of AFFINITY®. These plastomers are available as copolymers of propylene, butene, hexene, or octene, as well as terpolymers. The main characteristics of metallocenes are (Simon, 1994)

1. Low-molecular weight components which impart the resins with high extractable fraction are eliminated. This has the benefit of being a much purer resin for food contact applications. It also reduces odor and off-taste flavor.
2. Initiation seal temperatures are lower and sealing initiation temperatures are wider than HDPE. Strong hot-tack strength, and seal strength are shown by these resins so they can be used as a coextruded and/or blended heat seal layer.
3. Mechanical properties like puncture resistance, spencer impact, and blocking are improved with respect to resins produced by Ziegler-Natta catalysts. Haze and gloss are improved due to the absence of high-molecular weight fraction in the metallocene resins.
4. New metallocene PEs are expected to replace some PVC and produce new stretch films, sealant shipping bags and have application in taste-sensitive packaging (Manders; 1995). Other applications include meat, poultry, and fish requiring low sealing temperatures; coextruded structures for cereal and cake mix liners; and coffee pouch laminations. SSC resins can be blended with LDPE and HDPE.

8.3.2 Polyvinyl Chloride

8.3.2.1 General

PVC is a homopolymer of vinyl chloride (CH_2=CHCl). Of commercial PVC in packaging, 80% is produced by an addition polymerization reaction in a liquid suspension; other methods included emulsion and solution. Rigid PVC (used for making pipes) has a T_g = 180°F (82°C) and is very difficult to process. Flexible PVC material used in packaging is obtained by incorporating plasticizers. Plasticizers are additives that by a "lubricating" action at a molecular level, soften rigid polymers making them more flexible. Plasticizers decrease T_g and processing temperatures of a polymer. The addition of a liquid plasticizer to PVC then, permits the production of a flexible film with a moderate oxygen permeability.

TABLE 8.13
PVC Plasticized* Film and Resin Properties

	°C	°F
Melting temperature	75–105°C	167–221°F
Glass transition temperature	1.22–1.40	
Specific gravity	9.7–2.4 kPa	1.4–3.5 kpsi
Tensile strength at break	20	20
Bursting strength, mil (Mullen)	42.4–112 kN/m	210–290 g/mil
Initial tearing strength	10.5–175 kN/m	60–1000 lb/in
Propagating tearing strength	143–160°C	277–320°F
Seal temperature		
Permeability		
Water, at 37.8°C	330–2000[a]	85–510[c]
Oxygen, at 25°C	389–3900[b]	100–1000[d]
CO_2, at 25°C	1170–2330	300–6000[d]
Resistance to		
Acids	Good	
Alkali	Good	
Grease and oil	Fair	
Water	Excellent	

* Calendared and extruded.

[a] Units in g·µm/m²·d·kPa.

[b] Units in cc(STP)·µm/m²·d·kPa.

[c] Units in g·mil/100 in²·d·atm.

[d] Units in cc(STP)·mil/100 in²·d·atm.

Adapted from *Modern Plastic Encyclopedia* (1987).

PVC blow molded bottles are produced with plasticized PVC. The manufacture of a wide variety of packaging materials from PVC is possible because of the miscibility of the polymer with a range of plasticizers. Formulations to produce specific products made of PVC are mostly proprietary, for direct food contact, however, the additives need to be FDA sanctioned. DOA [di(2-ethyl hexyl)adipate] is the most common plasticizer used for PVC. Stabilizers such as Ca/Zn salts, which avoid the decomposition of PVC and the corresponding product of HCl, are also incorporated in PVC during compounding. The processing of PVC is carried out by conventional methods, e.g., injection molding, extrusion, blow film and blow molding.

8.3.2.2 Properties

PVC shows good clarity, good barrier properties, puncture resistance, and good sealability. PVC films provide good toughness and resilience. Properties of PVC are shown in Table 8.13.

8.3.2.3 Applications

Most PVC films are used for packaging food products particularly red and fresh meat. The oxygen permeability of PVC film is well suited to maintain the necessary oxygen requirements of the meat. This is necessary to keep the red color of the meat and its appearance of freshness. PVC is also used to wrap fresh fruits and vegetables. Almost all poultry producers in the U.S. use PVC stretch films for chilled, tray-packed poultry parts. PVC is available as stretch-wrap film. Examples of PVC packaging application include: bottles for milk, dairy products, edible oil, cosmetics, detergents, liquors, food wrap butter, and margarine; box lid for fresh, frozen, and cured meat; and, blister packaging fish, produce, and pharmaceutical products. PVC is also used for blood and intravenous-solutions tubing and bags.

8.3.2.4 PVC Concerns and the FDA

In the polymerization process of PVC slightly less than 100% of vinyl chloride monomer (VCM) is converted to polymer. This means that relatively high values of VCM may remain unreacted and trapped in the resin. The resin is subsequently submitted to a process in which VCM is removed. By repeated applications of vacuum, VCM is eliminated from the resin to reach concentration values of less than 1 ppm in the resin.

PVC is used extensively in food contact applications such as meat, oil, and water. The FDA has never banned or limited the use of PVC, but in the mid 1970s had expressed concern regarding its use in food due to the discovery of residual VCM in PVC. The FDA has not cleared VCM for food contact because VCM is a carcinogen in large doses, at least in laboratory animals. Currently, the industry produces PVC with extremely low levels of VCM in the resin, and the amount of VCM that might migrate to food is well below the sensitivity of analytical methods. It can be said that the concentration of VCM in food, by the action of migration from PVC containers, is sufficiently low and should not generate concern.

In the 1990s, PVC is now the center of a different controversy. Several European countries have banned the use of any PVC packaging because of the fear that during incineration of solids waste, HCl gases and chlorinated organic compounds (in which dioxins can be found) are generated and emitted into the environment. This increases the impact of the acid rain and poses health risks to humans. Japan, where a large portion of the solids waste is incinerated, has developed technology that prevents the emission of such unwanted compounds. However, some European countries maintain the ban on PVC.

8.3.2.5 Suppliers of PVC (Flexible Unfilled)

Alpha Gary Co. (Leominster, MA); Borden, Inc. (Andover, MA); Colorite Plastics Co. (Rigefield, NJ); Novatec Plastics & Chemicals Co., Inc. (Eatontown, NJ); A. Shulman, Inc. (Akron, OH); Shintech, Inc. (Houston, TX); Synergistics Industries, Inc. (Farmingdale, NJ); Teknor Apex Co. (Pawtucket, RI); Union Carbide Corp. (Danbury, CT); Vi-Chem Corp. (Grand Rapids, MI); and Vista Chemical Co. (Houston, TX).

8.3.3 Vinylidene Chloride Copolymers

8.3.3.1 General

Vinylidene chloride copolymers, known as Saran® or PVDC, were developed by the Dow Chemical Co. during the 1930s. These polymers result from the copolymerization of vinylidene chloride (VDC) ($CH_2{=}CCl_2$) with vinyl chloride, methyl acrylate, or acrylonitriles. Many commercial Saran polymers contain two or more comonomers. VDC homopolymer has a melting point of 198°C to 205°C, but it decomposes at 210°C. These conditions make VDC homopolymer, or PVDC, difficult to process. By copolymerization the melting point of the copolymers are decreased to a range of 140 to 175°C, making the melt-processing feasible. Saran polymer contains 2 to 10% plasticizer (e.g., dibutyl sebacate or diisobutyl adipate), and heat stabilizers. The most notable attribute of Saran copolymers are their extremely low permeability to gases and liquids and chemical resistance, which are comparable to EVOH resins.

8.3.3.2 Forms of Saran®

Saran is available in the following forms: F-Resins (with acrylonitrile as copolymer) used as solvent-soluble polymer for barrier coating; aqueous emulsion latexes for barrier coatings; and extrusion resins which are melt processable in rigid multilayer coextruded containers, extrusion of films, and sheets.

F-resins include F-239, and F-278 types. These resins are used to coat plastic films such as cellophane and polyester to give water permeability values ranging from 2.0 to 1.3 g·μm/m²·d·kPa, and oxygen permeability around 0.09 cc·μm/m²·d·kPa. Resin F-310 is used for paper coating. Heat sealing temperature of F-resins are in the 100 to 130°C range, (Dow Chemical Co. Form 190-305-1084).

Latexes are applied to coat paper, paperboard, and plastics films such as PP and PE. Also PET, PVC, PS, and PE rigid containers can be coated with latexes. Barrier properties of latexes are similar to those of F-Resins, (Dow Chemical Co. Form 190-309-1084).

Extrusion resins are used for flexible packaging in monolayer, and multilayer (coextruded or laminated) structures for meat and other food applications. For nonrefrigerated foods in rigid containers, extrusion resins can be coextruded with PP or PS resins. Extrusion resins are poorer barrier that F-Resins or latexes, (Dow Chemical Co. Form 190-320-1084). Saran HB Films (with vinyl chloride as comonomer) are a better barrier than F-Resins having an oxygen permeability of 0.04 cc·μm/m²·d·kPa, (Dow Chemical Co. Form 500-1083-586).

8.3.3.3 Applications

As indicated, different processing methods are available to Saran resins including extrusion, coextrusion, laminating resin, and latex coating to meet specific packaging requirements. Also injection molding, blown-film extrusion film and cast film are common industry processes for the resins. The main applications of Saran resins are in food packaging as barrier materials to moisture, gases, flavors, and odors. Monolayer films are widely used in household wrap.

Multilayer films, generally coextrusions with polyolefins are used to package meat, cheese and other moisture or gas-sensitive foods. The structures usually contain 10 to 20% of VDC copolymer and are commonly used as shrinkable films to provide a tight barrier around the food product. PVDC can be used as barrier layer in thermoformed containers made of a coextruded multilayer for shelf-stable and retortable single food packaging.

Industrial applications of monolayer films include laminations unit dose packaging drum and pack liners for moisture, oxygen and solvent-sensitive products in pharmaceutical and cosmetic packaging. FDA has cleared the use PVDC copolymer resins for direct food contact as specified in 21 CFR Sections 175.105 for adhesives, 175.320 for coating polyolefins, 176.170 for paper in contact with aqueous and fatty foods, 176.180 for contact with dry foods, and 177.1990 for resins.

Suppliers of PVDC include: Dow Plastics (Midland, MI).

8.3.4 Polystyrene

As other polymeric materials, polymers based on the polymerization of styrene, (CH_2=CHC_6H_5) are being produced by new technologies. New copolymerization methods, additives, rubber-modification and blending make polystyrene (PS) a very versatile packaging material. PS is hydrophobic, nonhygroscopic, easily extruded and a thermoformed material. Three types of PS are available: general purpose, impact, and Foams.

8.3.4.1 General Purpose Polystyrene (GPPS)

Although referred to as crystal PS, these are totally amorphous materials with no melting temperature, highly transparent, and with excellent optical properties. “Crystal” PS linear polymer has a T_g value ranging from 74 to 105°C, which makes it brittle and stiff at room temperature. There are three grades of GPPS: high heat, medium flow, and high flow (or easy flow). High heat resins have high molecular weight, contain few or no additives, and are brittle. They are used as extruded foams and thermoformed materials for electronic packaging, injection molded jewel box, high quality cosmetic containers and CD jewel boxes.

TABLE 8.14
Polystyrene Oriented Film and Resin Properties

	Amorphous °C	°F
Melting temperature		
Glass transition temperature	74–105°C	165–221°F
Specific gravity	1.05–1.06	
Tensile strength at break	14–70 MPa	2–10 kpsi
Tensile modules, stiffness	2280–3280 MPa	330–475 kpsi
Flexural strength	69–100 MPa	10–14.6 kpsi
Flexural modulus, 23°C	2620–3380 MPa	380–490 kpsi
Bursting strength, mil (Mullen)		16–35
Initial tearing strength	104–191 kN/m	270–495 g/mil
Propagating tearing strength	0.9 kN/m	5 lb/in
Permeability		
Water, at 37.8°C	460–660[a]	120–170[c]
Oxygen, at 25°C	970–1260[b]	250–350[d]
CO_2, at 25°C	3500	900[d]
Resistance to		
Acids	Good	—
Alkali	Good	—
Grease and oil	Poor	—
Water	Good	—

[a] Units in g·µm/m²·d·kPa.
[b] Units in cc(STP)·µm/m²·d·kPa.
[c] Units in g·mil/100 in²·d·atm.
[d] Units in cc(STP)·mil/100 in²·d·atm.

Adapted from *Modern Plastic Encyclopedia* (1987).

High flow resins have a low molecular weight and usually contain 3 to 4% mineral oil as additive. This makes crystal PS more flexible (less brittle) with lower distortion temperature. Typical applications include disposable medical ware, dinner ware, and coextruded sheets for thermoformed packaging.

Medium flow resins have an intermediate molecular weight, with 1 to 2% mineral oil as additive. These resins are used in blow molded bottles and coextruded materials for food and pharmaceutical packaging.

8.3.4.2 High Impact Polystyrene

High impact polystyrene (HIPS) contains particulates of rubber which are added to enhance the impact resistance. This produces an opaque material easy to process that can be thermoformed. Typical food packaging application are tubs for refrigerated dairy products, serving-size cups, lids, plates, and bowls. Limiting factors for HIPS are heat resistance, oxygen permeability, UV light stability, and resistance to oil and chemicals. According to Toebe et al. (1990) containers made of HIPS have an intense flavor scalping action on foods.

8.3.4.3 Expandable PS

Foam is a form of crystal PS supplied as a partially expanded bead. Expandable PS (EPS) foam has good shock absorbing and heat insulation characteristics. Application in food packaging includes egg cartons and meat trays.

Selected properties of PS are presented in Table 8.14. FDA has cleared the use of PS resins for direct food contact as specified in 21 CFR Section 177.1640.

8.3.4.4 Suppliers of Homopolymer PS

A. E. Plastics, Inc. (Elk Grove Village, IL), American Polymers (Worcester, MA); Amoco Chemical Co. (Chicago, IL); Bamberger Polymer Inc. (Success, NY); BASF Corp. (Wyandotte, MI); Chevron Chemical Co. (Houston, TX); Dow Plastics (Midland, MI); Federal Plastics Co. (Cranford, NJ); Fina Oil & Chemical Co. (Houston, TX); Hutsman Chemical Co. (Chesapeake, VA); RTP Co. (Winona, MN); A. Shulman, Inc. (Akron, OH); and Washington Penn Plastic Co. (Washington, PA).

8.3.5 Ethylene Vinyl Alcohol

8.3.5.1 General

Introduced in 1970 in Japan, EVOH is produced by a controlled hydrolysis of EVA copolymer. The hydrolytic process transforms the VA group in VOH, (CH_2=CHOH). The presence of OH in the backbone chain substituting a certain number of H atoms in PE has several profound effects on the polymer properties. First, the OH group is highly polar which increases the intermolecular forces, and at the same time becomes more hydrophilic than PE. Second, the OH group is small enough to give the polymer chain enough estereoregularity to form a polymer with high percent of crystallinity; even if it is randomly distributed in the chain it provides an excellent barrier to permeants. If the percent of OH in the olefinic backbone is zero, the product is PE, and at 100% VA the product becomes polyvinyl alcohol (PVOH).

Contrary to PE, PVOH has exceptionally high gas and odor barrier properties (the lowest of any polymers available), but is difficult to process, and is water soluble. When the percent of VOH in EVOH ranges from 52 to 70%, the ethylene-VOH copolymers obtained combine the processability and water resistance of PE and the gas and odors barrier characteristic of PVOH. EVOH copolymers are highly crystalline and their processing and barrier properties vary with respect to the equivalent percent of ethylene. When the ethylene percent is about 30%, gas and organic vapor barrier are exceptionally high but process conditions become more difficult. When ethylene content increases the water barrier and processability improve.

8.3.5.2 Properties

The most important characteristic of EVOH is the outstanding O_2 and odor barrier properties. Packaging structures with EVOH provides high retention of flavors and quality associated with oxygen reaction with the food product. EVOH also provides a very high resistance to oils and organic vapors. This resistance decreases somehow as the polarity of the penetrating compound increases. For example, the resistance to linear and aromatic hydrocarbons is outstanding, yet for ethanol and methanol it is low. It may, therefore, absorb up to about 12% of ethanol.

As indicated, the hydroxyl group OH makes the polymer hydrophilic, attracting of water molecules. The presence of water has a depressing effect in the oxygen barrier property. This poses an interesting challenge to the design of high barrier packages since external non-hydrophilic layers are necessary to protect the EVOH oxygen barrier characteristics. Selected properties for two EVOH copolymers are presented in Table 8.15.

8.3.5.3 Applications

EVOH can be coextruded in numerous combinations with PE or PP, and laminated or coated to several substrates including PET, PE, nylons, etc. EVOH can also be extruded in films, and processed in blow molding, injection molding, and coextrusion blow molding. Selected structures are listed in Table 8.16.

TABLE 8.15
Selected Properties of EVOH copolymers

Property	EVOH (32% ethylene)	EVOH (44% ethylene)
Density, g/cc	1.19	1.14
Ultimate tensile strength, MPA	80	59
Tear strength, N/mm	154	193
T_m, (T_g) in °C	181, (70)	164, (55)
Heat seal temperature, °C	179–238	177–238
Oxygen permeability, cc·µm/m²·d·kPa	0.03 (0% RH) 0.2 (65% RH)	0.15 (0% RH) 0.3 (65% RH)
WVTR, g·µm/m²·d·kPa at 38°C	250	92

Note: EVOH = ethylene vinyl alcohol; WVTR = water vapor transmissin rate; RH = relative humidity.

Adapted from EVAL Company of America.

TABLE 8.16
EVOH Applications for Selected Structures

Application	Structure
Processed meats, cheese, snacks	PET/EVOH/EVA Nylon/EVA/Nylon/Ionomer OPP/EVA/EVOH/EVA
Dairy, meat, coffee, condiments	Onylon 6/EVOH/Onylon 6
Red meat	LLDPE/EVOH/LLDPE
Tea, condiments	OPP/EVOH/LDPE
Aseptic packaging	LDPE/paperboard/ EVOH/PP/Ionomer
Yogurt	PP/EVOH/PP
Ketchup	PET/EVOH/PET
Cosmetics	LDPE/EVOH/LDPE
Pharmaceuticals	EVOH/LDPE

Note: PET = polyethylene terephthalate, EVOH = ethylene vinyl alcohol; EVA = ethylene vinyl acetate; PP = polypropylene; OPP = oriented polypropylene; LDPE = low density polyethylene; LLDPE = linear LDPE.

Adapted from Foster, R., 1986, *The Wiley Encyclopedia of Packaging Technology*, Bakker, M., Ed., John Wiley & Sons, New York, 270–275.

FDA has cleared the use of EVOH resins for direct food contact as specified in 21 CFR, Section 177.1360 up to 80% of VOH. Application in packaging include flexible and rigid containers. Typical applications are ketchup and barbecue sauce bottles, jelly preserves, vegetable juice, mayonnaise containers, and meat packages. Non-food applications include packaging of solvent and chemicals.

8.3.5.4 Suppliers

Eval Company of America (Lisle, IL); Nippon Goshei (Japan), and Kurary Co. (Japan).

8.3.6 NYLON

8.3.6.1 General

Nylons are a family of condensation, linear, thermoplastic polyamides that contain the amide group (–CONH–) as a recurring part of the chain. Polyamides can be produced by the reaction of diacid with a diamine or by the polymerization of single amino acids such as ε-caprolactam to produce nylon 6, Kohan (1973).

8.3.6.2 Properties

In general nylons are clear, thermoformable, very strong, and tough materials over a broad range of temperatures. They are a good barrier to gas, oil, and aromas (see properties in Table 8.17). Nylons are polymers with strong intermolecular forces taking place by the presence of H-bonding between the –C=O and HN– groups of different chains. These high intermolecular forces are combined with crystallinity to yield tough high-melting thermoplastic materials. For instance, Nylon 6,6 has a melting point of 269°C (516°F). In addition, nylons have good puncture resistance, impact strength, and temperature stability. Furthermore, the flexibility of the aliphatic portion in the chain permits film orientation that enhances strength. By reacting comonomers (for example, 2 different di-acids), amorphous nylons can be produced, e.g., 6I/6T (Selar®, PA, trade mark from DuPont). 6I/6T is a copolymer of hexamethylene adipamine and isophthalic and terephthalic acids (Blatz, 1989).

Since the amide group is polar, nylons are moisture sensitive or hydrophilic. Left in its normal environmental conditions at 65 to 80% RH (relative humidity), nylons can easily absorb 6 to 8% of its weight of water, depending on their chemical composition. Complete sorption isotherms of Nylon 6 and amorphous nylon 6I/6T at three temperatures are given by Hernandez (1994). The amount of water in a nylon sample can be described as a function of relative humidity by a sorption isotherm curve.

Oxygen permeability in nylons is affected by their moisture content. As indicated in Figures 8.2 and 8.3, in the case of semicrystalline nylons such as nylon 6, oxygen permeability increases above an equilibrium RH of 30 to 40%, while in amorphous 6I/6T it stays constant after a decrease from 0%, (Hernandez, 1994).

8.3.6.3 Applications

Nylons are melt-processable using conventional extrusion. Film manufacture can be produced by either cast-film process or blown film process. During film production, diverse degrees of crystallinity are obtained depending on the temperature quenching rate. When the cooling rate is increased, a less crystalline nylon is obtained since the polymer was not given sufficient time to form crystals. The biaxial orientation of nylon (BON) films provides increased transparency, crack resistance, mechanical properties, and barrier characteristics. The increase in amorphousness produces improved transparency and thermoformable film.

Nylons are used in coextrusion with other plastic materials providing strength and toughness to the structure. Polyolefins are commonly used in nylon coextrusions to provide heat sealability, moisture, and low cost. Nylon is used to extrusion coat paperboard to obtain heavy duty paperboard.

Blow molding process is used with nylon resins to produce industrial containers. Thermoformed nylons are employed for disposable medical devises, meat and cheese packaging and are in thermoform/fill/seal packaging.

Important attributes of nylons for packaging are their excellent thermoformability, flex-crack resistance, abrasion resistance, grease, and odor barrier, mechanical strength (tensile, burst and impact) up to above 200°C.

TABLE 8.17
Nylon 6 Film and Resin Properties

Melting temperature	210–220°C	410–428°F
Glass transition temperature	°C	°F
Specific gravity	1.12–1.14	—
Tensile strength at break[a]	41.4–166 MPa	6–24 kpsi
Tensile modules, stiffness[a,b]	690–1700 kPa	100–247 kpsi
Flexural strength[a,b]	400 kPa	58 kpsi
Flexural modulus, 23°C[a,b]	966 kPa	140 kpsi
Initial tearing strength	386–463 kN/m	1000–1200[a] g/mil
Propagating tearing strength	2.8–4.9 kN/m	16–28[c] lb/in
Folding endurance[a]	250,000	—
Permeability		
Water, at 37.8°C	660–620[d]	170–187[h]
Oxygen, at 25°C	10.0[e,f]–5.1[e,h]	2.6[f,g]–1.3[g,h]
CO_2, at 25°C	39–47	10–12[f,g]
N_2, at 25°C	3.5	0.9 [f,g]
Resistance to		
Acids	Poor	—
Alkali	Fair	—
Grease and oil	Excellent	—
Water	Poor–Good	—

[a] Molding and extrusion compound.
[b] As conditioned to equilibrium at 50% RH.
[c] Units in g·mil/100 in^2·d·atm.
[d] Units in g·µm/m^2·d·kPa.
[e] Units in cc(STP)·µm/m^2·d·kPa.
[f] Cast.
[g] Units in cc(STP)·mil/100 in^2·d·atm.
[h] Biaxially oriented.

Adapted from *Modern Plastic Encyclopedia* (1987).

The most common nylons used in food packaging is nylon 6 and nylon 6,6. FDA has cleared the use of nylon resins for direct food contact as specified in 21 CFR, Section 177.1500. For most applications nylons are combined with other materials that add moisture barrier and heat sealability, e.g., LDPE, ionomer, EVA. Multilayer films containing a nylon layer are used principally in vacuum-packing bacon, cheese, bologna, hot dogs, and other processed meats. Coextrusion such as nylon 6/EVOH/nylon 6 provides a unique combination of mechanical and barrier properties. PVDC copolymer coating on nylons are available for an improved oxygen, moisture vapor, grease barrier properties. Nylon based structures are used in MAP involving CO_2 flushing for poultry, fish, and fresh meat.

8.3.6.4 Suppliers of Nylon 6

The following are suppliers of Nylon 6 (molding and extrusion compound): Adell, Inc. (Baltimore, MD); Allied Signal, Inc. (Morristown, NJ); ALM Co. (Wayne, NJ); Ashley Polymers, Inc. (Brooklyn, NY); BASF Co. (Wyandotte, MI); Bamberger Polymers, Inc. (Success, NY); Bayer co. (Pittsburgh, PA); Com Alloy International Co. (Nashville, TN); Custom Resins Division of Bemis Co. (Henderson, KY); DuPont Co. (Wilmington, DE); EMS, Inc. (Sumter, SC); Hoechst Celanese Co. (Chatham, NJ); Nylon Corporation of American

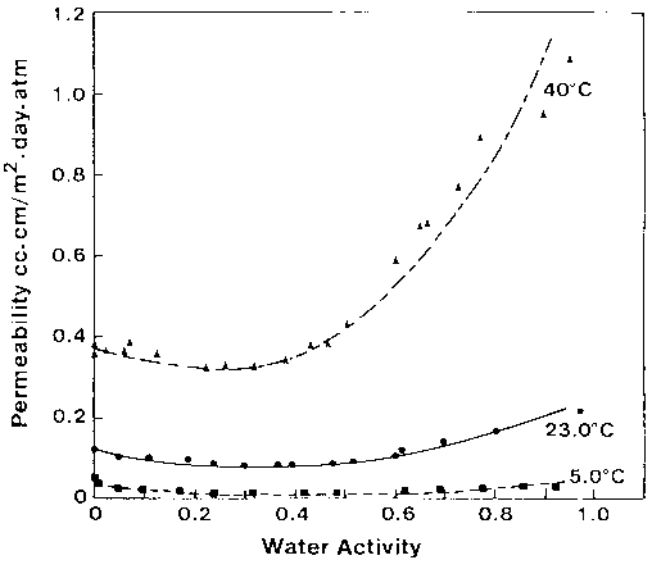


FIGURE 8.2 Oxygen permeability of Nylon 6. (From Hernandez, R. J., 1994, *J. Food Eng.*, 22:502. With permission.)

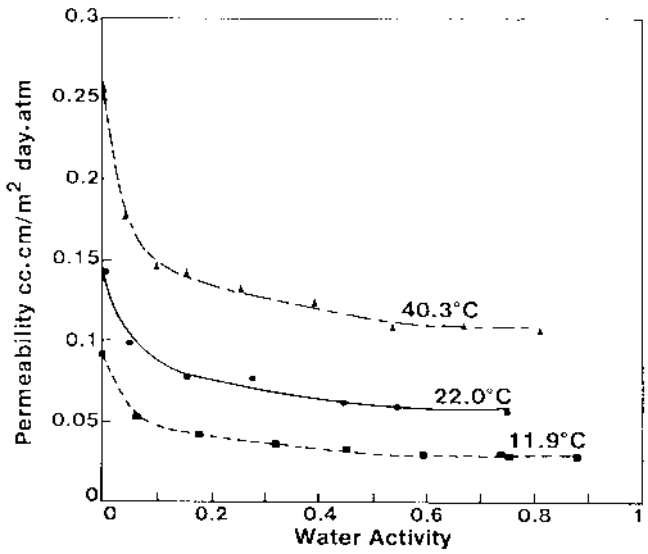


FIGURE 8.3 Oxygen permeability of Nylon 6I/6T. (From Hernandez, R. J., 1994, *J. Food Eng.*, 22:502. With permission.)

(Manchester, NH); Polymer Resources (Farmington, CT); Polymers International, Inc. (Spartanburg, SC); A. Shulman, Inc. (Akron, OH); Texapol Co. (Bethlehem, PA); and Thermofil, Inc. (Brighton, MI).

8.3.7 Polyethylene Terephthalate

8.3.7.1 General

PET is a linear, thermoplastic polyester produced by the esterification reaction of glycol and terephthalic acid. Due to the step-wise type of reaction which imparts high steroregularity to

TABLE 8.18
PET Film and Resin Properties

Melting temperature	212–265°C	413–509°F
Glass transition temperature	70–80°C	158–176°F
Specific gravity	1.35–1.41	
Tensile strength at break	48.3–72.5 MPa	7–10.5 kpsi
Tensile modules, stiffness	2760–4140 MPa	400–600 kpsi
Flexural strength	83–124 MPa	12–18 kpsi
Flexural modulus, 23°C	2400–3100 MPa	350–450 kpsi
Bursting strength, mil (Mullen)	55–80	—
Initial tearing strength	79.3–116 kN/m	50–300 g/mil
Propagating tearing strength	175–525 kN/m	1000–3000 lb/in
Folding endurance[a]		>100,000
Permeability		
Water, at 37.8°C	66–86[a]	17–22[c]
Oxygen, at 25°C	11.6–23.3[b]	3.0–6.0[d]
CO_2, at 25°C	58.3–97.1[b]	75–25[d]
N_2, at 25°C	2.7–3.9[b]	0.7–1.0[d]
Resistance to		
Acids	Good	
Alkali	Poor	
Grease and oil	Good	
Water	Good	

Note: PET = polyethylene terephthalate.

[a] Units in g·μm/m²·d·kPa.
[b] Units in cc(STP)·μm/m²·d·kPa.
[c] Units in g·mil/100 in²·d·atm.
[d] Units in cc(STP)·mil/100 in²·d·atm.

From *Modern Plastic Encyclopedia* (1987).

the polymer chain, PET is a semicrystalline polymer. Homopolymer PET has become a very important packaging material in food packaging films and carbonated beverage bottles. Copolymerization with other monomers produces polyester resins of different degrees of crystallinity, including an amorphous material, which are used for containers and trays.

8.3.7.2 Properties

The great acceptance of PET as a carbonated beverage packaging material is due to its toughness and clarity, capability of being oriented, reasonable cost, and the development of high speed bottle processing technology. PET containers are lightweight, shatter-resistant, good barriers, and recyclable. PET is produced by the condensation of a diacid and a dialcohol. Oriented PET has good strength, toughness, and clarity. It resists weak acids, bases, and many solvents. See Table 8.18.

The presence of moisture during the extrusion of PET reverts the condensation reaction and produces some degree of depolymerization. Before extrusion then, PET must be dried to remove water molecules. Moisture content should be less than 0.005% to minimize hydrolytic breakdown and loss of properties. Films can be produced using chill roll. Injection molding is used to produce bottles. Molding material should be free from contamination to comply with FDA regulations.

8.3.7.3 Applications

PET is used for packaging food, distilled spirits, carbonated soft drinks, noncarbonated beverages, and toiletries. FDA has cleared the use of PET resins for direct food contact as specified in 21 CFR, Section 177.1315. Typical food products include, e.g., mustard, pickled foods, peanut butter, spices, edible oil, syrups, and cocktail mixers. PET is extensively used for extrusion coating and extrusion into film and sheet. Its crystalline form (CPET) is the basic material for oven-ware containers. Biaxially oriented PET is used in meat and cheese packaging. Thermoforming is a common operation applied to PET sheets. Other applications include ovenable boards, boil-in-bag, and sterilizable pouches. As the food processors continue to refine their technologies of low acid, high-particular entrees, aseptic packaging could become an important market for multilayer barrier containers such as PET/EVOH/PET.

Since FDA has accepted the use of regenerated PET (reclaimed PET that has undergone a rigorous chemical or mechanical recycling process to assure clean liners), it is expected that the use of this material in multilayer food packaging may reduce the cost of producing the thermoformable sheets. Under development is a three-layer amorphous PET sheet structure with a core layer of 60 to 70% regrind. The intended use of this structure is for bakery and refrigerated products. Since PET resists higher retort temperatures 127 to 135°C than copolymer PP, 121°C, the three-layer amorphous sheet could be used in retortable, aseptic packaging (Toensmeier, 1995).

8.3.7.4 Thermoplastic Copolyesters

The name copolyesters is applied to those polyesters whose synthesis is carried out by using more than one glycol and/or more than one diacid. The copolyester chain is less regular than homopolymer and the degree of crystallinity is lower, some of those are amorphous. PCTA is a polymer of cyclohexanedimethanol (CHDM) and terephthalic/isophthalic acids. This is an amorphous polyester, designed primarily for film forming and sheeting in food, pharmaceutical, and, in general, blister packaging applications. PETG is made with CHDH and glycol plus terephthalic acid. PETG, with a T_g of about 81°C, is a glossy, transparent, tough, sterilizable with gamma rays, and recyclable.

8.3.7.5 Polyethylene Naphthalate

Polyethylene naphthalate (PEN) is the last addition to the polyester family. Its packaging application has been directed to the beverage industry. PEN is a clear material, although less than PET, with enhanced gas-barrier characteristics. The oxygen permeability constant of PEN is five times lower than for PET. It has a T_g near 120°C (43° higher than for PET), and is stronger and stiffer than PET. These properties make PEN well suitable for hot fillings and an excellent material for carbonated beverages. Because of its absorbance of UV radiation, PEN may provide an extra protection to UV-sensitive products. PEN resins, presently more expensive than PET, can be processed by blow molding, injection molding, and extrusion molding. Containers made with this resin are returnable, refillable, and recyclable.

8.3.7.6 Suppliers

Suppliers of PET and copolyesters unfilled include: DuPont Co. (Wilmington, DE); Eastman Chemical Co. (Kingsport, TN); Hoechst Celanese Co. (Chatham, NJ); A. Shulman, Inc. (Akron, OH); Shell Chemical Oil Co. (Houston, TX); and Texapol Co. (Bethlehem, PA).

8.3.8 Polycarbonate

Polycarbonate (PC) is a glassy, amorphous thermoplastic material. It has excellent balance of toughness and clarity. It has a heat deflection temperature of about 130°C and a glass

transition temperature of 149°C. PC has major applications in the automobile industry and appliances markets and has good potential for packaging applications.

Commonly, PC is produced by the reaction of bisphenol-A and carbonyl chloride.

Toughness is the most impressive property of PC. For instance, PC is the material of choice for school window and sports equipment. Being tough and clear makes PC a material well suited for reusable bottles, particularly 19-l (5-gal.) water bottles or 1-gal milk bottles. Systems with washing stations have been developed for reusable PC bottles. PC films are odorless, have no taste, and do not become stained through normal contact with natural or synthetic coloring agents.

PC has good resistance to fruit juices, aliphatic hydrocarbons, and aqueous solutions of ethanol but is attacked by some solvents such as acetone and dimethyl ethyl ketone. Since PC is FDA approved, food-contact applications include microwave, ovenware, and food storage containers.

In Europe, most food applications include prebaked bread, biscuits, confectionery, meat, and processed cheese. Other emerging applications include hot fillings, modified atmospheric packaging, rigid packaging to substitute PVC, high gloss for paper, and barriers for fruit juice cartons.

PC finds application in medical-device packaging. It can be sterilized by commercial sterilization techniques such as ethylene oxide, autoclave sterilization, and gamma sterilization.

PC can be processed by injection molding, extrusion, coextrusion, and blow molding. Coextrusions with EVOH or polyamides are carried out with the help of adhesives. PC can be laminated or coextruded to PP, PE, PET, PVC, and PVDC. PC is a hydrophilic polymer and at ambient conditions can reach moisture levels of 0.35%.

8.3.8.1 Suppliers

Suppliers of PC include: Albis Co. (Rosenberg, TX); American Polymers (Worcester, MA); Ashley Polymers, Inc. (Brooklyn, NY); Bamberger Polymers, Inc. (Success, NY); Bayer Co. (Pittsburgh, PA); Dow Plastics (Midland, MI); Federal Plastics, Inc. (Cranford, NJ); General Electric Plastics (Pittsfield, MA); MRC Polymers, Polymer Resources (Farmington, CT); Progressive Polymers, Inc. (Jacksonville, TX); RTP Co. (Winona, MN); and Shuman (Charlotte, NC).

8.3.9 Silica-Coated and Aluminum-Coated Films

Silicon oxide (SiO_x) deposition on polymer substrates have been applied to packaging to provide a high barrier to gases and vapors. PET coated with silicon oxide has proved to acquire excellent barrier properties for water and oxygen. Its barrier properties are slightly affected by temperature variations but it maintains its transparency and is retortable and microwaveable. Three vacuum deposition processes (evaporation, sputtering, and plasma-based) are used to coat PET, LDPE, BOPP, and BON (Felts, 1993). Results showed that the SiO_x coatings made by plasma-enhanced chemical vapor deposition (PECVD) yielded the best oxygen barrier properties. Oxygen permeability values are much lower than those of EVOH. Silica-coated films are produced by Airco Coating Technology (Concord, CA). The permeation of organic vapors through silica-coated PET films have been measured by Sajaki and Giacin (1993).

Aluminum oxide (AlO_x) coatings produced by Flex Products (Santa Rosa, CA) and by A.D. Tech (Taunton, MA) are close rivals of silicon-oxide coatings. Aluminacoated films are also excellent barriers to gases and vapors, optically transparent, and microwaveable.

8.4 PLASTIC ADDITIVES

Pure resins are rarely processed into final products without the addition of highly selected compounds, called additives, that are incorporated during the process of extrusion and molding of a plastic resin or applied externally on the formed material. There are several reasons

for the addition of these compounds into the formulation of the final product: to improve the processing conditions; to increase the resin's stability to oxidation; to obtain a better impact resistance; to increase or decrease hardness; to control surface tension; to facilitate the extrusion and molding; to control blocking; to reduce cost; to increase flame resistance, etc.

The number and amount of additives incorporated in the compounding process of a resin vary greatly with the type of resin and application. In the case of PE, for instance, an antioxidant may be the only additive incorporated. In the case of PVC, several plasticizers, a filler, heat stabilizer, and colorant are normally incorporated. Many options are available to the manufacturer. In most cases the final formulation is considered proprietary information.

Additives are incorporated by the resin manufacturer and/or by the packaging converter. The presence of additives in packaging applications always raises the question of additive migration. Most of the additives diffuse within the polymer and tend to go to the surface of the material. When the packaged product is in direct contact with a compounded polymer there will be a transfer of the additive to the product. The additive transfer is controlled by the system's mass transfer coefficients and thermodynamics. Selected additives relevant to food packaging are reviewed.

8.4.1 Antifogging Agents

When condensation of water molecules takes place on the internal surface of the headspace of a package, a continuous thin layer of small droplets of water can be formed. On transparent films and structures, the layer of droplets of water produces the refraction of light in many directions. This phenomenon, called fogging, makes the film or structure appear opaque. This is not only aesthetically poor but also may produce damage in the packaged product. The droplets are formed when the polymer surface tension is lower than the surface tension of water, which prevents the formation of a continuous layer of water.

Antifogging additives function by increasing the critical surface tension of the polymer surface and allowing the molecules of water to wet the polymer surface.

Common antifogging agents are: fatty acid esters, such as, glycerol and sorbitol stearate, fatty alcohols and ethyloxylates of nonyl phenols. Antifogging agents are incorporated in the resin in levels ranging from 0.5 to 4%. Several factors are involved in the selection and use of these additives, e.g., polymer type (LDPE, LLDPE, PVC, EVA, PP, and PET), thickness of the structure or film, performance life, and whether the product is a food. In the latter case, FDA clearance is necessary for its application. Antifogging compounds can be applied on the surface of the material or compounded internally in the packaging material.

8.4.2 Antiblocking

Blocking is the tendency of two adjacent layers of polymer films to stick to each other by simple physical contact. Blocking is mainly determined by the smoothness of the surfaces. To reduce blocking the smoothness of the surfaces must be altered by the presence of tiny particulates imbibed within the polymer. Solid particulates, antiblocking agents are usually incorporated into polymers films to reduce the area of flat contact.

According to Radosta (1991), diatomaceus earth of 2 to 4 μm has been employed to reduce blocking in PE films, but talc also has important commercial use as an antiblock agent for LLDPE and LDPE. Diatomaceus earth is a class of compact, granular, or amorphous mineral composed of hydrated silica formed of fossil diatoms. Talc is a soft mineral of fine colloid particles with soapy feel, made of hydrated magnesium silicate, $4SIO_2$-$3MgO$-H_2O. The advantages of talc over diatomaceus earth include platelet morphology, particle size distribution, and the possibility of being coated to make it more compatible with PE. Its level range is between 0.1 to 0.5% of the resin.

When antiblocking agents are incorporated to PE films other important properties of the polymer are also affected. This includes an increase in stiffness, a decrease in the COF, and an increase of haze.

8.4.3 Antimicrobials

Antimicrobial agents preserve compounded polymeric materials from attack by microorganisms, i.e., bacteria, fungi, or mildews.

Most synthetic polymers in their pure state are not attacked by microorganisms, they are in general nonbiodegradable. However, when various low molecular additives are compounded within the polymer, conditions for microorganism attack are created.

The presence of plasticizers, lubricants, or heat stabilizers in the polymeric matrix are the target of the microbial activity. It has to be said, however, that different additives pose different resistance to be biodegraded. If the expected value of the shelf-life of a package is in the order of the time required for the package material to develop microbial attack it will be necessary to consider the use of an antimicrobial agent.

One of the most compounded polymers available in packaging is PVC which may contain an appreciable amount of plasticizers and lubricants (40 to 50% in weight percent). Among the most common preservatives used for polymers are 2-n-octyl-4 isothiazolin-3 and copper-8-quinoleate, the use level ranges from 0.1 to 1%. Antimicrobial agents for polymers are considered pesticides by the Environmental Protection Agency under the Federal Insecticide, Fungicide and Rodenticide Act (FIFRA).

8.4.4 Antioxidants

Polymeric materials chemically deteriorate during fabrication, processing, and storage due to a series of complex chemical oxidation reactions using atmospheric oxygen. Several factors promote the oxidation reactions, among them are high temperature during processing, ionizing radiation, mechanical stress, chemical attack, or simple storage. In an oxidative degradation process such as one generated in the extrusion process, covalent bonds in the polymer chain are broken and free radicals are formed. This process goes to a propagation and the termination process.

The oxidative degradation may considerably damage the polymer by chain scission and cross-linking. Usually, the average molecular weight changes and the MWD broadens. To prevent the damage on the polymer generated by the oxidative degradation, chemical additives called antioxidants are incorporated to the polymer during processing.

Two main types of antioxidants (AO) are available commercially, primary AO and secondary AO. Primary AO work by inhibiting the propagation of oxidation process. Examples of primary AO include hindered phenols, e.g., butylated hydroxy toluene (BHT), and secondary arylamines.

The secondary AOs work by decomposing the peroxide molecule into nonradical stable products. Examples of a secondary AO are phosphites and sulfur compounds. Because the role of primary and secondary AO differ in their mechanism of attack to prevent oxidative degradation, in practice both types of AO are used together to obtain the best results.

Saturated polymers containing tertiary carbon off the backbone, such as PP, are more susceptible to oxidation than saturated linear polymer containing only secondary carbon in the backbone, such as PE.

In packaging, three resins consume most of the AO produced: PP, PE, and HIPS. For PP a combination of hindered phenol and phosphite AO is commonly used and the total concentration is normally from 0.08 to 1%, depending on formulation and end use. For LDPE, 50 to 500 ppm of BHT is normally incorporated. There is a tendency, however, to employ less volatile additives to prevent its migration from the resin. For HDPE and LLDPE, AO is

less volatile than BHT. Polyphenols at a higher concentration are normally used in combination with phosphites. For HIPS hindered phenols are used in combination with UV absorbers.

Evaluation of the use of α-tocopherol, or vitamin E, as an AO for polyolefins is discussed by Laermer and Zambetti (1992).

In the case of PVC the degradation is mostly ionic. PVC breakdown occurs through dehydrochlorination. The reaction is autocatalyzed by HCl byproduct and further accelerated by oxygen. Organometallic compounds and salts derived from lead, cadmium, barium, zinc and tin, as well as epoxides and phosphites, are the most common stabilizers used for PVC.

8.4.5 Antistatics

In general, static electricity is generated on a polymer surface by friction or by rubbing it against another surface, and this may include a solid or just air. Accumulation of electricity is favored by the low conductivity of the polymers. In packaging, the fast moving film, whether in a continuous converting operation or in a form-fill-seal processing line for instance, promotes the generation of static electricity on the film.

Static can adversely affect a manufacturing operation or process by introducing uncontrolled electrical forces that may result in, e.g., folding and sticking surfaces. It may also create dangerous conditions such as spark formation, leading to vapor explosions. In most polymers, electric charges are accumulated on the surface because polymers have high resistivity which makes the surface able to conduct electrons and ions.

Polymer surface static is controlled by the presence of antistatic agents that make the surface more conductive, or less resistive. For example, the presence of water within a hydrophilic polymer, such as polyamides, which is in equilibrium with air at 65% RH will act as an antistatic agent and will prevent the static buildup. This action is not seen at low RH values. Since most polymers used in packaging are not hydrophilic, antistatic agents must be used to control static. These agents are, in general, cationic, ionic, or nonionic surfactants.

A common group of cationic antistatics is alkyl quaternary ammonium salts that are mostly employed in polar substrates such as PVC and styrenic polymers. Other types include alkyl phosphonium and alkyl sulfonium salts. Flexible PVC may have a content of up to 7% of these antistatics which are not cleared by the FDA. Sodium alkyl sulfonates, similar to common detergent, have gained wide acceptance as an anionic antistatic that also are used in PVC and styrenic polymers. Other anionic antistats include alkyl phosphonic, dithiocarbamic, and carboxylic acids.

For nonpolar polyolefins, nonionic antistatics are the most commonly used. Nonionic antistatics include ethoxylated fatty amines, fatty acid esters, ethanolamides, and PE glycol-esters. Dosages for LDPE is around 0.05%. Antistatic can be applied internally or externally. Internal antistatics are compounded with the resin and they act once they migrate to the surface of the polymer. External antistatics are applied directly to the surface by spraying or eventually by dipping the polymer in a solution of the antistatic. Testing of antistats are described by ASTM D 257 and measures the electric resistivity; or Federal Test Method Standard 101C Method 4046 that measures the generation or decay of static electricity.

8.4.6 Colorants

The use of colorants in plastics is almost exclusively driven by product appearance to influence consumers and by marketing considerations. Colorants do not add mechanical strength nor improve mass barrier properties. They may give an opaque appearance that can contribute to protection from light for a packaged product. Selecting, combining, and matching colors is a complicated art that only well-trained individuals are able to perform correctly. There are hundreds of different colorants used in the plastic industry, and there are as many types of colorants as there are different applications for plastics.

The present tendency of the plastic industry is to move away from toxic colorants, specially those based on heavy metals, i.e., chromium, cadmium, and lead. Similar to measuring optical properties of papers and paperboard, the characterization of a color for plastics is based on the measurement of color (hue), brightness, and opacity. Other important variables to be considered include dispersability in the plastic, migration, toxicity, light stability, and chemical resistance.

There is a world-wide movement to eliminate heavy metal colorants. The European Union had considered banning them in 1995. In 1993, in the U.S. there were 22 states that restricted or banned the use of heavy metal colorants. The use of organic colorants, or heavy-metal-free (HMF) colorants, is continuously increasing, and many colorant producer companies are replacing all heavy-metal-containing colorants. Colorants incorporated in plastic containers are in direct contact with food and have to be cleared by FDA.

There are several more important types of colorants used in plastics (Dick, 1987). These will be discussed.

8.4.6.1 Dyes

Dye is a colorant that is soluble in the plastic. Normally, dyes are low-molecular-weight organic compounds. They impart great transparency to the plastic, but migrate easily from it. Their tendency to migrate is the reason dyes have limited use in the plastic industry. Some dyes are very toxic and their use is regulated by U.S. Occupational Safety and Health Association (OSHA). Dyes include azo, diazo, pirazalones, anthraquinones, quiniphthalones, and quinolines dyes.

8.4.6.2 Organic Pigments

Organic pigments, unlike dyes, are insoluble in the plastic matrix. They are produced in the form of very fine particles which give the plastic an opaque appearance. Organic pigments tend to migrate less than dyes and similarly, some are very toxic. While handling these pigments OSHA directives must be followed. Examples of organic pigments include

Benzimidalones (yellow, red, orange)
Phthalocyanines (blue, green)
Quinacridones (violet, red, orange)
Dioxazines (violet)
Disazos (yellow, red)
Pyrazalones (orange, red)

8.4.6.3 Inorganic Pigments

Widely used in the plastic industry, inorganic pigments have neither the brightness nor the intensity of color that characterize organic pigments, however, they are less expensive, more opaque, and more stable to high temperature. Since they are very insoluble in the polymers, their migration tendency is less than the organic pigments. Many of the inorganic pigments are extremely toxic since they are oxides of heavy metals, such as chromium, lead, cadmium, or nickel. When manipulating these colorant OSHA guidelines must be followed. Example of inorganic pigments include

Titanium oxide (white)
Lead chromates (yellow, orange)
Zinc chromate (yellow)
Nickel titanate (yellow)

Chrome titanate (yellow)
Chromium oxide (green)
Iron oxides (brown, red, yellow, black)
Cadmium sulfoselenides (maroon, red, orange)
Cobalt alumate (blue)
Lead molybdate (orange)
Cadmium sulfide (orange)
Iron chromite (black, infrared reflective)

8.4.6.4 Lake Pigments

Lake pigments consist of a dye associated with an inorganic support such as alumina hydrate. They are used in packaging for visual effects.

8.4.6.5 Pearlescent Colorants

Pearlescent colorants impart a special pearly luster and provide iridescent effects. Titanium oxide-coated mice and ferric oxide-coated mice are the major pearlescents in use. They form thin platelets of high refractive index, which both reflect and transmit the incident light.

8.4.6.6 Colorants and the FDA

Besides economic factors, the use of colorants in plastic packaging requires both health and safety considerations. As indicated in Section 8.1.3, the FDA has made public a list of sanctioned colorants. Colorants for polymers are considered in Title 21 of CFR §178.3297. Colorants listed there "may be safely used as colorants in the manufacture of articles or components of articles intended for use in producing, manufacturing, packing, processing, preparing, treating, packaging, transporting, or holding food." There are also some provisions related to definition of colorant, migration to food, and conformation under Section 409 of the Federal Food, Drug and Cosmetic Act that should be reviewed when dealing with this subject.

Inorganic colorants listed in 21CFR §178.3297 includes aluminum, aluminum hydrate, aluminum and potassium silicate, aluminum silicate, barium sulfate, bentonite, calcium carbonate, calcium silicate, calcium sulfate, carbon black (channel process, prepared by the impingement process from stripped natural gas), chromium oxide green (Cr_2O_3), cobalt aluminate (with restrictions), diatomaceous earth, iron oxides, (kaolin-modified for use in olefin polymers up to 40%), magnesium oxides, magnesium silicate (talc), Sienna, silica, titanium dioxide, titanium dioxide-barium sulfate, ultramarines, zinc carbonate (limited use), zinc chromate (less than 10%), zinc oxide (limited use), and zinc sulfide (less than 10%).

Partial listing of organic colorants from 21CFR §178.3297 include all FD&C certified colors, C.I. Pigment Blue 15, C.I. Pigment Violet 19, C.I. Pigment Red 38, C.I. Pigment Orange 64, C.I. Pigment Yellow 95, C.I. Pigment Yellow 138, and C.I. Pigment Red 177. In recent years, the FDA has sanctioned few new colorants for food-packaging or extended the use of others. Some of them have limited thermal stability which probably make them unsuitable for use with high-heat resins like nylons and polycarbonate (Lachance, 1996). A final decision on colorants as with other additives for food-contact packaging should be done in accordance with the FDA regulations.

8.4.7 Heat Stabilizers

The major disadvantage of PVC is its poor thermal stability. Products made with PVC such as films and bottles degrade when they are heated at moderately high temperatures or subjected to gamma rays sterilization or even UV radiation, unless proper additives are present. Compounds classified as heat stabilizers can effectively hinder and reduce the degradation process

which makes the PVC become progressively yellow, to amber, to reddish brown, and finally black. The best way to control the degradation of PVC is to carefully select the correct heat stabilizer for a specific PVC application. PVC stabilizers are inorganic, organometallic compounds and organic compounds. Barium-cadmium, organotin and organolead compounds account for more than 90% of type total heat stabilizers used in the U.S. One of the most common organotin stabilizers is dibutyltin.

The additives in PVC bottles like dibutyltin, calcium-zinc compounds and methyltin for cooking oil and other food products must have FDA clearance. For flexible packaging materials the most common stabilizers are the mixed metals such as barium-zinc and calcium-zinc that are replacing the cadmium-zinc formulations. For rigid blow-molded containers and calendared sheets organotin formulations are the most commonly employed.

8.4.8 Plasticizers

A plasticizer is a substance that is incorporated into a rigid plastic to increase its flexibility, workability, and distensibility. By reducing the glass transition temperature and increasing chain lubricity, plasticizers also improve processing and extrusion characteristics, reduce the minimum required processing temperature, reduce the plastic's hardness and improve low temperature flexibility.

Not all plastics require the use of a plasticizer, but for certain plastics, such as PVC, the use of an appropriate plasticizer is essential for the desired end use. Indeed, PVC applications depend on the level of the plasticizer.

Without plasticizers, PVC is a semicrystalline, brittle polymer very difficult to process. At low levels of concentration the plasticizer helps to reduce the processing temperature. This prevents thermal degradation of the polymer.

At higher levels besides improving processing conditions, it reduces hardness and increases flexibility of the final product. PVC is a polymer well suited for plasticization and accounts for more than 80% of the total production of plasticizer. In order for a plasticizer to work it has to have a correct balance of different functional groups to fully compatibilize with the polymer. Normally they have a slightly to strong polar functionality for compatibility with polymer polar groups and nonpolar groups (hydrocarbon) for internal lubrication. Different ratios of polar/nonpolar groups make a plasticizer more suitable for one application than for another. To improve processing conditions at high temperatures a more polar plasticizer is preferred, such as dibuthyl phthalate. To improve application at low temperatures, that is, make the PVC more flexible by depressing T_g, a nonpolar plasticizer is better, such as dioctyl sebacate.

Common plasticizers are the phthalates and among them, diethylhexyl phthalate (COP) is the most widely used. Safety concerns of DOP were raised in the 1980s but never fully clarified. To date, no action has been taken to regulate the production or use of DOP. Both in the U.S. and Europe it appears that DOP is making something of a comeback.

8.4.9 UV Stabilizers

UV radiation from outdoor or from gamma radiation used for sterilization of medical and biomedical products can cause photo-oxidation in PS, polyolefins (especially PP), PVC, and other polymers. Highly energetic, UV photons are easily captured by a polymeric chain resulting in the breaking of covalent bonds and the producing of free radicals. Although the particular response to UV varies with each polymer due to different sensitivity, the global effect may be destructive of the polymer. Change of color, loss of flexibility and gloss, and degradation are some of the effects that can be seen by photo-oxidation. (UV radiation has similar deteriorative effects when reaching the human skin). To protect polymers from the destructive action of UV radiation, different approaches have been adopted.

One of them is to use "screen protector" agents that absorb the harmful UV radiation and emit a radiation of larger wavelength and lower energy. An example of this type is hydrobenzophenone used with PVC, PE, PP, cellulosics, and PET. The family of Tinuvin P, based on benzotriazoles, are commonly used although not as effective in polyolefins as the hydrogenzophenones. Pascall et al., 1995, described the decreasing lipid oxidation of soybean oil when an UV absorber, Tinuvin 326, is incorporated in the packaging material.

A second group of stabilizers may act by "quenching" a polymeric chain that has been excited by the UV photon to higher level of energy. An example is an organosalt of nickel used in PP and PE.

Finally, a third approach may be when the stabilizer acts by accepting free radicals, i.e., a free-radical scavenger. The highly efficient family of hindered amine light stabilizers (HALS) belongs to this group. HALS, contrary to phenolic and phosphite antioxidants, provide a regenerative radical trapping process. In this way several free radicals are eliminated before they are converted into inert derivatives. Applications of HALS include pigmented polymers, and radiation stabilizers for PP in biomedical products. The growing concern in the use of ethylene oxide in sterilization has increase the acceptance of gamma radiation in the sterilization of medical supplies. This requires that UV stabilizers must protect the polymeric materials used in this process. HALS have become very important UV stabilizers. In the market, there are many formulations of HALS and the correct selection must be a function of the polymer and the intended application. Combining different stabilizers trigger a synergistic effect and provide excellent protection to the polymer.

Carbon black is an inexpensive material that offers UV protection to polymers even at low concentrations. It can be used in PVC, PE, and PP.

8.4.10 Other Additives

Other additives may be incorporated into polymers, although they are not very important in packaging. The following types of additives may be found: flame retardants, fillers, coupling agents, mold-release agents, and processing aids. Blowing agents although not truly additives, are used to form plastic foams. Blowing agents can be chemical blowing agents (CBA) or physical blowing agents (PBA). CBA refers to the decomposition of organic compounds to generate the blowing gas; In PBAs, compressed gases are used and no change in chemical composition is involved. Fluorocarbons were widely used in the recent past as PBA, but they have been eliminated due to problems with the ozone layer. Expanded PS is fabricated with pentane. Expanded PE does not contain a blowing agent. Currently, expanded PET, PP, and PVC foams are produced by using endothermic CBS that produces a lesser amount of evolving gases. As indicated in Section 8.2.3, any additive used in food-contact packaging must comply with FDA regulations.

8.5 MASS TRANSFER IN PACKAGING SYSTEMS

Mass transfer in packaging systems is controlled by the type of packaging materials and the physical integrity of the package. Mass transfer through a package can occur in:

1. Package discontinuities, e.g., micro holes and cracks in the package walls and sealed areas and in closures; see Section 8.5.1
2. Permeation through the package wall, section 8.5.2
3. Partition equilibrium (covered elsewhere in this handbook)

8.5.1 Mass Transfer Through Micro Holes

Micro holes and cracks not only allow mass transfer between the interior of a package and the outside environment, but also may permit microbe penetration into the package. Some bacteria can penetrate holes as small as 0.4 μm in diameter (Axelson and Cavlin, 1991).

Modeling mass flow through package pores is relevant in packaging integrity testing, and in the use of perforated films for modified atmospheric packages.

Nondestructive package integrity tests are in general based on leak detection of gas through the packaging material. The change in pressure between the package headspace and the environment can be detected by a variety of methods (Floros and Gnanasekharan, 1992). Nondestructive testing methods can be classified in the following categories: visual optical, acoustic, pressure difference, and others. The gas exchange through micro holes in MAP increases the transfer rate of gases such as CO_2 and O_2.

Other package discontinuities may exist in bottles between the finish and the cap. To secure a good seal, the use of cap liners and adequate applied cap torque are necessary.

8.5.1.1 Diffusion through a Micro Hole in a Barrier Membrane

The barrier membrane can be a flexible material, a rigid container wall, a thermoformed blister package, or the seal line formed in a pouch by heat sealing or adhesion. The molecular transport through the pore comprises the diffusion due to concentration differences (Knudsen diffusion), and the hydrodynamic flow as a result of a pressure difference (Poiseuille flow).

Consider a cylindrical capillary pore of diameter d and length *l* equal to the wall thickness of the packages. The wall separates two gas mixtures, that inside of the package and that in the outside environment. Assume the inside pressure to be p_i and total external pressure is p_o. If the radius of the pore is smaller than the molecular mean free path λ of the diffusant gas, a particular molecule will more often collide with the pore walls rather than with another molecule (see Example 8.2). The value of d/λ can be less than 0.2, larger than 20, or in between. When $d/\lambda < 0.2$ the rate of diffusion is governed by the collisions of the gas molecules with the pore walls and follows Knudsen's law (Treybal, 1980).

8.5.1.2 Knudsen Diffusion

The flux of a gas, A, controlled by Knudsen diffusion is given by the following equation (Youngquist, 1970)

$$N_A = -D_{KA}\frac{dc_A}{dx} \tag{8.1}$$

where N_A is the molar flux of A in mol/m^{2}s, D_{KA} is the Knudsen diffusion coefficient in m^2/s, c_A is the concentration of A in mol/l, x is the axial distance in the porous. From the kinetic theory of gas D_{KA} is given by

$$D_{KA} = \frac{d}{3}\overline{v_A} \tag{8.2}$$

where $\overline{v_A}$ is the mean molecular velocity in m/s given by

$$\overline{v_A} = \left(\frac{8}{\pi}\frac{RT}{M}\right)^{1/2} \tag{8.3}$$

where R is the gas constant = 8314 N m/kg mol K; T is the temperature in Kelvin degrees; and M_A is the mass of one mole of gas, Kg-mol.

EXAMPLE 8.1

Calculate the velocity of a CO_2 molecule in a Knudsen diffusion process at 0°C.

TABLE 8.19

Values of $\overline{v_A}$ for Selected Gases

Gas	Molecular weight	Temperature 0°	15°C	25°C
O_2	32	425.1	436.6	444
N_2	28	454.5	466.8	474.8
He	4	1202.0	1256	1256.2
CO_2	44	362.5	372.4	378.8
G_2O	18	566.8	582.1	592.1
Air	28.8	448.1	460.2	468.1

Note: Values given in meters per second.

Solution

From Equation 8.3 and knowing that M = 44 kg·mol.

$$\overline{v_{CO_2}} = \left(\frac{8}{\pi}\frac{8.614\times 273.15}{44}\right)^{1/2} = 362.5\ \text{m/s}$$

From Equation 8.3 we have

$$\frac{\overline{v_A}}{v_B} = \left(\frac{M_B}{M_A}\right)^{1/2} \tag{8.4}$$

and

$$\frac{\overline{v_1}}{v_2} = \left(\frac{T_1}{T_2}\right)^{1/2} \tag{8.5}$$

From Equation 8.4 it can be seen that the lighter molecule has a higher velocity and therefore will be transferred faster than the heavier one. Values of $\overline{v_A}$ for selected gases are presented in Table 8.19.

At steady state, the Knudsen flux N (in mol/m²s) through a pore of area A, is obtained by integrating Equation 8.1.

$$N = A\frac{D_{KA}}{R\ell T}\left(p_i - p_{\text{(}}\right. \tag{8.6}$$

or

$$J = 706\ \ d^3\overline{v_A}\left(p_i - p_o\right)/\ell T \tag{8.7}$$

where J is the gas flow through the pore in ml(STP)/s; d is the porous diameter, in m; $D_{K\ell}$ is the velocity of the molecule from Equation 8.3 (or Table 8.19) in m/s; T is temperature in Kelvin; l is the thickness of the package wall in m; and p_i and p_o are the pressures inside and outside, respectively, in Pa. STP conditions are 0°C and 1 standard atmosphere.

TABLE 8.20
Molecular Mean Free Path for Selected Gases at 25°C and Pore Diameter for Knudsen Flow

Gas	$\sigma \times 10^{10}$ m	Pressure	λ μm	d = 0.2 λ μm
CO_2	3.34	0.2 atm	0.4	0.08
O_2	2.98	0.2 atm	0.5	0.1
N_2	3.15	0.8 atm	0.1	0.02
He	1.9	0.01 atm	24.9	5.0

8.5.1.2.1 Mean free path

Knudsen flow takes place in a pore when the pore diameter, d, is smaller than one fifth of the molecular mean free path λ. The mean path can be estimated from the following equation (Cunningham and Williams, 1980)

$$\lambda = \frac{k_B T}{\left(\pi\sqrt{2}\sigma^2 p\right)} \tag{8.8}$$

where k_B is Boltzmann's constant = 1.38×10^{-23} J/K; and σ^2 is the collision diameter of diffusing molecule. Equation 8.8, indicates that the molecular mean free path increases with temperature and decreases with the gas pressure. For most packaging situations T = 25°C = 298.7K and the pressure is 1 atm or less.

EXAMPLE 8.2

Calculate λ for O_2 at 25°C and p = 0.2 atm.

Solution

From Equation 8.8

$$\sigma = 2.98 \times 10^{-10}\text{m (CRC Handbook, 64th Ed.)}$$

$$p = 0.2 \times 1.013 \times 10^5 \text{ Pa}$$

$$\lambda = \frac{1.38\times10^{-23}\times293.15}{\pi\sqrt{2}\times\left(2.98\times10^{-10}\times0.2\times1.013\times10^5\right)} = 5\times10^{-7}\text{m}$$

Other values of λ are presented in Table 8.20.

The Knudsen flow can be calculated through a pore in a package wall by applying Equation 8.7.

EXAMPLE 8.3

Calculate the Knudsen flow of oxygen O_2 throughout a 0.1×10^{-6} m diameter pore in a package wall of 100×10^{-6} m thick, assuming the $p_i - p_o$ is 0.2 atm (2.0265×10^4 Pa) at 25°C.

Solution

Applying Equation 8.7 for $d = 0.1 \times 10^{-6}$ m; $(p_i - p_o) = 2.0265 \times 10^4$ Pa; T = 298.15 K; $l = 10^{-4}$ m. The value of $\bar{v}$ is given in Table 8.19.

$$J = 706 \times \left(1 \times 10^{-7}\right)^3 \times 444 \times 2.0265 \times 10^4 / \left(298.15 \times 1 \times 10^{-4}\right)$$

$$J = 2.1 \times 10^{-10}\,\text{mL (STP)/s} \quad \text{for each pore.}$$

The total gas volume V transferred through 1000 pores during 100 days is

$$V = 2.1 \times 10^{-10} \times 1000 \times 100 \times 86400 = 1.8\ \text{mL of } O_2 \text{ at STP.}$$

EXAMPLE 8.4

Calculate the Knudsen flow of helium throughout 100 pores of 5×10^{-6} m diameter in a package 100 µm thick if $p_i - p_o = 0.01$ atm (1.013×10^3 Pa) and at 25°C

Solution

Applying Equation 8.7 for $d = 5 \times 10^{-6}$ m; $(p_i - p_o) = 1.013 \times 10^3$ Pa; T = 298.15 K; $l = 1 \times 10^{-4}$ m. The value of $\bar{v}$ is given in Table 8.19.

$$J = 706 \times \left(5 \times 10^{-6}\right)^3 \times 1256 \times 1.013 \times 10^3 / \left(298.15 \times 1 \times 10^{-4}\right)$$

$$J = 3.8 \times 10^{-4}\ \text{mL (STP)/s for each pore}$$

This type of flow may be significant in leak detection methods.

8.5.1.3 Flow in an Intermediate Pore

For d/λ in the range of 0.2 to about 20, a transition flow consisting of both molecular and Knudsen diffusion, take place in the pore. This flow is given by the following equation (Treybal, 1980)

$$N_A = \frac{N_A}{N_A + N_B} \frac{D_{AB,\,eff}\, p_t}{R \ell T} \ln \frac{\dfrac{N_A}{N_A + N_B}\left(1 + \dfrac{D_{AB,\,eff}}{D_{K,\,A,\,eff}}\right) - y_{A,\,o}}{\dfrac{N_A}{N_A + N_B}\left(1 + \dfrac{D_{AB,\,eff}}{D_{K,\,A,\,eff}}\right) - y_{A,\,i}} \tag{8.9}$$

where A and B are the diffusing molecules; N_A and N_B are the flux in mole/area time; D_{AB} is the molecular diffusion coefficient of A through B; $D_{AB,eff}$ is the effective diffusion coefficient which reflects the effect of the pore structure; $D_{K,A}$ is the Knudsen diffusion coefficient of A; and $D_{K,A,eff}$ is the effective Knudsen diffusion coefficient of A. Equation 8.9 shows that the flux does not depend on the diameter of the pore, d.

The effective diffusion coefficient is a measure of the tortuous path through the holes. For porous material this value generally is not known. However in packaging material, we can assume that the length of the pinhole is equal to the thickness of the package wall, i.e., no tortuous path. In this case the molecular diffusion coefficient D_{AB} and the effective diffusion coefficient $D_{AB,eff}$ can be considered no different.

8.5.1.4 Flow through Large Pores

When the ratio d/λ is greater than 20, ordinary molecular diffusion predominates and the equation describing steady state flow is (Treybal, 1980; Youngquist, 1970)

$$N_A = \frac{N_A}{N_A + N_B} \frac{D_{AB,\,eff} P_t}{R \ell T} \ln \frac{N_A / (N_A + N_B) - y_{Ao}}{N_A / (N_A + N_B) - y_{Ai}} \tag{8.10}$$

where $Y_A = p_A/p_t$ is the mole fraction; p_A is the partial of component A; and p_t is the total pressure. Subscripts o and i indicate outside and inside the package. Also

$$D_{AB} \propto \frac{T^{3/2}}{p} \tag{8.11}$$

For binary mixtures we have (Treybal, 1980)

$$\frac{N_A}{N_B} = -\left(\frac{M_A}{M_B}\right)^{1/2} \tag{8.12}$$

where M is the molecular weight.

EXAMPLE 8.5 (SMALL PORES)

Calculate the transition flow of oxygen, throughout a 2.0 μm diameter pore in a package seal of 1×10^{-4} m thick and with an external partial pressure of 0.21 atm and 0 atm inside the package. Nitrogen is 1 atm inside and 0.79 atm outside. Total pressure is 1 atm. Additional information includes

$$\frac{d}{\lambda} = \frac{2 \times 10^{-6}}{0.5 \times 10^{-6}} = 4$$

The dissusivity of the O_2–N_2 system at O°C is given by Treybal (1980).

$$D_{O_2-N_2} = 1.81 \times 10^{-5}\ m^2/s$$

from Equation 8.2, and Tables 8.15 and 8.16.

$$D_{K,O_2} = \frac{d}{3} v_A = \frac{1 \times 10^{-7}}{3} \times 444 = 1.5 \times 10^{-5}\ m^2/s$$

Solution

From Equation 8.11, the dissusivity at 25°C and 1 atm is

$$D_{O_2-N_2} = 1.81 \times 10^{-5} \times \left(\frac{298}{273}\right)^{3/2} = 2.06 \times 10^{-5}\ m^2/s$$

From Equation 8.4

$$\frac{N_{N_2}}{N_{O_2}} = -\frac{N_{O_2}}{N_{N_2}} = -\left(\frac{32}{28.02}\right)^{1/2} = -1.069$$

Applying Equation 8.9 for the following condition,

$$y_{O_2,o} = 0.21\,\text{atm} \quad y_{O_2,i} = 0 \quad p_t = 1.01325\times10^5\ \text{N/m}^2 \quad \ell = 10^{-4}\ \text{m}$$

$$\frac{N_{O_2}}{N_{O_2}+N_{N_2}} = \frac{1}{1+\dfrac{N_{N_2}}{N_{O_2}}} = 14.49 \quad \frac{D}{}$$

Substituting value, Equation 8.9 finally becomes

Substituting values

$$N_{O_2} = \frac{-14.49\times1.81\times10^{-5}\times1.013\times10^5}{8314(29.8)\times10^{-4}}\,\ell n\,\frac{-14.49(1+1.2)-0}{-14.49(1+1.2)-1.21}$$

$$N_{O_2} = 7.0\times10^{-4}\ \text{kmol/m}^2\cdot\text{s}$$

$$J = N_{O_2}\times\text{pore Area}\times22,414\times10^3 = 7\times10^{-4}\times\frac{\pi}{4}\times\left(2\times10^{-6}\right)^2\times22,414\times10^3$$

$$J = 5.1\times10^{-3}\ \text{mL/s}$$

which is the flow per pore 2 μm in diameter.

EXAMPLE 8.6 (LARGE PORES)

For the same condition as the previous example, assume that the pore diameter is now 40 μm

$$\frac{d}{\lambda} = \frac{40\times10^{-6}}{0.5\times10^{-6}} = 80$$

Solution

Applying Equation 8.10

p_t = 1 atm = 1.012 × 10^5 Pa

$$\frac{N_{O_2}}{N_{O_2}+N_{N_2}} = -14.49, \quad \ell = 10^{-4}\ \text{m}, \quad T = 298\ \text{K}, \quad y_{O_2,o} = 0.21\,\text{atm}, \quad y_{O_2,i} = 0$$

$$N_{O_2} = \frac{-14.49\times1.81\times10^{-5}\times1.013\times10^5}{8314\times(298)\times10^{-4}}\ln\frac{-14.49-0}{-14.49-0.2}$$

$$N_{O_2} = 1.47\times10^{-3}\ \text{kmol/m}^2\cdot\text{s}$$

$$J = N_{O_2} \times \text{pore area} \times 22414 \times 10^3 = 1.47 \times 10^{-3} \times \frac{\pi}{4}\left(40 \times 10^{-6}\right)^2 \times 22414 \times 10$$

$$J = 4.1 \times 10^{-5}\ \text{mL/s per por 40 μm in diameter}$$

8.5.1.5 Hydrodynamic Flow of Gas (Poiseuille's Flow)

When there is a difference in absolute pressure across the porous solid, such as by action of a vacuum pump, a hydrodynamic flow through the straight capillary tube will occur. For a single gas obeying the ideal gas law and for relatively small velocities (Reynolds number <2100), the flow can be described by Poiseuille's Law (Treybal, 1980) where

$$J = \frac{\pi d^4\left(p_i - P_2\right)}{128\,\mu\ell} \tag{8.13}$$

where J is the flow in m^3/s through the pore; d is the pore diameter, ($d/\lambda > 20$), m^2; $p_i - p_2$ is the pressure differential in Pa; μ is the viscosity of gas in $N \cdot s/m^2 = kg/m^2s$; and l is the capillary length, equal to the package's wall thickness.

EXAMPLE 8.7 POISEUILLE'S FLOW

Assume that a package containing a processed meat with a headspace atmosphere composition of 80% N_2 and 20% of CO_2, is tested for seal integrity by a vacuum nondestructive test (Jensen, 1994).

Assume that the test lasts 24 s and is desired to reach a maximum level leak of 300 ppm of CO_2 in the vacuum chamber having a volume of 0.013 m^3. The thickness of the package is 62 μm. The inside pressure of the package p_i = 1 atm and the outside vacuum is 0.6 atm. The temperature of testing is 25°C. Estimate the size of the pore allowing this leak.

Solution

The viscosity of the mixture $\mu = (0.8 \times 0.180 + 0.2 \times 0.15) \times 10^{-4} = 0.174 \times 10^{-4}$ Pa·s (Perry and Green, 1984). With these values J can be calculated.

$$J = \frac{0.013 \times 300 \times 10^{-6}}{24 \times 0.2} = 8.125 \times 10^{-7}\ \text{m}^3/\text{sec}$$

If $\mu = 0.174 \times 10^{-4}$ Pa·s and $p_1 - p_2 = 0.4 \times 1.01325$ Pa, solving for d in Equation 8.13

$$d = \left[\frac{128\,\mu\ell\,J}{\pi\left(p_1 - p_2\right)}\right]^{1/4} = \left[\frac{128 \times 0.174 \times 10^{-4} \times 62 \times 10^{-6} \times 8.125 \times 10^{-7}}{\pi \times 0.4 \times 1.01325 \times 10^5}\right]$$

$$d = 30.6 \times 10^{-6}\ \text{m}$$

8.5.1.5.1 Leak detection

Test equipment for leak detection based on the measurement of trace gas can provide good information on the package integrity. However, calculating the size of an ideal pinhole is less certain because several factors are unknown. These factors include the real geometry of the leak and more importantly the number of the leak points. Other factors related to the test apparatus (such as sensitivity and sample procedure) may also affect the result. If more than one pinhole is present in the package, Equation 8.12 can be written as

$$J = \frac{\pi(p_1 - p_2)}{128\,\mu\ell} \sum_i^n d_i^4 \tag{8.14}$$

where n is the number of pinholes and d_i is the average diameter of each pinhole. However, a single pinhole having an equivalent flow to the n pinholes will have a diameter,

$$d^4 = \sum_i^n d_i^4$$

If the pores are considered all the same size

$$d_i = \frac{d}{n^{1/4}} \tag{8.15}$$

where d_e is the diameter of the equivalent pinhole. Equation 8.14 indicates that the flow J in Example 8.7 could also be produced by, for instance, 100 pores 9.5 μm in diameter.

8.5.2 Permeability

The concept of permeability is normally associated with the quantitative evaluation of the "barrier" property of a material. A material that is a good barrier has low permeability value.

Polymers unlike metals, glass, and ceramic, are permeable materials. The phenomenon of permeability takes place when a polymer wall separates two fluid phases that contain low molecular weight species having different values of activity in each of the phases. The molecules at the high side concentration, or activity, tend to diffuse through the polymer structure and reach the other side to eventually equalize concentration at both phases.

8.5.2.1 Barrier Material

The barrier property of a plastic structure is the physical resistance that it opposes to the passage of any molecule or compound able to diffuse through the polymer: oxygen, carbon dioxide, water, and odors from air or headspace; flavors, aromas, and components from food; and external compounds contained either in secondary packages (e.g., corrugated boxes), board components (like vanillin and o-vanillin), or remains of solvents. In packaging design, it is very important to know the barrier characteristics of a package. An optimum package design results from balancing the packaging material properties, product protection requirements, environmental and transport conditions, and cost considerations. The barrier characteristics of the polymeric material relates mainly to its chemical structure. A polymeric structure can be polar or nonpolar, and a polar polymer can be hydrophilic or not. Polar hydrophilic polymers are good gas and organic vapor barriers when dry but are poor gas barriers when wet (e.g., nylons and EVOH). Conversely, the barrier properties of polar nonhydrophilic polymers containing groups such as nitrile, chlorine, or fluorine, are not dependent on the presence of water molecules. Similarly nonpolar polymers, e.g., polyolefins, are not affected by the presence of water, but they are not as good a barrier as the polar polymer, except against a polar water molecule itself. We also may say that like permeates like.

8.5.2.2 Permeation Mechanism

Figure 8.4 illustrates the sorption and diffusion mechanisms that take place through a package film or sheet structure surrounded by two fluid phases, to determine a permeation process.

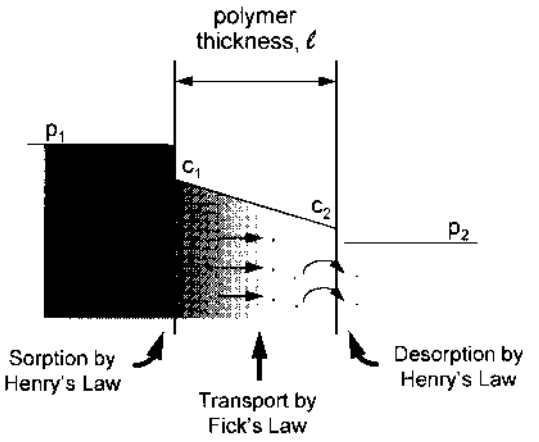


FIGURE 8.4 Permeation mechanism.

The permeation process involves three steps. (1) The permeant molecule from the contracting fluid phase at a partial pressure, p_1, penetrates the polymer surface. For pressure below one atmosphere, the value of the permeant concentration at the polymer interphase follows Henry's Law. (2) The permeant diffuses within the polymer film from the side of high concentration toward the side of low concentration according to Fick's laws. (3) The permeant leaves the opposite polymer interphase to diffuse in the adjacent continuous phase (liquid or gas phase) at a pressure p_2.

8.5.2.3 Permeability, WVTR, and Gas Transmission Rate

The solution of the diffusion equation through a nonporous polymer film at steady state is given by

$$F = -D\frac{\Delta c}{\ell} \tag{8.16}$$

where F is the flux through the film [or gas transmission rate (GTR)], Δc is the permeant concentration in the polymer/gas phase interphase, $c_1 - c_2$ and D is the diffusion coefficient. The value of c can be related to the partial pressure p through Henry's law of equilibrium

$$c = Sp \tag{8.17}$$

where S is the solubility coefficient in kg permeant/m^3 polymer · Pa. Where D is concentration-independent and the sorption equilibrium between the permeant and polymer follows Henry's law, Equations 8.16 and 8.17 can be combined to give

$$F = DS\frac{\Delta p}{\ell} = \frac{q}{At} \tag{8.18}$$

and

$$F\frac{\ell}{\Delta p} = P = DS \tag{8.19}$$

TABLE 8.21
Units of permeability, permeance, and Gas Transmission Rate

		Common Units	SI	Fundamental dimension	
Amount of mass	q	g, cm^3(STP), mol	kg	M	Mass
Thickness	l	cm/ mil	m	L	Length
Time	t	h, d	s	θ	Time
Area	A	cm^2, in^2	m^2	L^2	Length
Partial pressure	p	atm, psi, mmHg	Pa	F/L^2	Force/length

where P = permeability and coefficient; t = time, during which the permeation process takes place; l = thickness of the material with permeability P; Δp = difference of pressure at both sides of the film where P is the permeability coefficient; A = area of the package exposed to the permeation process with the same permeability value; and q = total quantity of the permeant throughout the exposed area during time t. A dimensional analysis of P indicates that the fundamental unit of P is time if the solubility coefficient is expressed in $Kg/m^2 \cdot Pa$

$$[P] = [D][S] = \left[\frac{L^2}{\theta}\right]\left[\frac{\theta^2}{L^2}\right] = [\theta] \text{ or sec in the SI}$$

Combining Equations 8.18 and 8.19 gives the well-known relation for P

$$P = \frac{q \cdot \ell}{t \cdot A \cdot \Delta p} \tag{8.20}$$

Tables 8.21 and 8.22 present units for Equation 8.20 and common conversion factors for permeability units, respectively. Permeability can be expressed in seconds or, most commonly, in any combination of the above units.

The relationship between water vapor transmission rate (WVTR), GTR, Permeance, normalized WVTR, and permeability coefficient P is indicated in Figure 8.5.

EXAMPLE 8.8

The gas transmission rate of oxygen through a film of PE, 1 mil thick is GTR = F = $3.5 \times 10^{-2} \frac{g}{h \cdot m^2}$ and the differential in partial pressure through the film Δp = 30 mmHg. Calculate permeance and permeability coefficient.

Solution

$$\text{Permeance} = \text{GTR.} \quad \frac{1}{\Delta p}$$

$$\frac{1}{\Delta p} = \frac{3.5 \times 10^{-2}\ g}{30\ h \cdot m^2\ mmHg} = 1.17 \times 10^{-3} \frac{g}{h \cdot m^2 \cdot mmHg}$$

$$\text{Permeance} = \frac{GTR}{\Delta p} \times \text{thickness} =$$

$$\frac{1.17 \times 10^{-3}\ g \times 2.54 \times 10^{-3} cm}{h \cdot m^2 \cdot mmHg} = 2.96 \times 10^{-6} \frac{g - cm}{h \cdot m^2 \cdot mmHg}$$

TABLE 8.22
Permeability Units Conversion Table

Convert from	Convert to	Multiplier
s	as	1×1^{-18}
s	$\frac{kg \cdot m}{m^2 \cdot s \cdot Pa}$	1
$\frac{kg \cdot m}{m^2 \cdot s \cdot Pa}$	$\frac{kg \cdot \mu m}{m^2 \cdot d \cdot kPa}$	8.64×10^{13}
$\frac{g \cdot mil}{m^2 \cdot d}$ at 100°F and 90% RH	$\frac{g \cdot \mu m}{m^2 \cdot d \cdot kPa}$	4.264
$\frac{kg \cdot \mu m}{m^2 \cdot d \cdot kPa}$	$\frac{g \cdot mil}{m^2 \cdot d\ at}$	3.989×10^3
$\frac{kg \cdot m}{m^2 \cdot s \cdot Pa}$	$\frac{g \cdot mil}{100\ in^2 \cdot d\ at}$	2.224×10^{16}
$\frac{g \cdot mil}{100\ in^2 \cdot d}$ at 100°F and 90% RH	$\frac{g \cdot \mu m}{m^2 \cdot d \cdot kPa}$	66.09
$\frac{kg \cdot m}{m^2 \cdot s \cdot Pa}$	$\frac{m^3(STP) \cdot m}{m^2 \cdot s \cdot Pa}$	$\frac{22.414}{MW}$
$\frac{m^3(STP) \cdot m}{m^2 \cdot s \cdot Pa}$	$\frac{cc(STP) \cdot mil}{100\ in^2 \cdot d \cdot atm}$	2.2237×10^{19}
$\frac{cc(STP) \cdot mil}{100\ in^2 \cdot d \cdot atm}$	$\frac{cc(STP) \cdot \mu m}{m^2 \cdot d \cdot kPa}$	3.883
$\frac{cc(STP) \cdot mil}{100\ in^2 \cdot d \cdot at}$	$\frac{cc(STP) \cdot mil}{m^2 \cdot d \cdot at}$	15.5
as	$\frac{cc(STP) \cdot mil}{m^2 \cdot d \cdot at}$	$\frac{1936.57}{MW}$
as	$\frac{cc(STP) \cdot mil}{100\ in^2 \cdot d \cdot atm}$	$\frac{498.47}{MW}$

* as = 1 atto sec = 1×10^{-18} sec; MW = molecular weight of permeant; RH = relative humidity. STR = standard temperature and pressure (0°C; 1 atm)

EXAMPLE 8.9

Calculate the water permeability coefficient of a polymer film 38.1 μm thick (1.5 mil) having a WVTR value of 0.1 g/dm² at 38°C (100°F) and 90% RH (ASTM conditions).

Solution

To calculate P, we need to multiply WVTR by the thickness over the pressure differential across the film.

$$P = WVTR \times \frac{1}{\Delta p}$$

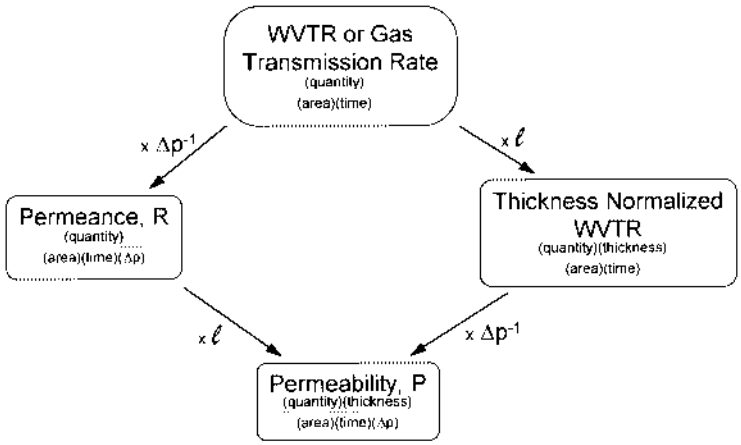


FIGURE 8.5 Relation between water vapor transmission rate (WVTR), gas transmission rate, permeance, thickness normalized WVTR, and permeability coefficient.

since

$$RH = \frac{p}{ps} \times 100$$

where p^s is the saturation vapor pressure of water,

$$p = \frac{p^s}{100} RH$$

therefore

$$\Delta p = p_o - p_i = \frac{p^s}{100}\left(RH_o - RH_i\right)$$

According to ASTM E 96 test $p_i = 0$ because it is in equilibrium with the desiccant. From Perry's Handbook page 3-45 (Perry and Green, 1984), p^s at 38°C: 49.7 mmHg

$$\Delta p = \frac{49.7}{100} \times 90 = 44.73\ \text{mmHg} = 5.88 \times 10^{-2}\ \text{atm} = 5.964\ \text{Pa}$$

$$P = \frac{WVTR \cdot \ell}{\Delta p} = \frac{0.1 \times 10^{-3} \times 38.1 \times 10^{-6}}{5964 \times 3600 \times 24} = 7.40 \times 10^{-18}\ \frac{\text{kg} \cdot \text{m}}{\text{m}^2 \cdot \text{s} \cdot \text{Pa}} = 9.8\ \text{as}$$

8.5.2.4 Variables Affecting Permeability

1. The chemical structure of the polymer and the permeant, determines the particular level of interaction. There is a value of permeability for each pair of polymer/permeant.
2. Polymer morphology; an increase in polymer crystallinity (density), orientation, or cross-linking, decreases permeability.

3. Humidity increases or decreases permeability (especially in hydrophilic polymers). Oxygen permeability increases with relative humidity for EVOH and Nylon 6. However, oxygen permeability decreases in amorphous nylon.
4. An increase in temperature increases permeability.
5. Fillers generally decrease permeability, however, the effect is complicated by the type, shape, and amount of filler and the interaction with permeant.
6. Concentration of the permeant, in general, is found to have no effect at low and moderate pressure for gases, and low-activity values for organic compounds in the range of Henry's Law. Strong effects can be found for organic compounds at high values of activity (Liu et al., 1991).
7. Plasticizers, usually, but not always, increase the permeability.
8. Film thickness does not affect, in principle, the permeability, the diffusion coefficient, or the solubility. However, film of different thicknesses may have different morphologies generated, e.g., by having different cooling characteristics during processing.
9. Molecular weight of a polymer has been found to have little effect on the permeability of a polymer except in the very low range of molecular weight.

8.5.2.4.1 Effect of temperature

The change in permeability with temperature is given by the following equation

$$P = P_o e^{-\frac{E_P}{RT}} \tag{8.21}$$

where E_p is the activation energy, R the gas constant, P_o is a pre-exponential term and T is temperature in Kelvin.

If a value of permeability P_1 is given at temperature T_1, the value of the permeability P_2 at T_2 can be calculated if E_p is known.

$$P_2 = P_1 \cdot \exp \frac{E_p}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{8.22}$$

That can be written as

$$P_2 = P_1 \cdot f \tag{8.23}$$

where

$$f = \exp \frac{E_p}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{8.24}$$

EXAMPLE 8.10

The permeability of oxygen in PET at 25°C is

$$P = 22 \frac{cc \cdot \mu m}{m^2 \cdot d \cdot kPa}$$

Calculate the value of permeability of PET at 50°C. Temperature = 25°C = 25 + 273.15 = 298.15 K.

Solution

From Table 8.23 is E_p = 32 KJ/mol = 7.6 kcal/mol

$$\frac{Ep}{R} = \frac{7600}{1.987} = 3{,}849\ K$$

$$\frac{1}{T_1} - \frac{1}{T_2} = \frac{1}{25+273} - \frac{1}{50+273} = .0002597\ K$$

From Equation 8.25

$$f = \frac{E_p}{e^p}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) = e^{3.849 \times 0.0002597} = 0.09996 = 2$$

Substituting in Equation 8.23

$$P_2 \cdot f = P_2 = P_1 \times 2.74 = 22 \times 2.74 = 60.3 \frac{cc \cdot \mu m}{m^2 \cdot d \cdot kPa}$$

Values of f are given in Table 8.20 and plotted in Figure 8.6 for values of P_1 at 25°C and from 0 to 50°C. E_p varies between 3 and 20 kcal/mol

EXAMPLE 8.11

For the above example calculate f from Table 8.24.

Solution

Ep = 7.6 kcal

T_2 = 50°C

f = 2.7 (interpolated between 2.49 and 2.84)

8.5.2.5 Measuring Permeability

Determination of WVTR is described in ASTM E96. Determination of permeability of O_2 and CO_2 is covered by ASTM D1434. For organic compounds there is not an ASTM standard, however, continuous and quasi-isostatic methods are discussed by Hernandez, et al. (1986).

A consistency analysis to measure the permeability based on the experimental data for the continuous flow method is discussed by Hernandez and Gavara, (1993).

8.5.2.6 Multilayer Structures

The permeability of a packaging wall made of a multilayer structure is given by the following equation

$$P_T = \frac{L_T}{\sum_i^n \frac{\ell_i}{P_i}} \tag{8.25}$$

where P_T is the total permeability coefficient of the structure; L_T total thickness, $L_T = \Sigma l_i$; n is the number of layers, and, l_i, and P_i are the thickness and permeability coefficient of each layer.

8.5.2.6.1 Permeance

The ratio $\frac{P_i}{\ell_i} = R$ is permeance. Equation 8.25 can then be written as

$$R_r = \left(\sum \frac{1}{R_i} \right)^{-1} \tag{8.26}$$

where R_T is the total permeance of the structure and R_i is the permeance of each layer.

8.5.2.6.2 WVTR

Similarly for WVTR

$$\frac{\Delta P_T}{(WVTR)_T} = \sum_i^n \left(\frac{\Delta p}{WVTR} \right)_i \tag{8.27}$$

or

$$(WVTR)_T = \frac{\Delta P_T}{\sum_i^n \left(\frac{\Delta P}{WVTR} \right)_i} \tag{8.28}$$

EXAMPLE 8.12

Calculate the total oxygen permeability of the following multilayer structure (units in cc $\mu m/m^2 \cdot d \cdot kPa$)

Solution

From Equation 8.25

$$\frac{L_T}{P_T} = \sum_1^3 \frac{\ell_i}{P_i}$$

$$P_T = \frac{L_T}{\sum_1^3 \frac{\ell_i}{P_i}}$$

$$L_T = 18 + 10 + 20 = 48\ \mu m$$

$$\sum_1^3 \frac{\ell_i}{P_i} = \frac{\ell_1}{P_1} + \frac{\ell_2}{P_2} + \frac{\ell_3}{P_3} = \frac{18}{1900} + \frac{20}{25} + \frac{20}{620} = 0.4417 \frac{m^2 \cdot d\ kPa}{cc}$$

$$P_T = \frac{48}{0.4417} = 109 \frac{cc \cdot \mu m}{m^2 \cdot d \cdot kPa}$$

The effect of temperature on the permeability of a multilayer structure is

$$P_T = \frac{L_T}{\sum_1^i \frac{\ell_i}{P_{1,i}\, f_i}} \tag{8.29}$$

where f_i is given by Equation 8.24 and can be obtained from Table 8.20 or Figure 8.6 for each layer, and $P_{1,i}$ is the permeability at temperature 1 for each layer i of the structure. Equation 8.29 can be written as

$$\left(\frac{P_T}{L_T}\right)^{-1} = \sum_1^i \frac{\ell_i}{P_{2i}\, f_i} \tag{8.30}$$

EXAMPLE 8.13

Calculate the total oxygen permeability P_T for the following structure at 40°C. Values of P were obtained at 25°C.

$f_1 = 2.29$, $f_2 = 2.34$, and $f_3 = 2.53$, obtained from Table 8.20.

$$L_T = \ell_1 + \ell_2 + \ell_3 = 48\ \mu m$$

Applying Equation 8.30

$$P_T = \left(\frac{18}{1{,}900 \times 2.29} + \frac{10}{25 \times 2.34} + \frac{20}{1{,}500 \times 2.53}\right)^{-1} 48$$

$$P_T = 266 \frac{cc \cdot \mu m}{m^2 \cdot d \cdot kPa}$$

Note: If this calculation were based only on the barrier layer, Nylon 6, neglecting the barrier contribution of both LDPE and PP, we would obtain

$$P_T = 280 \frac{cc \cdot \mu m}{m^2 \cdot d \cdot kPa}$$

8.5.2.7 Application of Permeability to Material Section and Shelf-Life Estimation

Gas permeability values presented in Figures 8.7 and 8.8 for easy comparison. Permeability values of organic compounds have been compiled by Hernandez and Giacin (1996).

Equation 8.20 is a simple but useful design equation for packages. It provides a basic relationship among the main variables associated with a packaging system: quantity of permeant transferred, thickness of the package, area, storage conditions (temperature and humidity), shelf-life, and permeability. More elaborate model can be found in the works of Labuza et al., (1972), Karel (1974), Kim (1992), and Pocas (1995).

Equation 8.20 is valid for steady state value. Also, it is assumed that the container does not have any pinholes or cracks. Besides its limitations, Equation 8.20 can be a first approx-

TABLE 8.23
Permeability, Diffusion and Solubility Coefficients

	Temperatures (°C)	P	Ep	S × E3	D × E10
Polyethylene LDPE (d = 0.914 g/cc)					
H_2	25	6.4E + 03		1.6E + 00	4.7E – 01
He	25	3.2E + 03	3.5E + 01	5.0E – 02	6.8E + 00
O_2	25	1.9E + 03	4.3E + 01	4.7E – 01	4.6E – 01
CO_2	25	7.0E + 02	3.9E + 01	2.5E + 00	3.7E – 01
N_2	25	6.3E + 02	4.9E + 01	2.3E – 01	3.2E – 01
CH_4	25	l.9E + 03	4.7E + 01	l.lE + 00	1.9E – 01
H_2O	25	5.9E + 04	3.4E + 01		
HDPE (d = 0.964 g/cc)					
He	25	7.4E + 02	3.0E + 01	2.8E – 02	3.1E + 00
O_2	25	2.6E + 02	3.5E + 01	1.8E – 01	1.7E – 01
CO_2	25	2.3E + 02	3.0E + 01	2.2E – 01	1.2E – 01
N_2	25	9.5E + 01	4.0E + 01	1.5E – 01	9.3E – 02
CH_4	25	2.5E + 02	4.lE + 01	5.lE – 01	5.7E – 02
H_2O	25	7.8E + 03			
Polypropylene (d = 0.907 g/cc) 50% crystallinity					
He	20	2.4E + 02	3.2E + 01		2.0E + 01
O_2	25	6.2E + 02	4.8E + 01		
CO_2	25	2.lE + 03	3.8E + 01		
N_2	25	8.0E + 01	5.6E + 01		
H_2O	30	4.4E + 04	4.2E + 01		
Poly (ethylene-co-propylene) 40/60 amorphous					
N_2	24.1	3.5E + 03	4.2E + 01	4.4E – 01	9.4E – 01
Polystyrene, biaxially oriented					
He	25	1.2E + 04			
O_2	25	1.lE + 03			
CO_2	25	3.5E + 03			
N_2	25	5.2E + 02			
H_2O	25	7.3E + 05	–8.0E + 00		
Polyacrylonitrile(Barex)					
O_2	25	3.5E + 00			
CO_2	25	1.0E + 01			
H_2O	25	4.2E + 05			
Polyvinyl acetate					
He	30	8.2E + 03	l.3E + 01	7.8E – 02	6.5E + 00
O_2	30	3.lE + 02	5.6E + 01	6.4E – 01	5.6E – 02
CH_4	25	2.0E + 01	8.3E + 01	1.4E + 00	1.7E – 03
Ethylene vinyl alcohol (E 32%)					
O_2 (0% RH)	25	3.0E – 02			
O_2 (65% RH)	25	2.0E – 01			
H_2O	25	3.1E + 05			
Ethylene Vinyl Alcohol (E 44%)					
O_2 (0% RH)	25	1.5E – 01			
O_2 (65% RH)	25	3.0E – 01			
H_2O	25	1.lE + 05			
PVC, unplasticized					
O_2	25	2.9E + 01	5.6E + 01	2.9E – 01	1.2E – 02
CO_2	25	1.0E + 02	5.7E + 01	4.7E – 00	2.5E – 03
N_2	25	7.7E + 00	6.9E + 01	2.3E – 01	3.8E – 03
CH_4	25	1.8E + 01	6.6E + 01	1.7E + 00	1.3E – 03
H_2O	25	1.8E + 05	2.3E + 01	8.7E + 02	2.4E – 02
O_2 (plasticized)	25	3.2E + 03			

TABLE 8.23 (continued)
Permeability, Diffusion and Solubility Coefficients

	Temperatures (°C)	P	Ep	S × E3	D × E10
Polyvinylidene chloride (Saran)					
O_2	30	3.3E + 00	6.7E + 01		
CO_2	30	1.9E + 01	5.2E + 01		
N_2	30	6.0E + 01	7.0E + 01		
H_2O	25	6.0E + 03	4.6E + 01		
H_2S	30	2.3E + 01	7.5E + 01		
Polytetrafluorethylene (Teflon)					
O_2	25	2.8E + 03	1.9E + 01	2.lE + 00	1.5E – 01
CO_2	25	6.5E + 03	1.4E + 01		
N_2	25	8.6E + 02	2.4E + 01	1.2E + 00	8.8E – 02
CH_4	90	3.3E + 03	3.4E + 01	1.7E + 00	2.2E – 01
Polyisoprene, rubber					
O_2	25	1.5E + 04	2.9E + 01	1.0E + 00	1.7E + 00
CO_2	25	9.9E + 04	2.2E + 01	9.2E + 00	1.3E + 00
N_2	25	6.lE + 03	3.6E + 01	6.lE – 01	1.2E + 00
H_2O	25	1.5E + 06			
CH_4	25	2.0E + 04	3.lE + 01	2.6E + 00	8.9E – 01
PET 40% crystallinity					
O_2	25	2.2E + 01	3.2E + 01	7.2E – 01	3.5E – 03
CO_2	25	8.0E + 01	1.8E + 01	2.0E + 01	6.0E – 04
N_2	25	3.9E + 01	3.3E + 01	4.5E – 01	1.3E – 03
H_2O	25	8.5E + 04	2.9E + 00		
CH_4					
PET amorphous					
O_2	25	3.8E + 01	3.8E + 01	9.8E – 01	4.5E – 03
CO_2	25	2.0E + 02	2.8E + 01	2.8E + 01	8.0E – 04
Polycarbonate(lexan)					
O_2	25	9.lE + 02	1.9E + 01	5.0E + 00	2.lE – 02
CO_2	25	5.2E + 03	1.6E + 01	1.2E + 01	4.8E – 03
N_2	25	1.9E + 02	2.5E + 01		

TABLE 8.23 (continued)
Permeability, Diffusion and Solubility Coefficients

	Temperatures (°C)	P	Ep	S × E3	D × E10
H_2O	25	9.lE + 05			6.8E – 01
Nylon 6					
O_2 (100% RH)	25	2.5E + 01	4.4E + 01		
CO_2	25	5.0E + 01	4.lE + 01		
N_2	25	3.5E + 00	4.7E + 01		
H_2O	25	1.2E + 02			
Nylon 6,6 drawn					
CO_2	25	4.5E + 01		1.5E + 01	
Nylon 11					
CO_2	40	6.5E + 02	3.4E + 01	4.9E – 01	1.9E – 02
Cellophane					
O_2(0% RH)	25	1.4E + 00			
O_2(76% RH)	25	5.7E + 00			
CO_2(0% RH)	25	3.0E + 00			
CO_2(76% RH)	25	4.7E + 01			
N_2(0% RH)	25	2.lE + 00			
N_2(76% RH)	25	4.8E + 00			
H_2O	25	1.6E + 07			

Note: These values are provided as a general guide. P = cc(STP) μm/m²·d·kPa; D = m²/s; S = cc(STP)/cc·kPa; E_p = kJ/mol; LDPE = low density polyethylene; HDPE = high density polyethylene; PET = polyethylene terephthalate; PVC = polyvinyl chloride; RH = relative humidity.

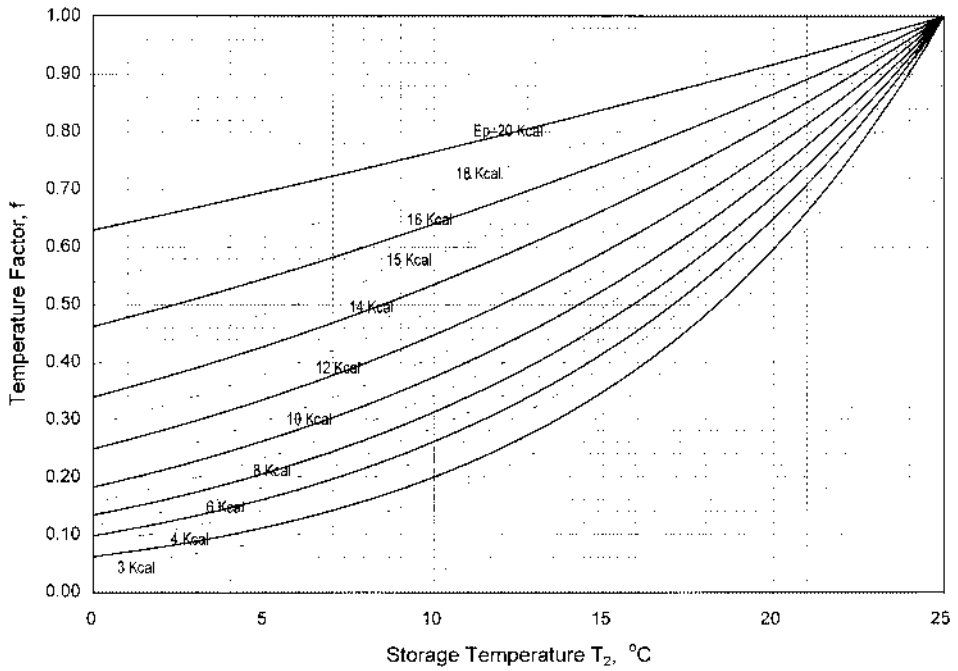


FIGURE 8.6a Values of f (Equation 8.23) for $0 < T_1 < 25°C$

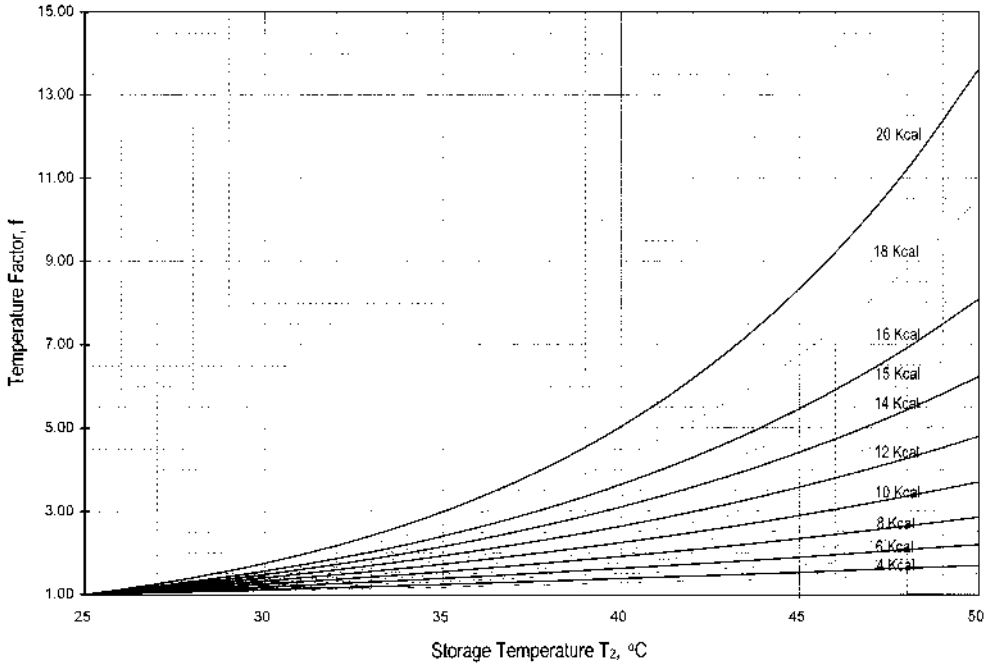


FIGURE 8.6b Values of f (Equation 8.23) for 25°C $<T_1<$50°C

imation designing tool in the selection of important package parameters. A careful analysis of the assumption and limitations however, must be practiced. Consider two cases, Δp constant and Δp variable. The simplest case in Equation 8.20 is when Δp can be considered constant. Consider the case of an oxygen-sensitive product for which the kinetic and type-of-product failure is known. Since the product reacts with any entering oxygen molecule the oxygen headspace concentration always is assumed to be zero.

EXAMPLE 8.14

Calculate the minimum packaging thickness for protection and loss of product. A water-based product has a compound that reacts with oxygen, producing unwanted effects. Analysis has shown that when the product reacts with an amount of oxygen equivalent to 0.005% (wt/vol), i.e., 50 ppm of oxygen, it is no longer acceptable for sale. Also, assume that PET is the packaging material and that the product volume is 500 ml. Further, the area of the package is around 400 cm^2 and it is expected that the package will be stored at 25°C and around 60% RH. Estimate the minimum thickness of the package to protect the product from oxygen for 6 months. In addition, for the calculated thickness, estimate the loss of water during the 6-month period.

Solution

From Equation 8.20 the thickness of the package is

$$\ell = \frac{PtA\,\Delta p}{q}$$

From Table 8.19 the permeability of PET at 25°C,

TABLE 8.24
Values of f (Equation 23)

	E_p (Kcal/mol)															
T_2 (°C)	3	4	5	6	7	8	9	10	11	12	13	14	15	16	18	20
0	0.629	0.538	0.461	0.395	0.338	0.290	0.248	0.213	0.182	0.156	0.134	0.115	0.098	0.084	0.062	0.045
2	0.654	0.568	0.493	0.428	0.372	0.323	0.280	0.243	0.211	0.183	0.159	0.138	0.120	0.104	0.078	0.059
4	0.681	0.599	0.527	0.463	0.408	0.359	0.315	0.278	0.244	0.215	0.189	0.166	0.146	0.129	0.100	0.077
6	0.708	0.631	0.562	0.501	0.447	0.398	0.355	0.316	0.282	0.251	0.224	0.199	0.178	0.158	0.126	0.100
8	0.736	0.664	0.599	0.541	0.488	0.441	0.398	0.359	0.324	0.293	0.264	0.239	0.215	0.194	0.158	0.129
10	0.764	0.699	0.639	0.584	0.534	0.488	0.446	0.408	0.373	0.341	0.312	0.285	0.260	0.238	0.199	0.166
12	0.793	0.734	0.680	0.629	0.582	0.539	0.499	0.462	0.428	0.396	0.366	0.339	0.314	0.291	0.249	0.213
14	0.823	0.771	0.723	0.677	0.635	0.595	0.557	0.522	0.489	0.459	0.430	0.403	0.378	0.354	0.311	0.273
16	0.853	0.810	0.768	0.728	0.691	0.655	0.622	0.590	0.559	0.531	0.503	0.477	0.453	0.429	0.386	0.348
18	0.885	0.849	0.815	0.783	0.751	0.721	0.692	0.665	0.638	0.612	0.588	0.564	0.542	0.520	0.479	0.442
20	0.916	0.890	0.865	0.840	0.816	0.792	0.770	0.748	0.726	0.705	0.685	0.666	0.647	0.628	0.593	0.559
22	0.949	0.933	0.916	0.901	0.885	0.870	0.855	0.840	0.825	0.811	0.797	0.783	0.770	0.757	0.731	0.706
24	0.982	0.976	0.971	0.965	0.959	0.953	0.948	0.942	0.937	0.931	0.925	0.920	0.914	0.909	0.898	0.888
25	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
26	1.016	1.022	1.027	1.033	1.038	1.044	1.049	1.055	1.061	1.066	1.072	1.078	1.084	1.090	1.101	1.113
28	1.051	1.068	1.086	1.104	1.123	1.141	1.160	1.180	1.199	1.219	1.240	1.260	1.281	1.303	1.347	1.392
30	1.086	1.117	1.148	1.180	1.213	1.247	1.281	1.317	1.354	1.392	1.431	1.471	1.512	1.554	1.642	1.735
32	1.122	1.166	1.212	1.259	1.309	1.360	1.413	1.469	1.526	1.586	1.648	1.713	1.780	1.850	1.997	2.157
34	1.159	1.217	1.279	1.343	1.411	1.482	1.557	1.635	1.718	1.804	1.895	1.991	2.091	2.196	2.423	2.674
36	1.196	1.270	1.348	1.431	1.520	1.613	1.713	1.818	1.930	2.049	2.175	2.309	2.451	2.602	2.933	3.305
38	1.235	1.324	1.421	1.524	1.635	1.754	1.882	2.019	2.166	2.323	2.492	2.673	2.868	3.077	3.541	4.075
40	1.273	1.380	1.496	1.622	1.758	1.905	2.065	2.238	2.426	2.630	2.850	3.089	3.349	3.630	4.264	5.010
42	1.313	1.438	1.574	1.724	1.888	2.067	2.264	2.479	2.714	2.972	3.254	3.564	3.902	4.273	5.124	6.144
44	1.353	1.497	1.656	1.831	2.026	2.241	2.478	2.741	3.032	3.354	3.710	4.103	4.539	5.020	6.142	7.514
46	1.394	1.558	1.740	1.944	2.172	2.426	2.710	3.028	3.383	3.779	4.222	4.716	5.269	5.886	7.346	9.168
48	1.436	1.620	1.828	2.062	2.326	2.624	2.961	3.340	3.768	4.252	4.796	5.411	6.105	6.887	8.766	11.158
50	1.478	1.684	1.918	2.185	2.490	2.836	3.231	3.681	4.193	4.776	5.441	6.198	7.061	8.044	10.438	13.546

	Polymer	Thickness (μm)	P_i at 25°C	Ep (kcal/mol)
Layer 1	LDPE	18	1,900	10.2
Layer 2	Nylon 6	10	25.0	10.5
Layer 3	PP	20	620	11.5

Layer no.	Polymer type	Thickness (μm)	P_i at 25°C $\left(\frac{cc \cdot \mu m}{m^2 \cdot d \cdot kPa}\right)$	Ep (kcal/mol) From Table
1	PE	18	1,900	10.3
2	Nylon 6	10	25.0	10.5
3	PP	20	1,500	11.5

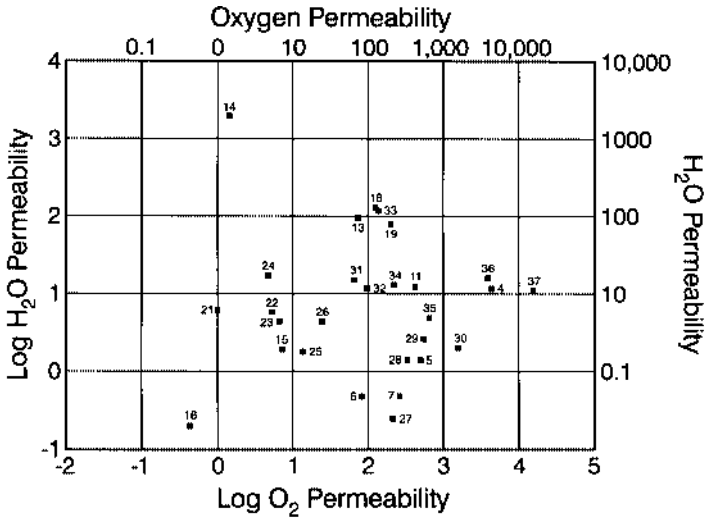
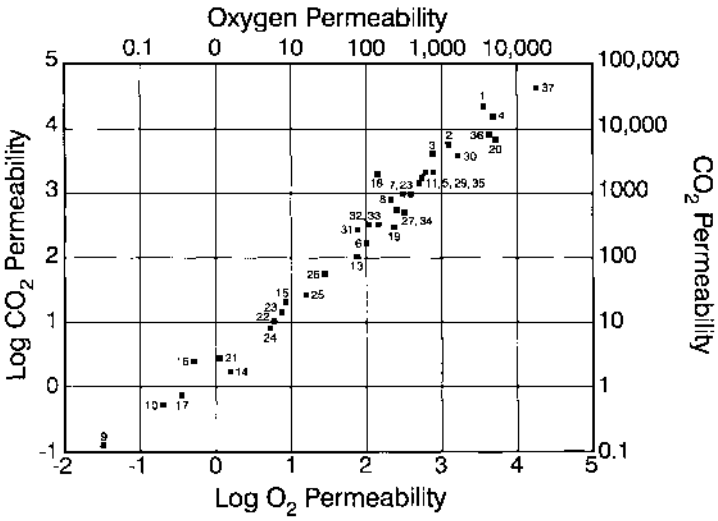


FIGURE 8.7 Oxygen and water vapor permeability chart. List of polymers: (1) Poly (1,3-butadiene); (2) gutta percha; (3) poly (chloroprene); (4) polyisoprene; (5) polyethylene (PE) d = 0.914; (6) PE, d = 0.964; (7) polypropylene; (8) poly (ethyl methacrylate); (9) poly (acrylonitrile); (10) poly (methacrylonitrile); (11) polystyrene; (12) poly (tetrafluoroethylene); (13) polyvinyl acetate; (14) polyvinyl alcohol; (15) polyvinyl chloride; (16) polyvinylidene chloride; (17) cellulose; (18) cellulose acetate; (19) cellulose nitrate; (20) ethyl acetate; (21) Barex; (22) Nylon 6.9/6.10; (23) phenoxy; (24) Nylon 6.6; (25) polyvinyl fluoride; (26) Nylon; (27) polytetrafluorethylene; (28) polybutene; (29) Surlyn; (30) butyl rubber; (31) SAN; (32) ABS; (33) polyurethane; (34) polycarbonate; (35) neoprene; (36) polybutadene; (37) silicone.



F**IGURE 8.8** Oxygen and CO_2 permeability chart. List of polymers: (1) Poly (1,3-butadiene); (2) gutta percha; (3) poly (chloroprene); (4) polyisoprene; (5) polyethylene (PE) d = 0.914; (6) PE, d = 0.964; (7) polypropylene; (8) poly (ethyl methacrylate); (9) poly (acrylonitrile); (10) poly (methacrylonitrile); (11) polystyrene; (12) poly (tetrafluoroethylene); (13) polyvinyl acetate; (14) polyvinyl alcohol; (15) polyvinyl chloride; (16) polyvinylidene chloride; (17) cellulose; (18) cellulose acetate; (19) cellulose nitrate; (20) ethyl acetate; (21) Barex; (22) Nylon 6.6; (23) phenoxy; (24) Nylon 6/6.6; (25) polyvinyl fluoride; (26) Nylon; (27) polytetrafluorethylene; (28) polybutene; (29) Surlyn; (30) butyl rubber; (31) SAN; (32) ABS; (33) polyurethane; (34) polycarbonate; (35) neoprene; (36) polybutadene; (37) silicone.

$t = 6$ months $= 180$ d

$A = 400\ cm^2 = 0.04\ m^2$

$\Delta p = 0.21$ at $= 21.27$ k Pa (assume $p_i = 0$ inside the package)

$$q = \frac{500}{32} \times \frac{0.005}{100} \times 22,414 = 17.5\ cc(STP)\ \text{of oxygen}$$

$$\ell = \frac{22 \times 180 \times 0.04 \times 22.27}{17.5} = 193\ \mu m\ (7.6\ mil)$$

The same equation can be used to calculate the loss of water. Since Δp is constant, there is enough water (inside the package) to keep the water activity unchanged during the package's shelf life. Solving for q

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

$$P_{H_2O} = 8.5 \times 10^4\ \frac{cc(STP)\mu m}{m^2 \cdot d \cdot kPa}$$ (from Table 8.19)

$t = 180$ d

$A = 0.04\ m^2$

$$\Delta p = p^s \times \left(\frac{100 - 60}{100}\right) = 1.267\ kPa$$

$p^s = 23.76\ mmHg = 3.17\ kPa$

$$q = \frac{8.5 \times 10^4 \times 180 \times 0.04 \times 1.267}{193} = 4,017\ cc(STP) = 3.20\ g\ \text{of water}$$

Equation 8.20 cannot be used if Δp changes during the shelf-life of the product. This is the case of moisture-sensitive products showing sorption isotherm curves. In simplified calculation, hysterisis of the sorption isotherms are not considered. However, the product's sorption isotherm needs to be known. The book by Iglesias and Chirife (1982) provides a valuable source of information on sorption isotherms.

For moisture-sensitive products the moisture content of the product varies with the relative humidity at which it is in equilibrium and vice versa. The relationship between the product moisture content and the relative humidity of the headspace is given by the product sorption isotherm. Assuming that the relative humidity outside the package (relative humidity of storage conditions, p_o) is constant, the Δp change through the shelf-life period is a function of the product moisture content, $\Delta p = p_o - p_i(M)$, where M is the product moisture content on a dry basis. A differential quantity dq of water exchanged through the package is equal

to the differential moisture content times the dry weight of the product W, dq = WdM. For moisture-sensitive products, the shelf-life can be written as

$$t = \frac{\ell W}{AP} \int_{M_i}^{M_2} \frac{dM}{p_o - p_i(M)} \tag{8.31}$$

where the limits M_1 and M_2 refer to the product's initial and final moisture content values, respectively. This equation estimates the value of the product's shelf-life which is defined as the time during which a packaged moisture-sensitive product remains in an acceptable or saleable condition under specific conditions of storage. Equation 8.31 relates the product's shelf-life with the area, thickness, mass of the product, and storage conditions. The validity of the above equations are subject but not limited to the following conditions.

1. There is a fast equilibrium between the product and the packages internal conditions.
2. The delay in reaching steady state condition of permeability through the package material is neglected
3. The temperature and external humidity are constant through the shelf-life period, t.
4. P is not affected by any other permeant.

For nonlinear isotherms, Equation 8.31 needs to be numerically integrated to solve for time t. Simplified solutions to Equation 8.31 can be obtained. For instance, if the portion of the sorption isotherm of interest can be linearized as

$$Y = a + bM$$

where Y is the relative humidity, the integration of 8.31 yields

$$t = \frac{\ell W}{PA\, p^s\, b} \ln \frac{Y_o - Y_{i,t=o}}{Y_o - Y_{i,t}}$$

where Y_o is the outside relative humidity; and Y_i is the headspace relative humidity.

EXAMPLE 8.15

A product with a dry weight W = 80 g and a b-value = 9.0 kg product/kg H_2O, will be stored at 23°C and 85% RH.

The initial equilibrium RH of the product $Y_{i,t=0}$ = 20%. The final equilibrium RH of the product $Y_{i,t}$ = 70%. The permeability of the package material is

$$P = 4 \times 10^{-2} \frac{kg\,\mu m}{m^2 \cdot d \cdot kPa}$$

For a package thickness of 53 µm, calculate the maximum package area to maintain the RH_i equilibrium of the product at or below 70% during 100 d.

Solution

l = 53 µm
W = 80 g = 0.08 kg
P = 4×10^{-2} kg µm/m^2 d kPa
p^s = 21.07 mmHg = 2.81 kPa
b = 9.0

$$\ln \frac{Y_o - Y_{i,t=o}}{Y_o - Y_{i,t}} = \frac{85-20}{85-70} = 1.466$$

$$A = \frac{53 \times 0.08}{4 \times 10^{-2} \times 100 \times 2.81 \times 9} \times 1.466 = 6.14 \times 10^{-2}\ m^2$$

8.6 CONCLUDING REMARKS

In this chapter, we have reviewed: (1) the economics of plastic containers; (2) major plastics used in food packaging and their properties; (3) main additives incorporated into plastics during processing; and (4) mass transfer applications of plastics in food packaging systems. Because of their unique combination of properties, technologies, and economics, plastics are versatile materials from which the food industry will continue to benefit.

REFERENCES

Albrant, P. D., 1996, Personal communication, Bekum America Co., Williamston, MI.

Alcoa, 1990, Form 992-100-6093, Crawfordville, IN.

Axelson, L. and Cavlin, S., 1991, Aseptic integrity and microhole determination of packages by gas leakages detection, *Pack. Tech. Sci.* 4:9–20.

Bezigian, T., 1996, Personal communication.

Blatz, P., 1989, Properties of films from blends of amorphous and crystalline nylons, AlChE Nat. Conf. April 2–6.

Brown, W. E., 1992, *Plastics in Food Packaging*, Dekker, New York.

Chirife, J. and Iglesias, H. A., 1982, *Handbook of Food Isotherms: Water Sorption Parameters for Food and Food Components*, Academic Press, NY.

CRC Handbook of Chemistry and Physics, 1983, 64th ed., CRC Press, Boca Raton, FL, F162.

Cunningham, R. E. and Williams, R. J., 1980, *Diffusion in Gases and Porous Media*, Plenum Press, New York.

Davis, D. S., 1992, Ethylene incorporation in polypropylene: effect on thermal-related properties, *J. Plastic Film Sheeting*, 8(4):101–108.

Dick, J. S., 1987, *Compounding Materials for the Polymer Industry*, Noyes Publications, NJ.

Felts, J. T., 1993, Transparent barrier coatings update: flexible substrates, *J. Plastic Film Sheeting* 9:201.

Fish, M., 1992, *Modern Plastic Encyclopedia*, 146.

Floros, J. D. and Gnanasekharan, V., 1992, Principles, technology and application of destructive and non-destructive package integrity testing, in *Advances in Aseptic Processing Technology*, Singh, R. K. and Nelson, P. E., Ed., Elsevier, London, ch.7.

Foster, R., 1986, Ethylene-vinyl alcohol copolymers (EVOH), in *The Wiley Encyclopedia of Packaging Technology*, Bakker, M., Ed., John Wiley & Sons, New York, 270–275.

Gibbs, D. S. and Wessling, R. A., 1983, Vinylidene chloride and poly(vinylidene chloride), in *Kirk-Othmer: Encyclopedia of Chemical Technology*, Interscience Publishers, New York, vol. 23, 764–798.

Gruenwald, G., 1987, *Thermoforming, A Plastic Processing Guide*, Technomics, Lancaster, PA.

Hernandez, R. J., 1994, Effects of water vapor on the transport properties of oxygen through polyamides packaging materials. *J. Food Eng.* 22:495–507.

Hernandez, R. J., Giacin, J. R., and Baner, A. L., 1986, The evaluation of the aroma barrier properties of polymer films, *J. Plastic Film Sheeting* 2(July):187–211.

Hernandez, R. J. and Gavara, R., 1993, Consistency test for continuous flow permeability experimental data, *J. Plastic Film Sheeting* 6(April):126–138.

Hernandez, R. J. and Giacin, J. R., 1996, Factors affecting permeation, sorption, and migration processes in packaging-product systems, Taub, I. and Singh, P. R., Eds., ACS Monograph Series,

Jensen, P. H., 1994, Testing of package integrity based on CO_2 on a trace gas, IAPRI Symposium, 9–12 October, Reims, France.

Karel, M., 1974, Packaging protection for oxygen-sensitive products, *Food Res.* 14:340.
Kim, J. N., 1992, An Application of the Finite Difference Method to Estimate the Shelf-Life of a Packaged Moisture Sensitive Pharmaceutical Tablet, M.S. Thesis, School of Packaging, Michigan State University, Ann Arbor, MI.
Kohan, M. I., Ed., 1973, *Nylon Plastics*, John Wiley & Sons, New York.
Kroschiwitz, J., Ed., 1987, *Polymers An Encyclopedic Sourcebook of Engineering Properties*, Encyclopedia Reprint Series, John Wiley, NY.
Labuza, T. P., Mizrahi, S., and Karel, M., 1972, Mathematical model for optimization of flexible film packaging of food for storage, *Trans. ASAE* 15:150.
Lachance, K., 1966, Meeting FDA regulations for food packaging made clear, *Packag. Technol. Eng.* 7:44.
Laermer, S. F. and Zambetti, F. F., 1992, Alpha-tocopherol (vitamin E)-the natural antioxidant for polyolefins, *J. Plastic Film Sheeting* 8:228–248.
Landvatter, G. R., 1994, Ethylene-vinyl acetate (EVA), in *Modern Plastics Encyclopedia Handbook*, McGraw-Hill, New York, 39.
Leonard, E. A., 1980, *Packaging Economics*, Books for Industry, New York.
Liu, K. I., Hernandez, R. J., and Giacin, J. R., 1991, The effect of water activity and vapor activity on the permeation of toluene vapor through a two-side PVDC coated oriented polypropylene film, *J. Plastic Film Sheeting* 7:56–67.
Manders, P. W., 1995, Polyethylene: new branches of the polymer family extend into specialized applications, *Modern Plastic Encyclopedia*, (Nov):B3-B6.
Mergenhagen, L. K., 1992, Ethylene acid copolymer in *Modern Plastics Encyclopedia*, McGraw-Hill, New York, 64.
Mobil, 1994, *Mobil OPP Films, Product Characteristics*, Mobil Chemical Company, Chadds Ford, PA.
Modern Plastic, Guide to Plastics, 1987, McGraw-Hill, New York.
McCrum, N. G., Bucley, C. P., and Bucknall, C. B., 1988, *Principle of Polymer Engineering*, Oxford University Press, New York.
Perry, R. H. and Green, D. W., 1984, *Perry's Chemical Engineers' Handbook*, 6th ed., McGraw-Hill, NY, 3–247.
Pascall, M. A., Harte, B., Giacin, J., and Gray, I., 1995, Decreasing lipid oxidation in soybean oil by a UV absorber in the packaging material. *J. Food Sci.*, 60(5):1116–1118.
Pocas, M. F., 1995, Modeling the moisture transfer of two-component food products in a flexible package, M.S. Thesis, School of Packaging, Michigan State University, Ann Arbor, MI.
Progelhof, R. C. and Throne, J. L., 1993, *Polymer Engineering Principles*, Hanser Publisher, New York.
Radosta, J. A., 1991, Talc anti-blocks for maximized LLDPE blown film performance, *J. Plastic Film Sheeting* 7:81–189.
Reed, R. W. and Vaughan, D., 1965, Surlyn A ionomer. I. The effect of ionic bonding on polymer structure. II. The effect of ionic bonding on solid state and melt properties, *Polymer Preprints* 1(1).
Rice, J., 1995, Opting for OPP, *Food Process.* Jan:71–73.
Sajaki, T. and Giacin, J. R., 1993, Permeation of ethyl acetate vapor through silica deposited PET films and composite structures, *J. Plastic Films Sheeting* 9:97.
Simon, D. F., 1994, Single-site catalysts produce tailor-made consistent resins, *Packaging Tech. Eng.*, April: 34–37.
Smith, M. A., 1986, High density polyethylene, in *The Wiley Encyclopedia of Packaging Technology*, Bakker, M., Ed., John Wiley & Sons, New York, 514–523.
Statz, R. J., 1994, Ionomer, in *Modern Plastics Encyclopedia Handbook*, McGraw-Hill, New York, 41–42.
Toebe, J. M., Hoojjat, H., Hernandez, R. J., Giacin, J. R., and Harte, B. R., 1990, Interaction of flavour components from an onion/garlic sour cream with HIPS, *Packag. Technol. Sci.* 3:133–140.
Toensmeier, P. A., 1995, *Modern Plastics*, Feb:44z–47.
Treybal, R. E., 1980, *Mass Transfer Operations*, 3rd ed., McGraw-Hill, New York, ch.2.
Van Drumpt, J., 1992, *Modern Plastic Encyclopedia*, Oct:150–154.
Van Krevelen, D. W., 1990, *Properties of Polymers*, 3rd ed., Elsevier, New York.
Young, G., 1966, New materials transform fresh-produce packaging, *Convert. Mag.* (July):78–79.
Youngquist, G. R., 1970, Diffusion flow of gases in porous solids, *Ind. Eng. Chem.* 62(8):52–63.