BARRIER POLYMERS

1. Introduction

Barrier polymers are used for many packaging and protective applications. As barriers they separate a system, such as an article of food or an electronic component, from an environment. That is, they limit the introduction of matter from the environment into the system or limit the loss of matter from the system or both. In many cases, the environment is simply room air, but the environment can be very different, such as in the case of protecting a submerged system from water.

All polymers are barriers to some degree; however, no polymer is a perfect barrier. Polymers only limit the movement of substances. When a polymer limits the movement enough to satisfy the requirements of a particular application, it is a barrier polymer for that application. Hence, barrier polymer finds definition in the application. A given polymer may be a good barrier for protecting one system from a component of an environment, but a poor barrier for protecting another system from a different component of the environment. This description of a barrier polymer is much wider than the traditional operational definitions that focus narrowly on oxygen permeabilities and water–vapor transmission rates (WVTR). This article discusses barrier polymers and the permeation process within the context of barrier applications. It also covers units of measure, physical factors affecting permeation, typical barrier structures, prediction and measurement of barrier properties, uses, and health and safety factors.

2. The Permeation Process

Barrier polymers limit movement of substances, hereafter called permeants. The movement can be through the polymer or, in some cases, merely into the polymer. The overall movement of permeants through a polymer is called permeation, which is a multistep process. First, the permeant molecule collides with the polymer. Then, it must adsorb to the polymer surface and dissolve into the polymer bulk. In the polymer, the permeant "hops" or diffuses randomly as its own thermal kinetic energy keeps it moving from vacancy to vacancy while the polymer chains move. The random diffusion yields a net movement from the side of the barrier polymer that is in contact with a high concentration or partial pressure of the permeant to the side that is in contact with a low concentration of permeant. After crossing the barrier polymer, the permeant moves to the polymer surface, desorbs, and moves away.

Permeant movement is a physical process that has both a thermodynamic and a kinetic component. For polymers without special surface treatments, the thermodynamic contribution is in the solution step. The permeant partitions between the environment and the polymer according to thermodynamic rules of solution. The kinetic contribution is in the diffusion. The net rate of movement is dependent on the speed of permeant movement and the availability of new vacancies in the polymer.

A few simple equations describe most applications of barrier polymers. Equation 1 is an adaptation for films of Fick's first law.

$$\frac{\Delta M_x}{\Delta t} = \frac{PA\Delta p_x}{L} \tag{1}$$

where $\Delta M_x/\Delta t$ is the steady-state rate of permeation of permeant x through a polymer film, P is the permeability coefficient (commonly called the permeability), A is the area of the film, Δp_x is the difference in pressure of the permeant on the two sides of the film, and L is the thickness of the film.

The permeability is the product of the diffusion coefficient D and the solubility coefficient S.

$$P = DS \tag{2}$$

The diffusion coefficient, sometimes called the diffusivity, is the kinetic term that describes the speed of movement. The solubility coefficient, which should not be called the solubility, is the thermodynamic term that describes the amount of permeant that will dissolve in the polymer. The solubility coefficient is a reciprocal Henry's law coefficient, as shown in equation 3.

$$C_{\mathrm{eq}} = Sp_x \tag{3}$$

where C_{eq} is the equilibrium concentration of permeant that will dissolve in a polymer when the permeant has a partial pressure of p_x.

A polymer can have a low permeability because it has a low value of D or a low value of S or both. A low value of D can result from either static or dynamic effects. Static effects include molecular packing in the amorphous phase, orientation, and the amount of crystallinity. Molecular packing affects the way permeant molecules move through the free volume or vacanies in the polymer host. When there is a small amount of free volume, movement is limited. Symmetric monomers lead to good packing, and hence lower diffusion rates. For example, vinylidene chloride, which is symmetric 1,1-dichloroethene [75-35-4], leads to a good barrier polymer because the adjacent molecular chains can pack together well. The analogue vinyl chloride [75-01-4], which is asymmetric monochloroethene, leads to a polymer that does not pack as well. The simple chain of high density polyethylene (HDPE) packs much better than the branched chain of low density polyethylene (LDPE). Hence, HDPE has better barrier properties than LDPE.

Orientation sometimes leads to lower permeability values (better barrier properties). Orientation can increase packing density, which lowers the diffusion coefficient D; it can also increase the difficulty of hopping or diffusing in a direction perpendicular to the film. In the latter case, movement in general may be fast, but movement through the film is limited. However, mere stretching does not always lead to orientation of the molecular chains. In fact, stretching can lead to void formation, which increases permeability.

Increased crystallinity can reduce permeability values because the crystal regions of a polymer are impenetrable in most semicrystalline polymers. Hence, the average value of the solubility coefficient S is reduced. It also means that movement must occur around the crystallites, which means that a longer distance must be traveled, thus lowering the effective value of D.

The dynamic effects on the diffusion coefficient are related to polymer chain mobility. Permeant movement is enhanced when there are fluctuations in the free volume of the polymer. As chains move with thermal motion, opportunities for diffusion or hopping increase. Spaces between polymer molecules that are too small for passage at one point in time can be adequate later as the molecules move. Ultimately, this effect is related to temperature in general and often to the glass transition temperature T_g in particular. As the temperature increases, thermal motion increases, and the probability of larger openings occurring increases. Below T_g, thermal motion is limited to short range; small openings occur at low rates. Above T_g, thermal motion is enhanced, longer range motion is common, and larger openings occur at usable rates. All the polymer–polymer interactions that affect T_g affect the permeability, including dipole–dipole interactions and efficient packing.

The common model of a polymer as a collection of noodles in a bowl is not adequate for diffusion. A better model is a collection of long, active worms. Movement through the collection is enhanced if the worms are widely spaced (static effect) and if they have agitated motion (dynamic effect).

A low solubility coefficient can result when the permeant does not condense readily or does not interact strongly with the polymer. Generally, those permanent gases that have low boiling temperatures have low solubility coefficients in polymers. They are inherently adverse to existing in a condensed state either as a liquid or in a polymer solution. Hence, molecules like oxygen have solubility coefficients that are many orders of magnitude lower than the solubility coefficients of heavy flavor molecules. When no specific interactions, such as dipole–dipole interactions or hydrogen bonding, occur between the polymer and the permeant, solution is minimal. All those effects that control solutions in general apply to the polymer solution. These effects are not fully understood, but progress is being made.

3. Units of Measure

To understand permeability or barrier property values, it is necessary to define the units of measure. These units are complicated and many different sets of units are in common use. Furthermore, from time to time the units of permeability are presented in confused or incorrect fashion in the literature.

The dimensions of permeability become clear after rearranging equation 1 to solve for *P*. The permeability must have dimensions of quantity of permeant (either mass or molar) times thickness in the numerator with area times a time interval times pressure in the denominator. Table 1 contains conversion factors for several common unit sets with the permeant quantity in molar units. The unit nmol/(m · s · GPa) is used herein for the permeability of small molecules because this unit is SI, which is preferred in current technical encyclopedias, and it is only a factor of 2, different from the commercial permeability unit, [cc(STP) · mil]/(100 in.^{2} · d · atm) where cc(STP) is a molar unit for absorbed permeant (nominally cubic centimeters of gas at standard temperature and pressure). The molar character is useful for oxygen permeation, which could ultimately involve a chemical reaction, or carbon dioxide permeation, which is often related to the pressure in a beverage bottle.

For permeation of flavor, aroma, and solvent molecules another metric combination of units is more useful, namely, (kg · m)/(m^2 · s · Pa). In this unit, the permeant quantity has mass units. This is consistent with the common practice of describing these materials. Permeability values in these units often carry a cumbersome exponent; hence, a modified unit, an MZU (10^{-20} kg · m)/(m^2 · s · Pa), is used herein. The conversion from this permeability unit to the preferred unit for small molecules depends on the molecular weight of the permeant. Equation 4 expresses the relationship where MW is the molecular weight of the permeant in daltons (g/mol).

$$\text{permeability in MZU} \times (10/\text{MW}) = \text{permeability in nmol}/\left(\text{m}^3\text{GPa}\right) \qquad (4)$$

The solubility coefficient must have units that are consistent with equation 3. In the literature, *S* has units cc(STP)/(cm^3 · atm), where cm^3 is a volume of polymer. When these units are multiplied by an equilibrium pressure of permeant, concentration units result. In preferred SI units, *S* has units of nmol/(m^3 · GPa).

$$\begin{aligned}&\text{solubility coefficient in cc(STP)}/\left(\text{cm}^3\text{atm}\right) \times \left(4.04 \times 10^{14}\right)\\&\quad = \text{solubility coefficient in nmol}/\left(\text{m}^3\text{GPa}\right)\end{aligned} \qquad (5)$$

Table 1. **Permeability Units[a] with Conversion Factors**

Multiply⟶ to obtain ↓	$\frac{\text{nmol}}{\text{m·s·GPa}}$	$\frac{\text{cc·mil}}{\text{100 in.}^2\text{·d·atm}}$	$\frac{\text{cc·mil}}{\text{m}^2\text{·d·atm}}$	$\frac{\text{cc·cm}}{\text{cm}^2\text{·s·atm}}$	$\frac{\text{cc·cm}}{\text{cm}^2\text{·s·cm Hg}}$	$\frac{\text{cc·20 }\mu\text{m}}{\text{m}^2\text{·d·atm}}$
$\frac{\text{nmol}}{\text{m·s·GPa}}$	1	2	0.129	4.390×10^{10}	3.336×10^{12}	0.1016
$\frac{\text{cc·mil}}{\text{100 in.}^2\text{·d}}$	0.50	1	6.452×10^{-2}	2.195×10^{10}	1.668×10^{12}	5.08×10^{-2}
$\frac{\text{cc·mil}}{\text{m}^2\text{·d·atm}}$	7.75	15.50	1	3.402×10^{11}	2.585×10^{13}	0.787
$\frac{\text{cc·cm}}{\text{cm}^2\text{·s·atm}}$	2.278×10^{-11}	4.557×10^{-11}	2.939×10^{-12}	1	76.00	2.315×10^{-12}
$\frac{\text{cc·cm}}{\text{cm}^2\text{·s·cm Hg}}$	2.998×10^{-13}	5.996×10^{-13}	3.860×10^{-14}	1.316×10^{-2}	1	3.046×10^{-14}
$\frac{\text{cc·20 }\mu\text{m}}{\text{m}^2\text{·d·atm}}$	9.84	19.68	1.27	4.32×10^{11}	3.283×10^{13}	1

[a] Throughout the *Encyclopedia* cm^3 (or mL) is used in preference to cc. However, the advantage of using cc here is an obvious visual aid in the complex units and there are further comments regarding cc vs cm^3 in the text.

Table 2. **Water Vapor Transmission Rate Units with Conversion Factors**

Multiply ⟶ to obtain ↓	$\frac{\text{nmol}}{\text{m·s}}$	$\frac{\text{g·mil}}{100\ \text{in.}^2\text{·d}}$	$\frac{\text{g·cm}}{\text{m}^2\text{·d}}$
$\frac{\text{nmol}}{\text{m·s}}$	1	0.253	6.43
$\frac{\text{g·mil}}{100\ \text{in.}^2\text{·d}}$	3.95	1	25.40
$\frac{\text{g·cm}}{\text{m}^2\text{·d}}$	0.155	3.94×10^{-2}	1

In the mass units for flavor, aroma, and solvent molecules, the solubility coefficient has units kg/($\text{m}^3 \cdot \text{Pa}$). Equation 6 shows how to convert from the mass units to the molar units.

$$\begin{aligned}&\text{solubility coefficient in kg}/\left(\text{m}^3\text{Pa}\right) \times \left(10^{21}/\text{MW}\right)\\&\quad = \text{solubility coefficient in nmol}/\left(\text{m}^3\text{GPA}\right)\end{aligned} \tag{6}$$

The diffusion coefficient has been commonly reported in cm^2/s in many applications. Hereafter, m^2/s will be used since it uses the basic SI units.

The water–vapor transmission rate is another descriptor of barrier polymers. Strictly, it is not a permeability coefficient. The dimensions are quantity times thickness in the numerator and area times a time interval in the denominator. These dimensions do not have a pressure dimension in the denominator as does the permeability. Common commercial units for WVTR are (g·mil)/(100 in.^2·d). Table 2 contains conversion factors for several common units for WVTR. This text uses the preferred nmol/(m·s). The WVTR describes the rate that water molecules move through a film when one side has a humid environment and the other side is dry. The WVTR is a strong function of temperature because both the water content of the air and the permeability are directly related to temperature. For the WVTR to be useful, the water–vapor pressure difference for the value must be reported. Both these facts are recognized by specifying the relative humidity and temperature for the WVTR value. This enables the user to calculate the water–vapor pressure difference. For example, the common conditions are 90% relative humidity (rh) at 37.8°C, which means the pressure difference is 5.89 kPa (44 mm Hg). The WVTR may be converted to a permeability by dividing by the specified pressure difference of the water vapor.

4. Small Molecule Permeation

4.1. Permanent Gases.

Table 3 lists the permeabilities of oxygen [7782-44-7], nitrogen [7727-37-9], and carbon dioxide [124-38-9] for selected barrier and nonbarrier polymers at 20°C and 75% rh. The effect of temperature and humidity are discussed later. For many polymers, the permeabilities of nitrogen, oxygen, and carbon dioxide are in the ratio 1:4:14.

The traditional definition of a barrier polymer required an oxygen permeability <2 nmol/(m · s · GPa) [originally, <(cc · mil)/(100 in.^2 · d · atm)] at room temperature. This definition was based partly on function and partly on conforming

Table 3. **Permeabilities of Selected Polymers**[a]

	Gas permeability nmol/(m · s · GPa)		
Polymer	Oxygen	Nitrogen	Carbon dioxide
vinylidene chloride copolymers	0.02–0.30	0.005–0.07	0.1–1.5
ethylene–vinyl alcohol (EVOH) copolymers, dry at 100% rh	0.014–0.095, 2.2–1.1		
nylon-MXD6[b]	0.30		
nitrile barrier polymers	1.8–2.0		6–8
nylon-6	4–6		20–24
amorphous nylon (Selar[c] PA 3426)	5–6		
poly(ethylene terephthalate) (PET)	6–8	1.4–1.9	30–50
poly(vinyl chloride) (PVC)	10–40		40–100
high density polyethylene	200–400	80–120	1200–1400
polypropylene	300–500	60–100	1000–1600
low density polyethylene	500–700	200–400	2000–4000
polystyrene	500–800	80–120	1400–3000

[a] Ref. 1; see Table 1 for unit conversion.
[b] Trademark of Mitsubishi Gas Chemical Co.
[c] Trademark of Du Pont.

to the old commercial unit of permeability. The old commercial unit of permeability was created so that the oxygen permeability of Saran Wrap brand plastic film, a trademark of The Dow Chemical Company, would have a numerical value of 1.

However, the traditional definition of a barrier polymer is a good starting point for food packaging. Table 4 contains the approximate oxygen tolerances of several food groups. This table and equation 1 can be used to analyze a hypothetical packaging situation. For a package with an area of 0.045 m^2 (70 $in.^2$) and a wall thickness of 50.8 μm (2 mil), the oxygen permeability

Table 4. **Estimated Maximum Oxygen Tolerance of Various Foods**[a]

Food or beverage	Maximum oxygen tolerance, ppm
beer (pasteurized)	1–2
typical autoclaved low acid foods	1–3
canned milk	
canned meats and vegetables	
canned soups	
baby foods	
fine wine	2–5
coffee (fresh ground)	2–5
tomato-based products	3–8
high acid fruit juices	8–20
carbonated soft drinks	10–40
oils and shortenings	20–50
salad dressings, peanut butter	30–100
liquor, jams, jellies	50 – 100+

Table 5. **Diffusion and Solubility Coefficients for Oxygen and Carbon Dioxide in Selected Polymers at 23°C, Dry**[a]

	Oxygen		Carbon dioxide	
Polymer	D, m^2/s	S, $nmol/(m^3 \cdot GPa)$[b]	D, m^2/s	S, $nmol/(m^3 \cdot GPa)$[b]
vinylidene chloride copolymer	1.2×10^{-14}	1.01×10^{13}	1.3×10^{-14}	3.2×10^{13}
EVOH copolymer[c]	7.2×10^{-14}	2.4×10^{12}		
acrylonitrile barrier polymer	1.0×10^{-13}	1.0×10^{13}	9.0×10^{-14}	4.4×10^{13}
PET	2.7×10^{-13}	2.8×10^{13}	6.2×10^{-14}	8.1×10^{14}
PVC	1.2×10^{-12}	1.2×10^{13}	8.0×10^{-13}	9.7×10^{13}
polypropylene	2.9×10^{-12}	1.1×10^{14}	3.2×10^{-12}	3.4×10^{14}
high density polyethylene	1.6×10^{-11}	7.2×10^{12}	1.1×10^{-11}	4.3×10^{13}
low density polyethylene	4.5×10^{-11}	2.0×10^{13}	3.2×10^{-11}	1.2×10^{14}

[a] Refs. (4–9).

[b] For unit conversion, see equation 5.

[c] 42 mol % ethylene.

needs to be <1.9 nmol/(m · s · GPa) to give 100 days of protection in air (2.1×10^{-5} GPa O_2) to 500 g of contents that could withstand up to 20 ppm (wt/wt) oxygen. A lower oxygen permeability is needed if the application requires greater oxygen protection, a longer storage time, or a thinner wall.

Poly(ethylene terephthalate) [25038-59-9], with an oxygen permeability of 8 nmol/(m · s · GPa), is not considered a barrier polymer by the old definition; however, it is an adequate barrier polymer for holding carbon dioxide in a 2-L bottle for carbonated soft drinks. The solubility coefficients for carbon dioxide are much larger than for oxygen. For the case of the PET soft drink bottle, the principal mechanism for loss of carbon dioxide is by sorption in the bottle walls as 500 kPa (5 atm) of carbon dioxide equilibrates with the polymer (3). For an average wall thickness of 370 μm (14.5 mil) and a permeability of 40 nmol/(m · s · GPa), many months are required to lose enough carbon dioxide (15% of initial) to be objectionable.

The diffusion and solubility coefficients for oxygen and carbon dioxide in selected polymers have been collected in Table 5. Determination of these coefficients is neither common, nor difficult. Methods are discussed later. The values of S for a permeant gas do not vary much from polymer to polymer. The large differences that are found for permeability are due almost entirely to differences in D.

4.2. Polymers with Good Barrier-to-Permanent Gases.

Those polymers that are good barriers to permanent gases, especially oxygen, have important commercial significance. They represent a diverse set of chemical structures shown in Figure 1.

Vinylidene chloride copolymers are available as resins for extrusion, latices for coating, and resins for solvent coating. Comonomer levels range from 5 to 20 wt %. Common comonomers are vinyl chloride, acrylonitrile, and alkyl acrylates. The permeability of the polymer is a function of type and amount of comonomer. As the comonomer fraction of these semicrystalline copolymers is increased, the melting temperature decreases and the permeability increases. The permeability of vinylidene chloride homopolymer has not been measured.

Vinylidene chloride copolymers are marketed under a variety of trade names. Saran is a trademark of The Dow Chemical Company for vinylidene chloride copolymers. Other trade names include Daran (W. R. Grace), Amsco Res (Union Oil), and Serfene (Morton Chemical) in the United States; Haloflex (Imperial Chemical Industries, Ltd.), Diofan (BASF), Ixan (Solvay and Cie SA), and Polyidene (Scott-Bader) in Europe.

Hydrolyzed ethylene–vinyl acetate copolymers [24937-78-8], commonly known as EVOH copolymers [25067-34-9], are usually used as extrusion resins, although some may be used in solvent-coating applications. As the ethylene fraction of these semicrystalline copolymers increases, the melting temperature decreases, the permeabilities increase, and the sensitivity to humidity decreases. The permeabilities as a function of polymer composition and humidity are shown in Figure 2. Vinyl alcohol homopolymer [9002-89-5] has a very low oxygen permeability in dry conditions; however, the polymer is water-soluble. Trade names for these barrier polymers include Eval, Soarnol, Selar OH, and Clarene. Table 6 lists the compositions of some commonly used EVOH copolymers.

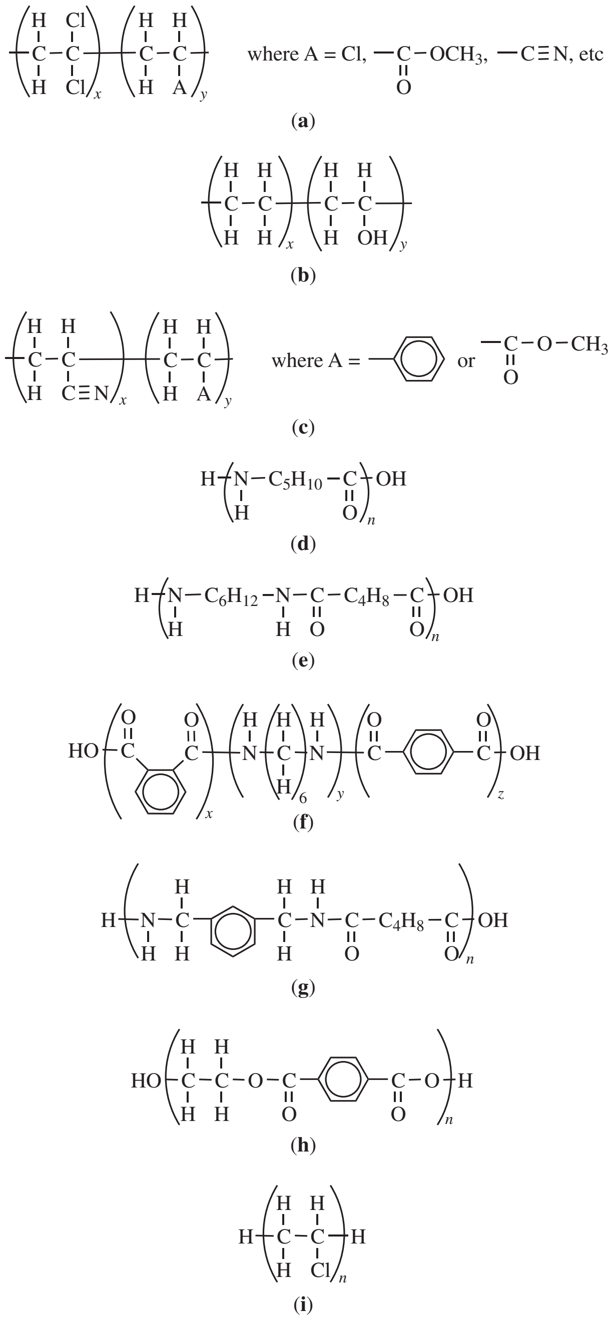

Fig. 1. Chemical structures of barrier polymers. (**a**) Vinylidene chloride copolymers; (**b**) hydrolyzed EVOH; (**c**) acrylonitrile barrier polymers; (**d**) nylon-6; (**e**) nylon-6,6; (**f**) amorphous nylon (Selar PA 3426), $y = x + z$; (**g**) nylon-MXD6; (**h**) PET; and (**i**) PVC.

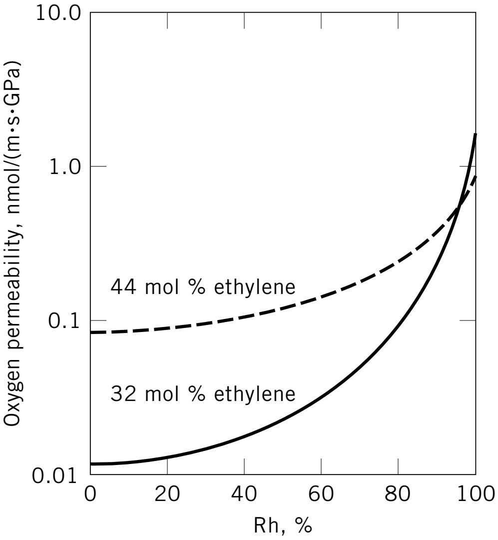

Fig. 2. Oxygen permeabilities of EVOH copolymers at 20°C (10). See Table 1 for unit conversions.

Copolymers of acrylonitrile [107-13-1] are used in extrusion and molding applications. Commercially important comonomers for barrier applications include styrene and methyl acrylate. As the comonomer content is increased, the permeabilities increase as shown in Figure 3. These copolymers are not moisture-sensitive. Table 7 contains descriptions of three high nitrile barrier polymers. Barex and Cycopac resins are rubber-modified to improve the mechanical properties.

Polyamide polymers can provide good-to-moderate barrier-to-permeation by permanent gases. Nylon-6 [25038-54-4] and nylon-6,6 [32131-17-2] have been available for many years. Nylon-6 and nylon-6,6 are moderate oxygen barriers

Table 6. **Composition of EVOH Copolymers**

Manufacturer	Name[a]	Ethylene, mol %
Du Pont	Selar OH 3003, 3007	30
	Selar OH 3803	38
	Selar OH 4416	44
Nippon Goshei	Soarnol D, DT	29
	Soarnol E, ET	38
Eval Company of America	Eval L	27
	Eval F	32
	Eval H	38
	Eval E	44
	Eval K[b]	38
Solvay	Clarene L	30
	Clarene P	36

[a] Names are trademarks of the individual manufacturer.
[b] Blend of 32 mol % and 44 mol % copolymers.

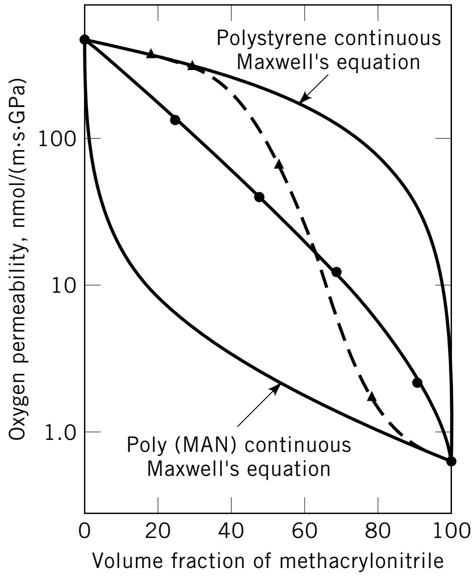

Fig. 3. Oxygen permeabilities of block (▲) and random (●) styrene–methacrylonitrile (MAN) copolymers [33961-16-9] (11). See Table 1 for unit conversions.

that are slightly humidity sensitive. They are, however, excellent barriers against migration of flavor and aroma compounds. New polyamides are being introduced. One of these is an amorphous nylon, Selar PA (Du Pont), which is a terpolymer of hexamethylenediamine [124-09-4] and a mixture of phthalic acids or acid chlorides (12). Nylon-MXD6 (Mitsubishi Gas Chemical Company) is a copolymer of *m*-xylyenediamine [1477-55-0] and adipic acid [124-04-9]. The amorphous nylons are unusual because the oxygen permeability actually decreases slightly as the humidity increases. Nylon-MXD6 [25805-74-7] is more typical; its oxygen permeability increases as the humidity increases. Research is active in the area of polyamide chemistry for new barrier polymers.

Two often, used polymers have adequate properties for some applications. Poly(ethylene terephthalate) is used to make films and bottles. This polymer is commonly made from ethylene glycol and dimethyl terephthalate [120-61-6] or

Table 7. **Compositions of High Nitrile Barrier Polymers**

Polymer[a]	Manufacturer	Chemical composition[b]
Lopac	Monsanto Co.	100% copolymer of 70% acrylonitrileand 30% styrene
Barex	Sohio	90% copolymer of 74% acrylonitrile and 26% methyl acrylate + 10% butadiene rubber graft
Cycopac	Borg-Warner Chemicals	90% copolymer of 74% acrylonitrile and 26% styrene + 10% butadiene rubber graft

[a] Names are trademarks of the individual manufacturer.

[b] Data from U.S. Food and Drug Administration (FDA) regulations for corresponding materials.

Table 8. **Permeability of Household Films at 25°C to Selected Permeants**

	Film type		
Permeant[a]	Plasticized vinylidene chloride copolymer[b]	Plasticized PVC[c]	Polyethylene[d]
oxygen, nmol/(m·s·GPa)	1.9	220	640
water vapor[e], nmol/(m·s)	0.055	0.30	0.19
d-limonene, MZU[f]	130	1.1×10^5	3.3×10^5
dipropyl disulfide, MZU[f]	1.1×10^4	3.3×10^6	6.8×10^6

[a] See Tables 1 and 2 for unit conversions.

[b] SaranWrap brand plastic film (trademark of The Dow Chemical Company).

[c] Reynolds plastic wrap (trademark of Reynolds Metals Co.).

[d] Handi-Wrap II brand plastic film (trademark of DowBrands, Inc.).

[e] Measured at 37.8°C, 90% rh.

[f] MZU = $(10^{-20}\ \mathrm{kg \cdot m})/(\mathrm{m^2 \cdot s \cdot Pa})$.

from ethylene glycol [107-21-1] and terephthalic acid [100-21-0]. PET is a moderate barrier-to-permanent gases; however, it is an excellent barrier to flavors and aromas. The oxygen permeability decreases slightly with increasing humidity. Poly(vinyl chloride) is a moderate barrier-to-permanent gases. Plasticized PVC is used as a household wrapping film. The plasticizers greatly increase the permeabilities. Table 8 lists the permeabilities of selected permeants in the three main household wrapping films.

Water–Vapor Transmission. Table 9 lists WVTR values for selected polymers. Comparison of Tables 3 and 9 shows that often there is a reversal of roles. Those polymers that are good oxygen barriers are often poor water–vapor barriers and vice versa, which can be rationalized as follows. Barrier polymers often rely on dipole–dipole interactions to reduce chain mobility and, hence, diffusional movement of permeants. These dipoles can be good sites for hydrogen

Table 9. **WVTR of Selected Polymers**[a]

Polymer	WVTR, nmol/(m·s)[b]
vinylidene chloride copolymers	0.005–0.05
HDPE	0.095
polypropylene	0.16
LDPE	0.35
EVA, 44 mol% ethylene[c]	0.35
PET	0.45
PVC	0.55
EVA, 32 mol % ethylene[c]	0.95
nylon-6,6, nylon-11	0.95
nitrile barrier resins	1.5
polystyrene	1.8
nylon-6	2.7
polycarbonate	2.8
nylon-12	15.9

[a] At 38°C and 90% rh unless otherwise noted (13).

[b] See Table 2 for unit conversions.

[c] Measured at 40°C.

bonding. Water molecules are attracted to these sites, leading to high values of S. Furthermore, the water molecules enhance D by interrupting the attractions and chain packing. Polymer molecules without dipole–dipole interactions, such as polyolefins, dissolve very little water and have low WVTR and permeability values. The low values of S more than compensate for the naturally higher values of D.

5. Large Molecule Permeation

The permeation of flavor, aroma, and solvent molecules in polymers follows the same physics as the permeation of small molecules. However, there are two significant differences. For these larger molecules, the diffusion coefficients are much lower and the solubility coefficients are much higher. This means that steady-state permeation may not be reached during the storage time of some packaging situations. Hence, large molecules from the environment might not enter the contents, or loss of flavor molecules would be limited to sorption into the polymer. However, since the solubility coefficient is large, the loss of flavor could be important solely from sorption in the polymer. Furthermore, the large solubility coefficient can lead to enough sorption of the large molecule that plasticization occurs in the polymer, which can increase the diffusion coefficient.

Table 10 contains some selected permeability data including diffusion and solubility coefficients for flavors in polymers used in food packaging. Generally, vinylidene chloride copolymers and glassy polymers such as polyamides and EVOH are good barriers to flavor and aroma permeation whereas the polyolefins are poor barriers. Comparison to Table 5 shows that the large molecule diffusion coefficients are 1000 or more times lower than the small molecule coefficients. The solubility coefficients are as much as 1 million times higher. Equation 7 shows how to estimate the time to reach steady-state permeation t_{ss} if the diffusion coefficient and thickness of a film are known.

$$t_{\mathrm{ss}} = \frac{L^2}{4D} \tag{7}$$

For d-limonene diffusion in a 50-μm thick vinylidene chloride copolymer film, steady-state permeation is expected after 2000 days. For a 50-μm thick LDPE film, steady-state permeation is expected in <1 h. If steady-state permeation is not achieved, the effective penetration depth L^* for simple diffusion, after time t has elapsed, can be estimated with equation 8.

$$L^* = 2(Dt)^{1/2} \tag{8}$$

For a food container, the amount of sorption could be estimated in the following way. For simple diffusion, the concentration in the polymer at the food surface could be estimated with equation 3, which would require a knowledge of the partial pressure of the flavor in the food. This knowledge is not always available, but methods exist for estimating this when the food matrix

Table 10. **Examples of Permeation of Flavor and Aroma Compounds in Selected Polymers at 25°C,[a] Dry[b]**

Flavor/aroma (compound)	Cas Registry Number	Permeant formula	P, MZU[c]	D, m^2/s	S, kg/(m$^3 \cdot$ Pa)[d]
Vinylidene chloride copolymer					
ethyl hexanoate	[123-66-0]	$C_8H_{16}O_2$	570	8.0×10^{-18}	0.71
ethyl 2-methylbutyrate	[7452-79-1]	$C_7H_{14}O_2$	3.2	1.9×10^{-17}	1.7×10^{-3}
hexanol	[111-27-3]	$C_6H_{14}O$	40	5.2×10^{-17}	7.7×10^{-3}
trans-2-hexenal	[6728-26-3]	$C_6H_{10}O$	240	1.8×10^{-17}	0.14
d-limonene	[5989-27-5]	$C_{16}H_{16}$	32	3.3×10^{-17}	9.7×10^{-3}
3-octanone	[106-68-3]	$C_8H_{16}O$	52	1.3×10^{-18}	0.40
propyl butyrate	[105-66-8]	$C_7H_{14}O_2$	42	4.4×10^{-18}	9.4×10^{-2}
dipropyl disulfide	[629-19-6]	$C_6H_{14}S_2$	270	2.6×10^{-18}	1.0
EVA copolymer					
ethyl hexanoate			0.41	3.2×10^{-18}	1.3×10^{-3}
ethyl 2-methylbutyrate			0.30	6.7×10^{-18}	4.7×10^{-4}
hexanol			1.2	2.6×10^{-17}	4.6×10^{-4}
trans-2-hexenal			110	6.4×10^{-17}	1.8×10^{-2}
d-limonene			0.5	1.1×10^{-17}	4.5×10^{-4}
3-octanone			0.2	1.0×10^{-18}	2.0×10^{-3}
propyl butyrate			1.2	2.7×10^{-17}	4.5×10^{-4}
LDPE					
ethyl hexanoate			4.1×10^{6}	5.2×10^{-13}	7.8×10^{-2}
ethyl 2-methylbutyrate			4.9×10^{5}	2.4×10^{-13}	2.3×10^{-2}
hexanol			9.7×10^{5}	4.6×10^{-13}	2.3×10^{-2}
trans-2-hexenal			8.1×10^{5}		
d-limonene			4.3×10^{6}		
3-octanone			6.8×10^{6}	5.6×10^{-13}	1.2×10^{-1}
propyl butyrate			1.5×10^{6}	5.0×10^{-13}	3.0×10^{-2}
dipropyl disulfide			6.8×10^{6}	7.3×10^{-14}	9.3×10^{-1}
HDPE					
d-limonene			3.5×10^{6}	1.7×10^{-13}	2.5×10^{-1}
menthone	[1074-95-9]	$C_{10}H_{18}O$	5.2×10^{6}	9.1×10^{-13}	4.7×10^{-1}
methyl salicylate	[119-36-8]	$C_8H_8O_3$	1.1×10^{7}	8.7×10^{-14}	1.6
Polypropylene					
2-butanone	[78-93-3]	C_4H_8O	8.5×10^{3}	2.1×10^{-15}	4.0×10^{-2}
ethyl butyrate	[105-54-4]	$C_6H_{12}O_2$	9.5×10^{3}	1.8×10^{-15}	5.3×10^{-2}
ethyl hexanoate			8.7×10^{4}	3.1×10^{-15}	2.8×10^{-1}
d-limonene			1.6×10^{4}	7.4×10^{-16}	2.1×10^{-1}

[a] Values for vinylidene chloride copolymer and EVA are extrapolated from higher temperatures.

[b] Permeation in the vinylidene chloride copolymer and the polyolefins is not affected by humidity; the permeability and diffusion coefficient in the EVA copolymer can be as much as 1000 times greater with high humidity (14–17).

[c] MZU = $(10^{-20}\,\text{kg} \cdot \text{m})/(\text{m}^2 \cdot \text{s} \cdot \text{Pa})$; see equation 4 for unit conversions.

[d] See equation 6 for unit conversions.

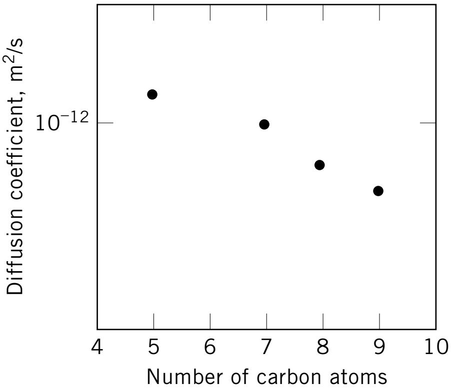

Fig. 4. Diffusion coefficient at 30°C of esters in a low density polyethylene film (18).

is water-dominated. The concentration in the polymer at the depth of penetration is zero. Hence, the average concentration C_{avg} is as from equation 9.

$$C_{\text{avg}} = 0.5Sp_x \tag{9}$$

The quantity sorbed ΔM_{sorb}, is simply the volume of polymer affected times the average concentration. The volume affected is the package area times L^*. The result is equation 10.

$$\Delta M_{\text{sorb}} = A(Dt)^{1/2}Sp_x \tag{10}$$

In this equation, A and t are observable. The pressure of the flavor must be obtained from an external reference, and D and S must be measured or estimated. If steady state is achieved, the quantity sorbed is given by equation 11. In either case the quantity sorbed can be important.

$$\Delta M_{\text{sorb}} = 0.5ALSp_x \tag{11}$$

The scalping of flavor and aroma by a package can be minimized by placing a barrier material as near as possible to the food. The ingress of undesirable permeants from the environment can be minimized by placing a barrier polymer between the food and the environment, not necessarily near the food.

Figures 4 and 5 show how the diffusion coefficient and solubility coefficient vary for a series of linear esters in LDPE film. The trends are generally true for other permeants in other films. As the size of the permeant increases, the diffusion coefficient decreases and the solubility coefficient increases. Since the increase in solubility coefficient is larger than the decrease in the diffusion coefficient, the permeability actually increases as the permeant size increases.

6. Physical Factors Affecting Permeability

Several physical factors can affect the barrier properties of a polymer. These include temperature, humidity, orientation, and cross-linking.

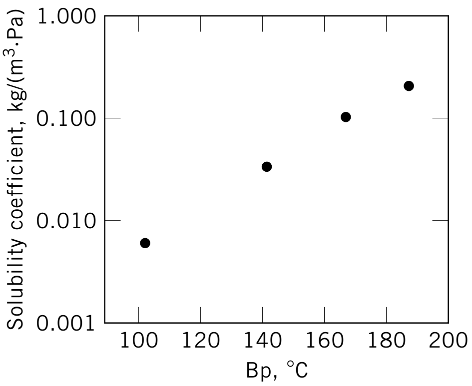

Fig. 5. Solubility coefficient at 30°C vs boiling point of ester in a low density polyethylene film (18). For unit conversion see equation 6.

6.1. Temperature.

The permeability varies with temperature according to equation 12, where P_o is a constant, E_p is the activation energy for permeation, R is the gas constant, and T is the absolute temperature.

$$P = P_o \exp\left(-E_p/RT\right) \tag{12}$$

The temperature dependence of the permeability arises from the temperature dependencies of the diffusion coefficient and the solubility coefficient. Equations 13 and 14 express these dependencies where D_o and S_o are constants, E_d is the activation energy for diffusion, and ΔH_{sol} is the heat of solution for the permeant in the polymer.

$$D = D_o \exp(-E_d/RT) \tag{13}$$

$$S = S_o \exp(-\Delta H_{sol}/RT) \tag{14}$$

The activation energy for diffusion is always positive and increases with increasing permeant size. Figure 6 shows this for diffusion in PVC. The heat of solution is near zero for small permanent gases such as oxygen; however, it becomes increasingly negative with increasing permeant size because the main contribution to the heat of solution is the heat of condensation. Equation 15 shows the relationship among the three exponential factors.

$$E_p = E_d + \Delta H_{sol} \tag{15}$$

Although, in principle, this sum could be negative and give a negative activation energy for the permeability, no examples are known. The permeability increases with increasing temperature.

Figure 7 shows generally how the permeability varies with temperature. Equation 12 is useful above and below the T_g, but not at the T_g. The main contribution to this effect is the diffusion coefficient. Above T_g, the diffusion process

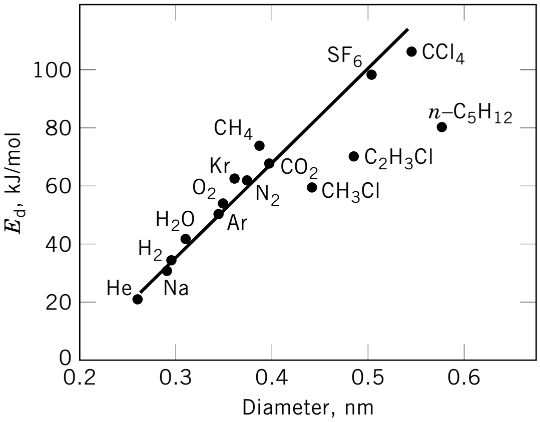

Fig. 6. Activation energy for diffusion in PVC as a function of penetrant mean diameter (19). To convert J to cal, divide by 4.184.

is controlled by motions of the polymer chains; hence, the activation energy is large. Below T_g, the diffusion process is controlled by the movement of the permeant; therefore, the activation energy is smaller. There is growing evidence with theoretical support that, above T_g, E_d decreases slightly with increasing temperature. Hence, the curve in Figure 7 would be concave downward above T_g.

For oxygen, the permeabilities increase ~10% per degree in polymers that are above their T_g such as vinylidene chloride copolymers and polyolefins. The

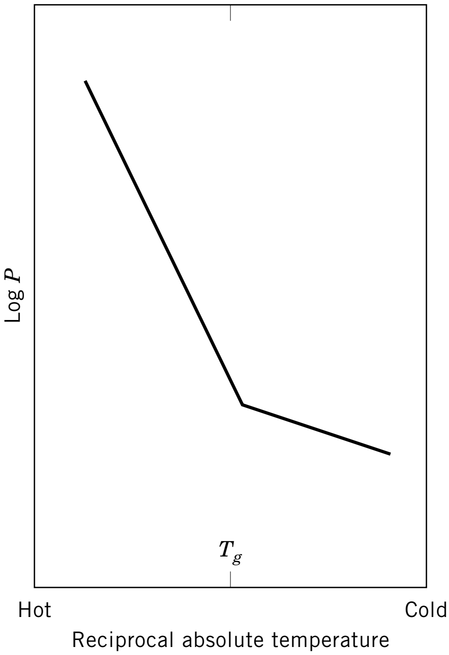

Fig. 7. Relationship of permeability and temperature.

Table 11. **Effect of Orientation on Oxygen Permeability for Certain Polymers**

Polymer	Degree of orientation, %	Oxygen permeability,[a] nmol/(m·s·GPa)[b]
polypropylene	0	300
	300	160
polystyrene	0	840
	300	600
polyester	0	20
	500	10
copolymer of 70% acrylonitrile and 30% styrene	0	2.0
	300	1.8

[a] At 23°C.

[b] See Table 1 for unit conversions.

permeabilities increase ~5% per degree in polymers that are below their T_g such as acrylonitrile copolymers, EVOH, and PET.

6.2. Humidity. When a polymer equilibrates with a humid environment, it absorbs water. The water concentration in the polymer might be very low as in polyolefins or it might be several weight percent as in EVA copolymers. Absorbed water does not affect the permeabilities of some polymers including vinylidene chloride copolymers, acrylonitrile copolymers, and polyolefins. Absorbed water increases the permeabilities in some polymers including EVA copolymers and most polyamides. Figure 2 shows how the oxygen permeability in an EVA copolymer increases with increasing humidity. A few polymers show a slight decrease in the oxygen permeability with increasing humidity. These include PET and the new amorphous nylon.

6.3. Orientation. The effect of orientation on the permeability of polymers is difficult to assess because the words orientation and elongation or strain have been used interchangeably in the literature. Diffusion in some polymers is unaffected by orientation; in others, increases or decreases are observed. The circumstances of the orientation (elongation) are important. Table 11 shows the effect of orientation on the oxygen permeability of four polymers. In each case a slight reduction in permeability occurs with orientation. In another study, however, no difference in oxygen or nitrogen permeability was observed between biaxially oriented polystyrene films and films that were cast from toluene solutions (20). Vinylidene chloride copolymer films show no difference in oxygen permeabilities between biaxially oriented (700%) and unoriented films. When increases in permeability have been observed, the creation of microcracks has been suspected.

6.4. Cross-Linking. Cross-linking has been shown to decrease the diffusion coefficient. The effect is greater for large permeants. To be effective, the cross-links need to be closer than ~30 − 40 nm. Such a high extent of cross-linking is a severe handicap for commercial applications; hence, little research is being done in this area for barrier materials.

7. Barrier Structures

Barrier polymers are often used in combination with other polymers or substances. The combinations may result in a layered structure either by coextrusion, lamination, or coating. The combinations may be blends that are either miscible or immiscible. In each case, the blend seeks to combine the best properties of two or more materials to enhance the value of a final structure.

7.1. Layered Structures. Whenever a barrier polymer lacks the necessary mechanical properties for an application or the barrier would be adequate with only a small amount of the more expensive barrier polymer, a multilayer structure via coextrusion or lamination is appropriate. Whenever the barrier polymer is difficult to melt process or a particular traditional substrate such as paper or cellophane [9005-81-6] is necessary, a coating either from latex or a solvent is appropriate. A layered structure uses the barrier polymer most efficiently since permeation must occur through the barrier polymer and not around the barrier polymer. No short cuts are allowed for a permeant. The barrier properties of these structures are described by the permeance P^*, which is described in equation 16 where P_i and L_i are the permeabilities and thicknesses of the layers.

$$\frac{1}{P^*} = \frac{L_1}{P_1} + \frac{L_2}{P_2} + \cdots \frac{L_i}{P_i} \tag{16}$$

The permeance can be used in equation 17 (which is a modification of eq. 1) to estimate package performance.

$$\frac{\Delta M_x}{\Delta t} = P^* A \Delta p_x \tag{17}$$

Figure 8 shows how the permeance varies for a hypothetical two-layer sheet as the relative thicknesses shift for a barrier layer with a permeability of 0.1

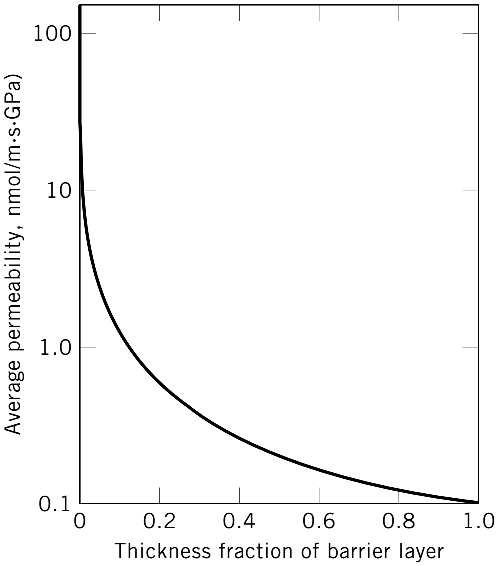

Fig. 8. Average permeance of a two-layer structure. See Table 1 for unit conversions.

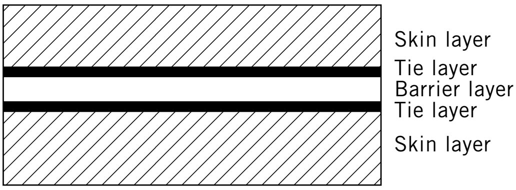

Fig. 9. Symmetric five-layer barrier coextruded sheet.

units and a nonbarrier layer with a permeability of 100 units. Figures 9 and 10 show profiles of coextruded sheet. Figure 9 shows a typical symmetric five-layer sheet, which is the simplest case and three extruders are necessary. One extruder supplies the outer layers that give structural integrity and toughness, eg, polypropylene. Another extruder supplies the barrier layer, and a third extruder supplies the adhesive tie layers that hold the structure together. A fourth extruder would be necessary if the outermost layers are different. Figure 10 shows an asymmetric sheet with a recycle layer. An additional extruder is needed to supply this layer to the coextrusion die. Both Figures 9 and 10 are drawn to scale. Figure 10 represents a recycle layer that is 30–50% of the total structure. Recycle at 30–50% has been demonstrated and reported for containers with a barrier layer of a vinylidene chloride copolymer (21–23). Development with other barrier polymers is continuing.

A typical coextruded sheet has a total thickness of 1270 μm (50 mil). After the container is formed by one of several methods, the sheet might then yield a wall thickness of 510 μm. The barrier layer in the container is typically in the range of 25–75 μm.

A thin layer of a barrier polymer can be coated onto a substrate. For example, a water-borne latex can be used to coat paper or a polymer such as polypropylene or PET. Commonly, two coats are applied to give a total barrier thickness of 5 μm. Two coats are useful so that minor holes in the first layer can be covered with the second layer. Adhesion of the coating is important for all substrates and hold out (minimizing wasteful soaking-in) is important for paper. Hence, sometimes the first layer is different from the second layer or the substrate receives a surface treatment before coating. A typical application is a vinylidene chloride copolymer latex on oriented polypropylene film for packaging snack foods. The most significant commercial application of solvent coating with barrier polymers is a special vinylidene chloride resin dissolved in a polar solvent coated onto cellophane or PET. Ethylene–vinyl alcohol polymers are potentially applicable for

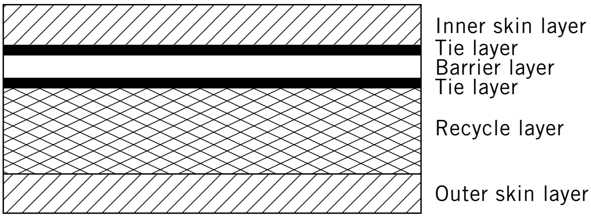

Fig. 10. Barrier sheet with recycle layer.

solvent coating. Inorganic coatings on polymers have the potential to enhance the barrier. However, commercial development is not significant.

7.2. Immiscible Blends. When two polymers are blended, the most common result is a two-phase composite. The most interesting blends have good adhesion between the phases, either naturally or with the help of an additive. The barrier properties of an immiscible blend depend on the permeabilities of the polymers, the volume fraction of each, phase continuity, and the aspect ratio of the discontinuous phase. Phase continuity refers to which phase is continuous in the composite. Continuous for barrier applications means that a phase connects the two surfaces of the composite. Typically, only one of the two polymer phases is continuous, with the other polymer phase existing as islands. It is possible to have both polymers be continuous. The aspect ratio L/W refers to the shape of the particles in the discontinuous phase. It is the average dimension of this phase parallel to the plane of the film L divided by the average dimension perpendicular to the film W. Plates in the plane of the film would have a high aspect ratio. Spheres or cubes would have an aspect ratio equal $=1$.

Figure 11 shows the theoretical permeabilities that are expected for a two-phase blend of polymers. The two solid curves represent calculations based upon Maxwell's equation (24) for an aspect ratio of 1 for the discontinuous phase. The dotted line is a prediction of the permeability using Nielsen's model (25) when a barrier polymer with an aspect ratio of 8 is discontinuous in a nonbarrier matrix. Figure 12 shows the expected result of a phase inversion for a two-polymer blend. The discontinuous phase is assumed to have an aspect ratio of 1. At some critical

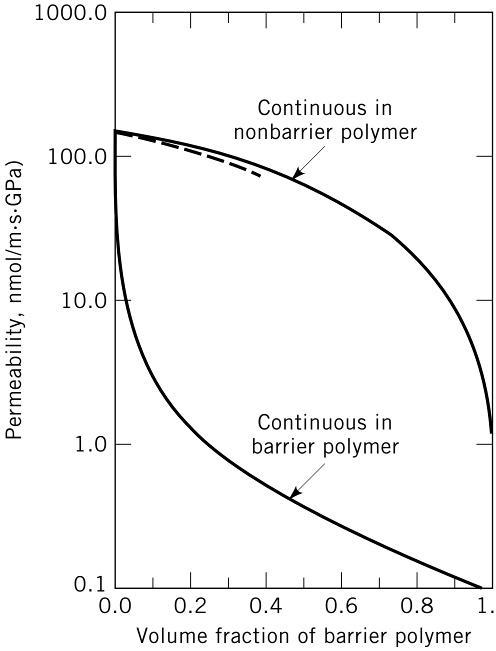

Fig. 11. Calculated permeabilities for a two-phase blend using Maxwell's result. Discontinuous phase has aspect ratio of 1.0. See Table 1 for unit conversion.

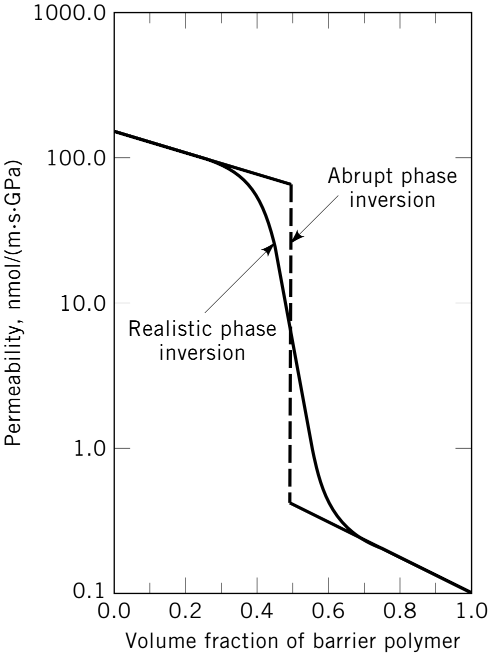

Fig. 12. Permeabilities for a two-phase blend with a phase inversion. Discontinuous phase has aspect ratio of 1.0. See Table 1 for unit conversion.

composition, the composite switches from being continuous in one polymer to being continuous in the other. Figure 12 is really a special case of Figure 11. Selar RB is a blend of polyethylene and nylon-6. Polyethylene is the majority constituent and forms the continuous phase. The product has its best barrier when it can be used in processes that impart orientation to the product. This gives a high aspect ratio to the nylon-6 and enhanced barrier to the article. Blends of polyethylene and EVOH are being developed.

Block copolymers of styrene and methacrylonitrile appear to behave like immiscible blends (11). Another case of immiscible blends is an inert filler in a polymer matrix. Although the inorganic fillers are assumed to have permeabilities nearly equal to zero, the filler must be wetted by the polymer to be effective at lowering the permeability of the host polymer. Table 12 shows the effect of a surface treatment on calcium carbonate to enhance wetting by polyethylene. With good wetting the permeability is reduced; with poor wetting the permeability is increased. Selar OH Plus resins are an example of filled polymers. By using 23.1 wt% mica flakes in an EVA alcohol copolymer, the permeability can be reduced with optimum processing to as low as 20% of the permeability of the unfilled polymer. Crystallinity in polymers acts like inert filler and lowers the permeability. However, since the amount of crystallinity in a given polymer is rarely under the control of the user, it is not considered here. Some orientation efforts can lower the permeability if the aspect ratio of the crystallites is increased.

Table 12. **Effect of Calcium Carbonate Fillers on Oxygen Permeability of LDPE**

$CaCO_3$, volume %	Type $CaCO_3$	Oxygen permeability,[a] nmol/(m · s · GPa)[b]
0		960
15	untreated	~ 2000
25	untreated	~ 4000
15	treated	500
25	treated	300

[a] At 23°C.

[b] See Table 1 for unit conversion.

7.3. Miscible Blends. Sometimes a miscible blend results when two polymers are combined. A miscible blend has only one amorphous phase because the polymers are soluble in each other. There may also be one or more crystal phases. Simple theory (26) has supported the empirical relation for the permeability of a miscible blend. Equation 18 expresses this relation, where P_{mb} is the permeability of the miscible blend and ϕ_1 and ϕ_2 are the volume fractions of polymer 1 and 2.

$$\ln P_{\mathrm{mb}} = \phi_1 \ln P_1 + \phi_2 \ln P_2 \tag{18}$$

This relationship is shown in Figure 13 where polymer 1 has a permeability 1000 times higher than that of polymer 2. Published data have small negative

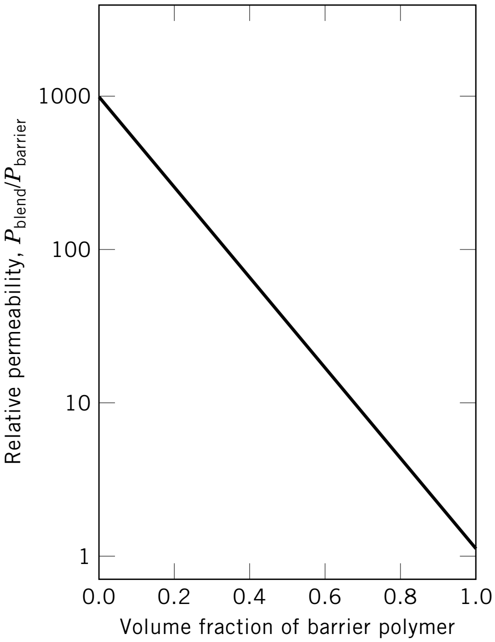

Fig. 13. Theoretical permeabilities for miscible blends of two polymers.

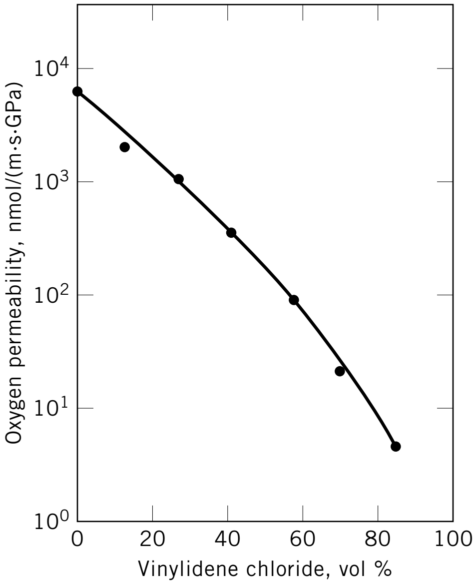

Fig. 14. Oxygen permeabilities of vinylidene chloride–*n*-butyl acrylate copolymers (27). See Table 1 for unit conversion.

deviations from this theoretical relationship. Part of the deviation can be explained by densification of the blend relative to the starting components. Random copolymers, which are forced (by covalent bonds) to imitate combinations of two materials, have permeabilities that are similar to miscible blends. However, the deviations from equation 18 tend to be positive. A series of styrene–MAN copolymers were studied (11) and slight positive deviations were found. Figure 14 shows the oxygen permeabilities of a series of vinylidene chloride–*n*-butyl acrylate copolymers [9011-09-0].

Plasticized polymers have been observed to behave like miscible blends. The permeabilities of oxygen, carbon dioxide, and water vapor in a vinylidene chloride copolymer increase exponentially with increasing plasticizer (4,5,28). About 1.6 parts plasticizer per hundred parts polymer is enough to double the permeability.

8. Predicting Permeabilities

Reasonable prediction can be made of the permeabilities of low molecular weight gases such as oxygen, nitrogen, and carbon dioxide in many polymers. The diffusion coefficients are not complicated by the shape of the permeant, and the solubility coefficients of each of these molecules do not vary much from polymer to polymer. Hence, all that is required is some correlation of the permeant size and the size of holes in the polymer matrix. Reasonable predictions of the permeabilities of larger molecules such as flavors, aromas, and solvents are not easily made. The diffusion coefficients are complicated by the shape of the permeant,

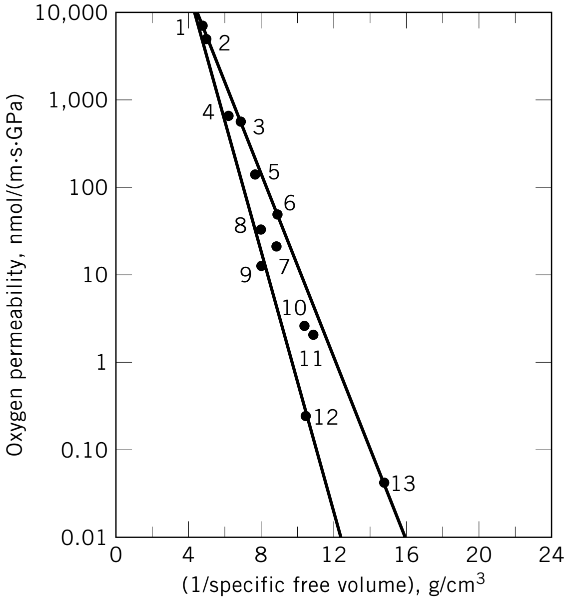

Fig. 15. Oxygen permeability vs 1/specific free volume at 25°C (30). 1. Polybutadiene; 2. polyethylene (density 0.922); 3. polycarbonate; 4. polystyrene; 5. styrene-*co*-acrylonitrile; 6. PET; 7. acrylonitrile barrier polymer; 8. poly(methyl methacrylate); 9. PVC; 10. acrylonitrile barrier polymer; 11. vinylidene chloride copolymer; 12. polymethacrylonitrile; and 13. polyacrylonitrile. See Table 1 for unit conversions.

and the solubility coefficients for a specific permeant can vary widely from polymer to polymer.

The permachor method is an empirical method for predicting the permeabilities of oxygen, nitrogen, and carbon dioxide in polymers (29). In this method, a numerical value is assigned to each constituent part of the polymer. An average number is derived for the polymer, and a simple equation converts the value into a permeability. This method has been shown to be related to the cohesive energy density and the free volume of the polymer (2). The model has been modified to liquid permeation with some success.

A less empirical model based solely on the specific free volume of the polymer has been proposed (30). Once the density and the intrinsic volumes of the polymer components are known, the specific free volume can be calculated. A correlation between the specific free volume and the oxygen permeabilities of several polymers is shown in Figure 15. The model seems to give better predictions for polymers with higher permeabilities. This model is for low molecular weight gases such as oxygen, nitrogen, and carbon dioxide.

For larger molecules, independent predictions of the diffusion coefficients and the solubility coefficients are required. Figure 16 shows how the diffusion coefficient varies as a function of permeant size in PVC. The two sets of data represent glassy PVC, which is below its T_g and plasticized PVC, which is above its T_g. Other glassy polymers show the steep slope, and other rubbery polymers show the shallow slope. The points near the lines represent spherical

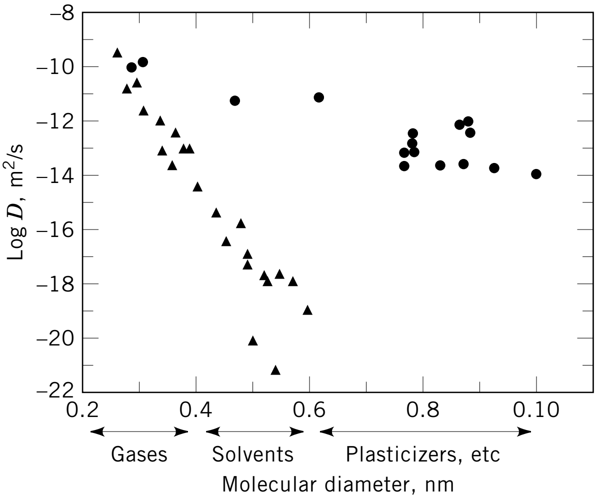

Fig. 16. Diffusivities of penetrants in rigid (▲) and plasticized (•) PVC vs molecular diameter at 30°C (31).

permeants whereas the points above the lines represent linear permeants. Predicting the diffusion coefficient for a permeant in a polymer requires knowing one other diffusion coefficient in the polymer. Figure 4 shows how the diffusion coefficient varies for permeant molecules slightly larger than shown in Figure 16.

The solubility coefficients are more difficult to predict. Although advances are being made, the best method is probably to use a few known solubility coefficients in the polymer to predict others with a simple plot of S vs $(\delta_{\text{poly}} - \delta_{\text{perm}})^2$, where δ_{poly} and δ_{perm} are the solubility parameters of the polymer and permeant, respectively. When insufficient data are available, S at 25°C can be estimated with equation 19, where $\kappa = 1$ and the resulting units of cal/cm^3 are converted to kJ/mol by dividing by the polymer density and multiplying by the molecular mass of the permeant and by 4.184 (16).

$$S = \kappa\left(\delta_{\text{poly}} - \delta_{\text{perm}}\right)^2 \tag{19}$$

The boiling temperature of a permeant can be used to predict the solubility coefficient only when the solubility coefficients of other permeants of the same chemical family are known.

9. Measuring Barrier Properties

Measuring the barrier properties of polymers is important for several reasons. The effects of formulation or process changes need to be known, new polymers need to be evaluated, data are needed for a new application before a large investment has been made, and fabricated products need to have performance verified. For some applications a full range of data is necessary, including P, D, and S plus the effects of temperature and humidity.

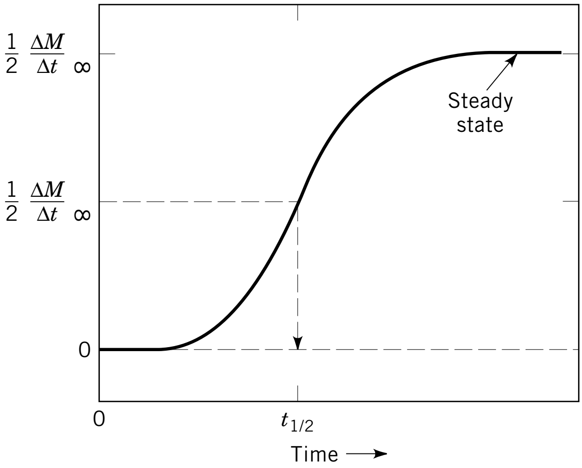

Fig. 17. Determining the diffusion coefficient from instantaneous transmission rates.

9.1. Oxygen Transport. The most widely used methods for measuring oxygen transport are based upon the Ox-Tran instrument (Modern Controls, Inc.). Several models exist, but they all work on the same principle. The most common application is to measure the permeability of a film sample. Typically, oxygen is introduced on one side of the film, and nitrogen gas sweeps the other side of the film to a coulometric detector. The detector measures the rate that oxygen comes through the film. The detector response at steady state can easily be converted to $\Delta M_{\mathrm{oxygen}}/\Delta t$ (eq. 1). Simple algorithms come with the instruction manual for calculating the permeability. The detector response can be monitored as a function of time to determine D, which is demonstrated in Figure 17. During the transient time before steady state is achieved, the transmission rate increases. First $t_{1/2}$, the time for the transmission rate to rise to 50% of the steady-state rate, must be found. Then equation 20 (32) is used where L is the film thickness. After P and D are known, S can be calculated.

$$D = \frac{L^2}{7.2 t_{1/2}} \tag{20}$$

The instrument has a heating element that allows for measurements at selected temperatures. The humidity can be controlled by passing the test gases through bubblers, monitoring the humidity, and adjusting the flow rates. This method requires some sophistication and is preferred when such testing is routine. The sandwich method is preferred for infrequent testing (33). With this method, pads that have been treated with saturated salt solutions are placed beside the film and encapsulated with thin polyethylene layers. The polyethylene offers almost no barrier to the oxygen and does a good job of holding the humidity near the test film.

Containers can be tested with the Ox-Tran instrument. However, care must be taken to obtain a good seal around the base of the container. A generous amount of epoxy glue is recommended.

9.2. Water Transport. Two methods of measuring WVTR are commonly used. The newer method uses a Permatran-W (Modern Controls, Inc.). In this method a film sample is clamped over a saturated salt solution, which generates the desired humidity. Dry air sweeps past the other side of the film and past an infrared detector, which measures the water concentration in the gas. For a calibrated flow rate of air, the rate of water addition can be calculated from the observed concentration in the sweep gas. From the steady-state rate, the WVTR can be calculated. In principle, the diffusion coefficient could be determined by the method outlined in the previous section. However, only the steady-state region of the response is serviceable. Many different salt solutions can be used to make measurements at selected humidity differences; however, in practice, $CaSO_4{\cdot}7H_2O$ is used nearly always because it gives a humidity of 90% as required by the traditional commercial applications. Typical experiments take between several hours and a day to complete.

The other method is the ASTM cup method (34). In this method, a desiccant is placed in a waterproof dish. The dish is covered with the experimental film and placed in an environmental chamber. The temperature and humidity are set for the conditions of interest, typically 37.8°C and 90% rh. At regular intervals, the dish is removed and weighed. After a few days enough data have been gathered to describe a steady-state rate of weight gain, and the WVTR can be calculated. Typical experiments take about a week to complete.

9.3. Carbon Dioxide Transport. Measuring the permeation of carbon dioxide occurs far less often than measuring the permeation of oxygen or water. A variety of methods are used; however, the simplest method uses the Permatran-C instrument (Modern Controls, Inc.). In this method, air is circulated past a test film in a loop that includes an infrared detector. Carbon dioxide is applied to the other side of the film. All the carbon dioxide that permeates through the film is captured in the loop. As the experiment progresses, the carbon dioxide concentration increases. First, there is a transient period before the steady-state rate is achieved. The steady-state rate is achieved when the concentration of carbon dioxide increases at a constant rate. This rate is used to calculate the permeability. Figure 18 shows how the diffusion coefficient can be determined in this type of experiment. The time lag t_L is substituted into equation 21. The solubility coefficient can be calculated with equation 2.

$$D = \frac{L_2}{6t_L} \tag{21}$$

9.4. Flavor and Aroma Transport. Many methods are used to characterize the transport of flavor, aroma, and solvent molecules in polymers. Each has some value, and no one method is suitable for all situations. Any experiment should obtain the permeability, the diffusion coefficient, and the solubility coefficient. Furthermore, experimental variables might include the temperature, the humidity, the flavor concentration, and the effect of competing flavors.

Any of the mathematical methods discussed previously to calculate P, D, and S in a single experiment are applicable to flavor permeation. Two cautions

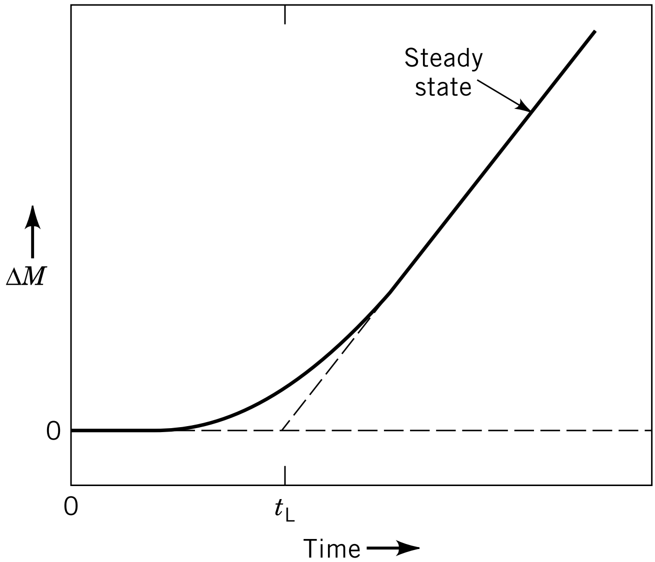

Fig. 18. Determining the diffusion coefficient from cumulative transmission.

are necessary. First, since the diffusion coefficients are typically low, the time to reach steady state can be long. The instrument must give stable responses for long times or something must be done to speed the experiment. The latter can be accomplished by using a thinner film or by raising the temperature. Second, the solubility coefficients are usually high. This means that the supply of permeant molecules could become depleted or the film could become altered. Recognizing the potential for depleting the flavor reservoir or for altering the experimental film is important. Using a thinner film or a constant supply of fresh permeant can help. Also working at high flavor concentrations should be done only when modeling performance that involves high concentrations.

Experimental data that show the effect of environmental variables have been given earlier. The most commonly misconstrued facet of the data is the effect of concentration on the permeability. The permeabilities of flavors in polymers have been correctly reported to be both independent and strongly dependent on the flavor concentration. However, to assume that there is disagreement would be incorrect. At very low concentrations, as commonly observed in foods, the permeabilities are independent of concentration. However, at high concentrations, as observed in some foods and in neat flavor oils, the permeabilities are quite concentration-dependent. The entire trend has been observed (35,36). Figure 19 shows that the permeability of ethyl propionate [105-37-3] in dry PVA is not affected by permeant concentration until the partial pressure of the permeant exceeds ~30% of the equilibrium vapor pressure. Above that concentration, the permeability is strongly dependent on the permeant concentration. This topic is important to include here because many techniques lack the sensitivity to work at low permeant concentrations. Then, at high concentrations, great variation is observed from experiment to experiment and from experimenter to experimenter. The variation does not necessarily diminish

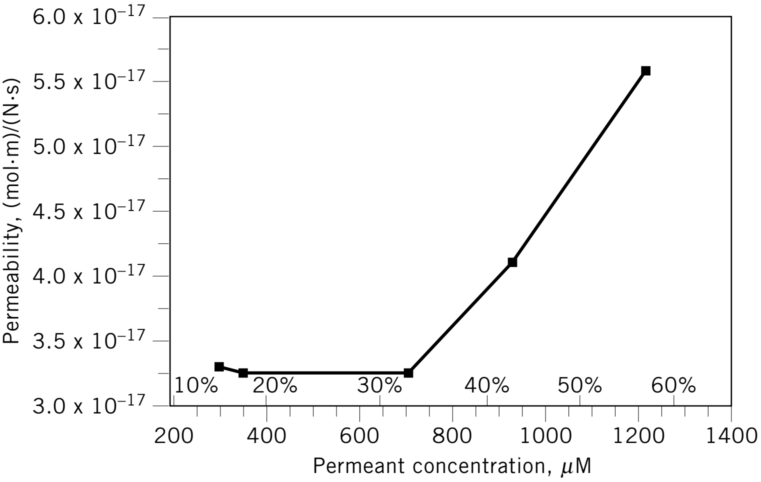

Fig. 19. Permeation of ethyl propionate at various concentrations through PVA at 25°C, 0% rh. Percentages on x-axis represent partial pressure of the permeant as a fraction of the equilibrium vapor pressure.

the quality of the measurement; it merely reflects the strong concentration dependence.

10. Safety and Health Factors

The use of safe materials is vital for barrier applications, particularly for food, medical, and cosmetics packaging. Suppliers of specific barrier polymers can provide the necessary details, such as material safety data sheets, to ensure safe processing and use of barrier polymers.

11. Applications

The primary application for barrier polymers is food and beverage packaging. Barrier polymers protect food from environmental factors that could compromise both taste and shelf life. They also help retain desirable flavors and aroma. Barrier polymers are also used for packaging medical products, agricultural products, cosmetics, and electronic components and in moldings, pipe, and tubing.

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