

1.0 Nature of Barrier Polymeric Materials

Barrier materials possess the ability to restrict the passage of gases, vapors, and organic liquids through their boundaries. Plastic films and sheeting, coatings, laminates, fabrics, metal foils, and many other types of materials are constructed to achieve an economic and efficient barrier layer. Polymeric materials dominate the barrier materials used in the packaging industry, and are found in other applications ranging from window films to clothing, because of their superior properties and low cost.

1.1 Transport of Gases and Vapors

The permeability or transmission rate of gases and vapors through any polymeric material is dependent upon two factors; the solubility of a gas or vapor and the rate of diffusion through the barrier. The solubility function is dependent upon the chemical relationship between the permeant molecule and the polymer; and the rate of diffusion is dependent upon the size of the permeant molecule and the amorphous configuration of the barrier polymer. The permeability coefficient measures relative permeation behavior and is used to compare the permeability of different polymers. The gases and vapors most often studied are water vapor, oxygen, carbon dioxide, and nitrogen.^[2030]

Gas (oxygen) transmission rate, OTR, is usually reported in cubic centimeters of gas that pass through a square meter of film in 24 hrs when the gas pressure differential on one side of the film, at a specified temperature, is one atmosphere greater than that on the other side. Water vapor transmission rate, WVTR, is reported as grams of water which will pass through a given area of material in a specified time, the usual units are grams per 1 square meter per 24 hrs at a specified temperature and humidity differential.^[1080]

The method by which a gas or vapor (the penetrant) permeates a polymer matrix is postulated to occur as follows:

- 1 Absorption into the polymer.^[1005]
- 2 Diffusion (qv) through the polymer matrix.^[1005]
- 3 Desorption through the polymer wall and evaporation for the surface.^[1005]

Permeability is the proportionality constant in the general equation for mass transport of a penetrant across a barrier.^[1020]

1.2 Mass Transport of a Gas

$$\frac{\Delta m_{\text{gas}}}{\Delta t} = \frac{P A \Delta p}{\ell}$$

P	=	permeability of barrier
$\Delta m_{\text{gas}} / \Delta t$	=	transmission rate
A	=	area of barrier
ℓ	=	thickness of barrier
Δp	=	partial pressure difference across the barrier

Permeability, as a property of a material, is the product of permeance and thickness. Permeance is the ratio of the gas transmission rate (the quantity of a given penetrant through a unit of the parallel surfaces of a barrier material in unit time under specified test conditions) to the difference in partial pressure of the penetrant on both sides of the barrier material. The unit of permeability is $\text{cm}^3 \cdot \text{mm}/\text{m}^2 \cdot \text{day} \cdot \text{atm}$, the unit for gas transmission rate ($\Delta m/A\Delta t$) is $\text{cm}^3(\text{STP})/\text{m}^2 \cdot \text{day}$.^{[1005][1020]}

For conventional polymer films it is often found that the oxygen permeability is a reciprocal function (inversely proportional) of the film thickness. The following equation allows for the definition of a permeation coefficient, P , that does not depend upon the film thickness, l :

$$P_{O_2} = \text{OTR } l$$

In this case, P_{O_2} is a material constant of the barrier polymer as far as the structure (crystallinity, orientation of the molecular chains, etc.) of the film does not vary. The necessary thickness of a film to reach a desired OTR can be calculated based on the permeability of the film of a different thickness.^[1074]

Moisture vapor permeability is measured in terms of weight of penetrant rather than volume and is measured at specified relative humidity conditions on each side of the film. As in the case of gases, vapor permeation rates for gauges other than unit thickness are often estimated by assuming that the permeation rate is inversely proportional to thickness.

In this publication, gas permeability and vapor permeability are listed under the *Permeability (normalized units)* heading in each chapter and take into consideration thickness in the normalized units of $\text{cm}^3 \cdot \text{mm}/\text{m}^2 \cdot \text{day} \cdot \text{atm}$ and $\text{g} \cdot \text{mm}/\text{m}^2 \cdot \text{day}$, respectively. Source document data is also presented and often denotes a transmission rate for a given thickness. Because the mathematical results are a good estimate, they are presented as normalized units. However, test results for various thickness may not be the same as the calculated result.

1.3 Special Situations—Coatings and Laminates

The oxygen transmission rate, OTR, of coated and uncoated films and the permeability $\text{OTR}_{\text{coating}}$ of the coating itself can be calculated by using the “laminated” equation:^[1020]

$$\text{OTR}_{\text{coating}} = \frac{\text{OTR}_{\text{uncoated}} \times \text{OTR}_{\text{coated}}}{\text{OTR}_{\text{uncoated}} - \text{OTR}_{\text{coated}}}$$

1.4 Factors Affecting Permeability

Permeation. Permeation is the rate at which a gas or vapor passes through a polymeric material. Permeation rate can be affected by many factors including polymer characteristics, i.e., the chemical make-up of the polymer and its physical state, the penetrating gas or vapor, and the environment.^[1005]

Polymer Characteristics. Polymer characteristics are properties which are affected by molecular organization of the polymer. Pendant chains, degree of chain motion, degree of crystallinity, and polarity must all be taken to account. Formulation,

processing properties and results, such as the degree of cross-linking, the presence of additives such as plasticizers, and the presence of pinholes and microvoids also affect the permeability properties.^[2030]

Crystallinity is an important factor because the crystallites themselves are impermeable. Thus, a permeant must seek out amorphous zones in order to penetrate a material. A lower degree of crystallinity yields greater permeability. The polymer state with the highest degree of crystallinity provides the least amount of permeation, thus the better barrier. Increased molecular orientation also reduces permeability, in effect making the path to permeate more difficult. Improved packing order and increased crystallinity of the barrier material increases its density and again, decreases permeability.^[1005] A similar effect is observed on radiation cross-linking of the material such as polyethylene.

Inert fillers affect barrier properties. Fillers with a high degree of compatibility and adhesion to the polymer matrix decrease permeability and improve barrier properties, and vice versa. For those polymers that must be plasticized or modified to achieve some desired effect, the alteration tends to make the resulting material more permeable.^[1005] Plasticizers generally increase the permeability of films and the permeability will vary with plasticizer content.

Physical interaction between penetrant and barrier material such as the formation of hydrogen bonds or the interaction between polar and functional groups may slow down the permeation.

Penetrant. Penetrant substances move through the material. Permeation depends upon the nature of the penetrant. The rate of passage of a permeating species through a polymer matrix is governed by its solubility in the polymer and the relationship between the size of the penetrant molecule and the interstices in the polymer. The type of penetrant is important since polymer characteristics that result in low permeability to one gas could cause high permeability to another gas. For example, highly polar polymers such as poly(vinyl) alcohol or cellophane, are excellent gas barriers but poor moisture vapor barriers. Conversely, nonpolar hydrocarbon polymers, although good barriers to water vapor, are poor barriers to gases.^[1005]

Permanent gases are usually inert toward barrier polymeric materials and their permeation rates are inversely proportional to their molecular size. The permeation of other gases and vapors depends strongly on the ease of their condensation and on their affinity to the barrier material. A readily soluble penetrant will produce swelling of the polymer, resulting in an

increased permeability coefficient. A less soluble penetrant will be “blocked” from penetration and the permeability will not be affected.

Environment. Environment can strongly affect permeability. Permeation rates are affected by temperature, humidity, and pressure.

Temperature. Permeation rates are affected by temperature, following the classical Arrhenius relationship. According to a common rule of thumb, permeability increases by 30–50% for every 5°C rise in temperature.^[1005]

Temperature affects the transport equation (above) in two ways. The flow of a gas (Δm gas) is directly affected by changes in temperature, and the partial pressure difference (Δp) is also affected by temperature. Whenever there is a difference in relative humidity between the inside and outside of a film, there will be a difference in partial pressure from one side of the barrier layer to the other. Thus, the permeability coefficient is also a function of the temperature and a measurement of the permeability coefficient or the vapor transmission rate is not valid without a reference to the test temperature.^[1020]

Solubility coefficients of permanent gases such as oxygen and sparingly soluble gases and vapors increase with increasing temperature, resulting in increased permeability. In contrast, solubility coefficient of readily condensable gases and vapors, such as sulfur dioxide and ammonia, decrease with increasing temperature, resulting in decreased permeability.

Permeability to water vapor usually increases with increasing temperature, depending upon the moisture content of the barrier material and its nature. Permeability to organic vapors generally increases with increasing temperature, but is complicated by the swelling of the barrier material.

Humidity. Absorbed water has a plasticizing effect on some barrier materials and can lead to increased permeability. Polar polymers, typified by cellophane and poly(vinyl) alcohol, lose their barrier properties when plasticized by water or exposed to high humidity. On the other hand, the diffusion of water in some materials is concentration dependent and the water vapor transmission rate is affected by the relative humidity differential. Therefore, the relative humidity of the test environment has to be known to make a correct interpretation of the permeability measurements.

Humidity is critical in the use of cellophane as meat-wrap where high oxygen transmission is desired. In an environment of < 35% relative humidity, cellophane is relatively impermeable to oxygen. As the

humidity increases, i.e., when it absorbs water as from a piece of meat, the cellophane becomes swollen and allows the permeation of oxygen.

The same phenomenon is present with a cellophane-polyethylene laminate. The laminate will show a greater permeability to water vapor when tested with the cellophane toward the high humidity than when the polyethylene is toward the high humidity. When next to the moisture, the cellophane absorbs more water and contributes greater permeability to the laminate.

Pressure. Permanent gases at pressures close to standard obey Henry’s law on proportionality and their solubility coefficient is proportional to the partial pressure of the gas. As a result, their permeation rates, reduced to unit pressure, are generally independent of the pressure.

Henry’s law on proportionality is true for gases that become liquid at far from standard temperature and pressure (1 atm and 0°C, respectively), primarily air, oxygen, argon, and carbon dioxide. The vapors of substances, such as water and acetone, that are liquid at pressures and temperatures close to standard do not obey Henry’s law.

The permeation rates of sparingly soluble vapors, such as water vapor in polyolefins, may be proportional to the vapor pressure differential across the barrier wall. The permeation rates of readily soluble penetrants that do not obey Henry’s law have a complex relation to pressure. For these penetrants, test pressure must be reported for the permeability data to be valid.

1.5 Polymers 101

The following explanation and examples were drawn from “The Macrogalleria” website developed by the Department of Polymer Science at the University of Southern Mississippi.^[1057]

Polymers generally fall into one of three categories:

- **Thermoset.** This is a hard and stiff cross-linked material that does not become moldable when heated. Rubbers are thermosets.
- **Thermoplastic.** This material can be molded and shaped when it is heated, often referred to as “plastic.” Most barrier materials fall into the thermoplastic category.

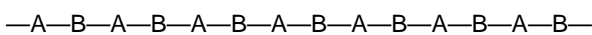
- *Thermoplastic Elastomer*. Thermoplastic elastomers (TPEs) perform like rubber and process like plastic. Specialty TPEs often demonstrate barrier properties.

Amorphous and Crystalline. Thermosets and thermoplastics can be categorized as either crystalline or amorphous. A crystalline polymer is any polymer that is arranged in a regular order or pattern. An amorphous polymer is a polymer whose chains are not arranged in ordered crystals. However, crystalline polymers are not entirely crystalline but have two components: the crystalline portion and the amorphous portion. Thus, the term semi-crystalline can be used to describe these polymers. The amorphous portion of a crystalline polymer can make up 40–70% of the polymer. Higher crystallinity generally leads to better barrier properties.

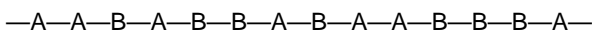
1.6 Molecular Design

When a polymer is made by linking only one type of small molecule, or monomer, together, it is called a *homopolymer*. When two different types of monomers are joined in the same polymer chain, the polymer is called a *copolymer*. Two monomers, *A* and *B*, can be made into a copolymer in many different ways.

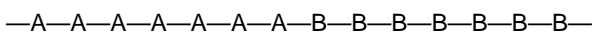
When the two monomers are arranged in an alternating fashion, the polymer is called an *alternating copolymer*:



In a *random copolymer*, the two monomers may follow in any order:

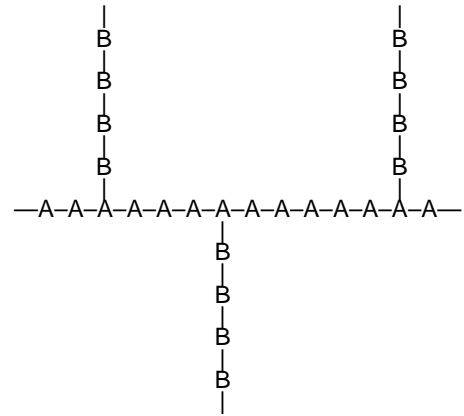


In a *block copolymer*, all of one type of monomer are grouped together, and all of the other are grouped together. A block copolymer can be thought of as two homopolymers joined together at the ends:



A common block copolymer is poly(styrene-butadiene-styrene) (SBS) rubber. It is used for the soles of shoes and for tire treads.

A *graft copolymer* results when chains of a polymer made of monomer *B* are grafted onto a polymer chain of monomer *A*:



One kind of graft copolymer is high impact polystyrene, or HIPS for short. It is a polystyrene backbone with chains of polybutadiene grafted onto the backbone. The polystyrene gives the material strength, but the rubbery polybutadiene chains give it resilience to make it less brittle.

1.7 Elastomers 101

Elastomer means rubber. Some polymers which are elastomers include polyisoprene or natural rubber, polybutadiene, polyisobutylene, and polyurethanes. Elastomers are special because they can be stretched to many times their original length, and can return to their original shape without permanent deformation.

To help elastomers bounce back even better it helps to cross-link them. Cross-linking is the forming of covalent links between the different polymer chains, joining them all into a single networked molecule. Most objects made of rubber contain only one molecule. When the polymer chains are joined together, it is even harder to pull them out of their original positions, causing the polymer to bounce back even better when stretched.

A thermoplastic elastomer is an elastomer modified to behave like a thermoplastic during processing (melting) and an elastomer during use, or an elastomer in which the molecules are tied together when the rubber is being used, but allows the chains to separate when being processed.

The idea behind thermoplastic elastomers is the notion of a *reversible cross-link*. Normal cross-linked polymers cannot be reused because they don't melt. They don't melt because the cross-links tie all the polymer chains together, making it impossible for the material to flow. Normal cross-links are covalent, chemically bonding the polymer chains together into one molecule. The reversible cross-link uses noncovalent, or secondary, interactions between the polymer chains to bind them together. These interactions include hydrogen bonding and ionic bonding.

Through the use of noncovalent interactions to form cross-links, a thermoplastic is created because the noncovalent bonds are broken by heating. This allows the material to be processed, and most importantly, recycled. When it cools again, the cross-links reform giving the material rubber-like properties.

2.0 Collected Comparative Barrier Properties of Plastics and Elastomers

It is often valuable to understand how a material performs when compared to other materials used in similar applications. For example, will polyethylene or nylon allow more water vapor to permeate? Will EVOH or PVDC supply less oxygen transmission? With comparative data, trends between and within material families can be easily studied and broad designations, such as high barrier or low barrier, can be

made. This chapter was created to provide such a resource.

The following tables and figures detail transmission rates for water vapor, d-limonene, oxygen, and other gases of multiple materials on the same table/figure. From the tables/figures it can be determined which family of material will provide more or less permeability when compared to the included materials under stated conditions.

The data presented was gathered from many different sources including material and product manufacturers, academic resources, and industry reference texts, and is provided as a reference guide to determine general trends. Barrier properties, like many other properties of polymers, are dependent upon a multitude of conditions, including but not limited to: processing conditions, test procedure, film thickness, relative humidity, material structure, and molecular design.

The data is presented in the format under which it was published. Any detail available from the source document has been included, i.e., test method, temperature, relative humidity, and thickness. Many materials are found in multiple comparisons and caution is recommended when comparing between tables and figures since testing parameters may not be constant and are not always known. It is recommended the user look for trends within the table/figure only.

The material chapters that follow offer more detailed presentation of each material and will, where appropriate, refer the user to this chapter for more detailed comparative information.

Index by Material

Material	Location
Acrylonitrile-butadiene-styrene, ABS	Table 1, Figure 15, Figure 16
Butadiene Rubber, BR	Table 5, Table 7
Butyl Rubber, IIR	Table 5, Table 6, Table 7
Chloroprene Rubber (Neoprene), CR	Table 5, Table 6, Table 7
Copolyester, PETG	Table 1, Figure 8, Figure 9
Cyclic Olefin, COC	Figure 1
Epichlorohydrin, ECO	Table 7
Epoxy	Figure 7
Epoxides	Table 3
Ethylene Propylene Diene Monomer, EPDM	Table 5, Table 6, Table 7
Ethylene-vinyl acetate, EVA	Table 1
Ethylene-vinyl alcohol, EVOH	Table 1, Table 4, Figure 1, Figure 2, Figure 3, Figure 4, Figure 5, Figure 6, Figure 7, Figure 10, Figure 14, Figure 15
Fluoropolymers, FPM or FKM	Table 2, Table 7, Table 9, Figure 1
Hypalon, CSM	Table 7
Isoprene Rubber, IR	Table 5, Table 7
Liquid-crystal polymer, LCP	Table 1, Figure 1, Figure 2, Figure 3
Low Density Polyethylene, LDPE	Table 1, Table 8, Figure 1, Figure 14
High Density Polyethylene, HDPE	Table 1, Table 4, Table 8, Figure 1, Figure 4, Figure 8, Figure 9, Figure 14, Figure 15, Figure 16
Natural Rubber, NR	Table 5, Table 6, Table 7
Nitrile	Table 1, Table 4, Figure 5, Figure 6, Figure 8, Figure 9, Figure 10
Nitrile Butadiene Rubber, NBR	Table 5, Table 6, Table 7
Nylon, amorphous	Table 4
Nylon 6, PA 6	Table 1, Table 4, Figure 1, Figure 3, Figure 4, Figure 8, Figure 9, Figure 15, Figure 16
Nylon 66 PA 66	Figure 3
Nylon MXD6	Figure 5, Figure 7, Figure 8, Figure 9, Figure 10
Nylon, modified	Figure 6
Oriented Nylon MXD6	Figure 2
Oriented Nylon 6, O-PA 6	Figure 1, Figure 2

Material	Location
Parylene	Table 3
Polyacrylate, ACM	Table 7
Polyacrylonitrile, PAN	Figure 15, Figure 16
Polyamide	Table 8
Polybutylene Terephthalate, PBT	Figure 15, Figure 16
Polycarbonate, PC	Figure 15, Figure 16
Polyetherimide, PEI	Figure 15, Figure 16
Polyethylene Terephthalate, PET	Figure 4, Figure 6, Figure 15, Figure 16
Polyethylene Terephthalate Polyester, PETG	Figure 15
Oriented PET, O-PET	Figure 1, Figure 2
Polyethylene, Chlorinated, CPE	Table 7
Polyethylene, Crosslinked, XPE	Table 7
Polyethylene Napthalate, PEN	Figure 7
Polypropylene, PP	Table 1, Table 2, Figure 4, Figure 8, Figure 9, Figure 14, Figure 15, Figure 16
Oriented Polypropylene, O-PP	Figure 1
Polyphenylene Ether, PPE	Figure 15, Figure 16
Polystyrene, PS	Table 1, Figure 8, Figure 9, Figure 15, Figure 16
Polycarbonate, PC	Table 1, Table 4, Figure 15
Poly(vinyl) chloride, PVC	Table 1, Table 2, Table 8, Figure 8, Figure 9, Figure 15, Figure 16
Polyester, PET	Table 1, Figure 8, Figure 9
Polyurethane (elastomer)	Table 8
Poly(vinylidene) chloride, PVDC	Table 1, Table 2, Table 4, Figure 1, Figure 2, Figure 4, Figure 5, Figure 6, Figure 10, Figure 17
Silicone, VSi	Table 3, Table 7, Figure 16
Styrene Butadiene Rubber, SBR	Table 5, Table 6, Table 7
Thiokol Rubber	Table 7
Urethane, AU	Table 3
Silicone, VSi	Table 5, Table 7
Vinyl Acrylic Ethylene, VAE	Table 7
Vinylidene Chloride-vinyl Chloride Copolymer	Table 8

Index by Permeant (and Condition)

Permeant	Location
Carbon Dioxide	Table 3, Table 6, Table 8, Table 9
Carbon Dioxide vs. Relative Humidity	Figure 6
Helium	Table 6, Table 9
Hydrogen	Table 3, Table 6
d-Limonene	Figure 3, Figure 14
DI Water	Figure 13
Nitric Acid	Figure 12
Nitrogen	Table 3, Table 6, Table 8, Table 9
Oxygen	Table 1, Table 3, Table 6, Table 8, Table 9, Figure 1, Figure 4, Figure 8, Figure 15
Oxygen vs. Relative Humidity	Figure 2, Figure 5, Figure 7, Figure 10
Propane	Table 6
Toluene	Figure 11
Water Vapor	Table 1, Table 2, Table 3, Table 4, Table 6, Table 9, Figure 1, Figure 4, Figure 9, Figure 16

Table 1. Oxygen and Water Vapor^[1080]

Plastic	Permeability	
	Oxygen (cc/100 sq in.)	Water (grams/100 sq in.)
Low-Density Polyethylene (LDPE)	300 - 400	1.0 - 1.5
High-Density Polyethylene (HDPE)	100 - 200	0.3 - 0.5
Polypropylene (PP)	150 - 200	0.2 - 0.5
Polystyrene (PS)	300 - 400	5 - 10
Polycarbonate (PC)	200 - 300	3 - 8
Nitrile	0.8	3 - 5
Poly(vinyl) chloride (PVC)	5 - 10	0.9 - 2
Polyester (PET)	10	0.9
Copolyester (PETG)	25	1.2
Nylon 6 (PA)	1 - 3	6 - 22
Poly(vinylidene) chloride (PVDC)	0.1	0.01
Ethylene-vinyl alcohol (EVOH) (dry)	0.01	6

Table 2. Water Vapor^[2015]

Structure	MVTR
60 μ PVC/ 45 μ aluminum foil/25 μ oriented polyamide (cold form foil)	0.00
75 μ UltRx 3000 (homopolymer)/200 μ PVC	0.08
51 μ UltRx 2000 (homopolymer)/200 μ PVC	0.11
23 μ SupRx 900 (homopolymer)/200 μ PVC	0.23
15 μ Rx 160 (homopolymer)/200 μ PVC	0.36
90 g/m ² · PVDC/PVC triplex	0.25
60 g/m ² · PVDC/coated PVC	0.50
33 μ Cx 130E (coextrusion)/200 μ PVC	0.78
40 g/m ² · PVDC/coated PVC	0.75
300 μ Polypropylene	1.00
250 μ PVC	3.00

- ASTM F1249: 38°C, 90% RH (g/m² · 24 hrs).
- Key: UltRx 3000, UltRx 2000, SupRx 900, Rx 160, and Cx 130E are Honeywell Aclar Fluoropolymer PCTFE products.

Table 3. Various Gases and Moisture Vapor²⁰¹⁸

Polymer	Gas Permeability at 25°C, [cm ³ (STP) mil]/(100 in ² /day · atm)				Moisture Vapor Transmission
	N ₂	O ₂	CO ₂	H ₂	90% RH, 37°C, (g mil/100 in ² · day) **
Parylene N	7.7	39	214	540	1.5
Parylene C	1.0	7.2	7.7	110	0.21
Parylene D	4.5	32	13	240	0.25
Epoxides	4	5 - 10	8	110	1.79 - 2.38
Silicones	—	50,000	300,000	45,000	4.4 - 7.9
Urethanes	80	200	3,000	—	2.4 - 8.7

Table 4. Moisture Barrier Properties^[2022]

Polymer	95% RH, 23°C (73°F) WVTR, (g/100 in ² · day · atm)
Extrudable PVDC	0.3
HDPE	0.3
Selar PA 3426*	2.0
EVOH	4.0
Acrylonitrile Copolymer	5.0
Polycarbonate	6.4
Nylon 6	12.4

* Selar PA 3426: Amorphous Nylon

Table 5. Rubbers^[1104]

Low Permeability	
Exxon Chemical Exxpro elastomers	Excellent
NR/IR BR/SBR	Fair
EPDM	Fair
CR	Good
NBR	Good
Silicone	Poor

Table 6. Relative Permeabilities of Various Rubbers to Gases^[1109]

Polymer	H ₂	He	N ₂	O ₂	CO ₂	C ₃ H ₈	H ₂ O
IIR (Butyls)	7	8	0.3	1	5	14	100
SBR		13	1.7				
EPDM		21	5				450
NR			9	23	150	170	2000
NBR	12	10	0.6	2	18		
CR	13		1.2	4	26		900

Table 7. Impermeability to Gases for Various Rubbers^[1114]

Rubber	Impermeability	Rubber	Impermeability
NR	Fair	VSi	Poor/Fair
IR	Fair	CSM	Good
SBR	Fair	ACM	Fair/Good
IIR	Excellent	FPM	Good/Excellent
BR	Fair	ECO	Excellent
EPDM	Fair	CPE	Good
CR	Fair/Good	X PE	Good
NBR	Good	VAE	Good
T	Excellent	PNR	Good/Excellent
AU	Poor/Fair		

Table 8. Permeability to Gases for Various Rubbers^[1112]

Gas Permeability (m ³ /mm/m ² /24 hrs) · 10 ⁻⁴ , [(ft ³ /mil/ft ² /24 hrs) · 10 ⁻⁴]			
Polymer	Oxygen	Nitrogen	Carbon Dioxide
Estane Polyester type 90 Hardness	1.3 (2.6)	0.7 (1.4)	8.0 (18.2)
Vinylidene Chloride-vinyl Chloride Copolymer	0.04 (0.08)	--	0.2 (0.41)
Polyvinyl Chloride	2.6 (5.2)	--	16.6 (33.6)
Low Density Polyethylene	9.4 (19.1)	3.1 (6.2)	49.4 (100.0)
High Density Polyethylene	12.0 (24.2)	17 (3.4)	133.4 (270.0)
Polyamide	59.8 (121.0)	1.7 (3.4)	133.4 (270.0)

Table 9. Oxygen, Nitrogen, Helium, Carbon Dioxide, Air, and Water Vapor Through Fluoropolymers

Material Family	FLUOROPOLYMERS							
Material Grade	PTFE	PFA	FEP	ETFE	CTFE	ECTFE	PVDF	PVF
Reference Number	1134							

MATERIAL CHARACTERISTICS

Sample Thickness (mm)	0.1
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TEST CONDITIONS

Temperature (°C)	23
Test Method	ASTM D1434 for gases, DIN 53122 for water vapor

PERMEABILITY (source document units)

Gas Permeability (cm ³ /m ² · day · bar)								
Air	2000	1150	600	175	--	40	7	50
Oxygen	1500	--	2900	350	60	100	20	12
Nitrogen	500	--	1200	120	10	40	30	1
Helium	3500	17000	18000	3700	--	3500	600	300
Carbon Dioxide	15000	7000	4700	1300	150	400	100	60
Vapor Permeability (g/m ² · day · bar)	5	8	1	2	1	2		7

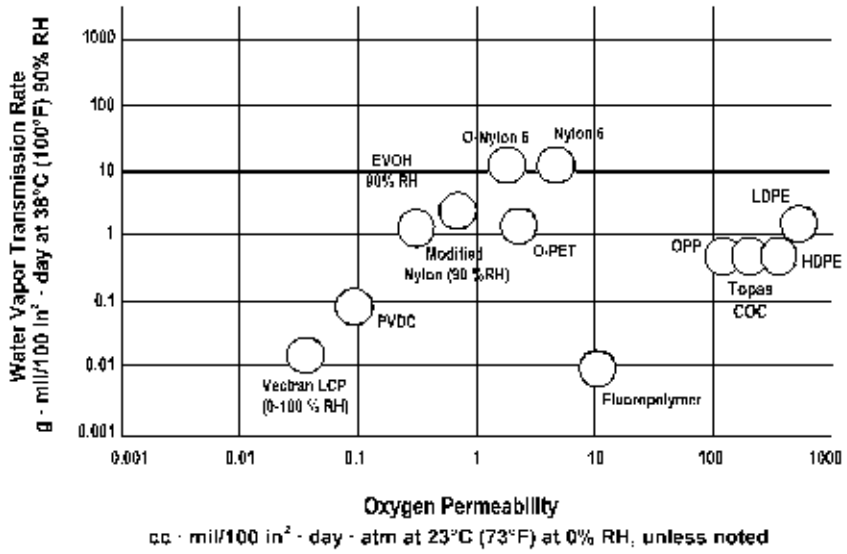


Figure 1: Oxygen and water vapor.^[1002]

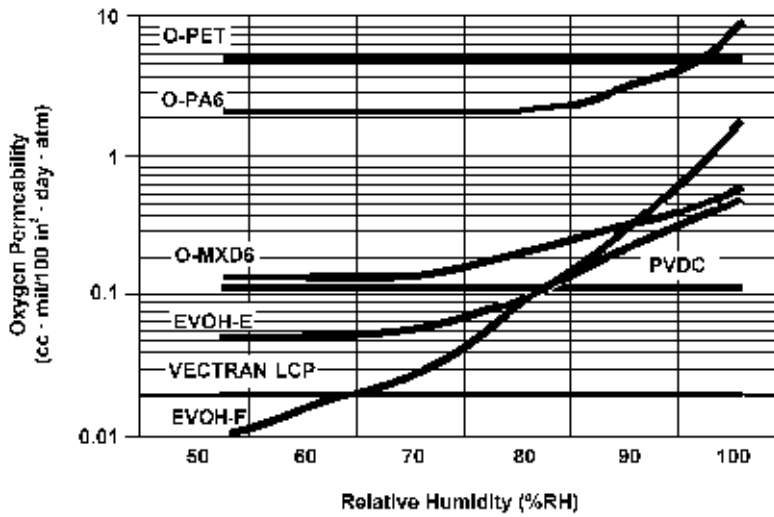


Figure 2: Comparative oxygen permeability at increasing relative humidity.^[1002]

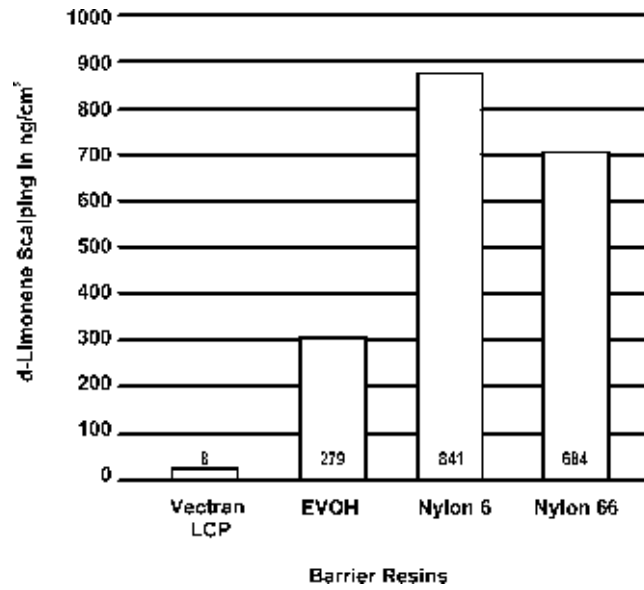


Figure 3: Flavor scapling (d-limonene from orange juice).^[1002]

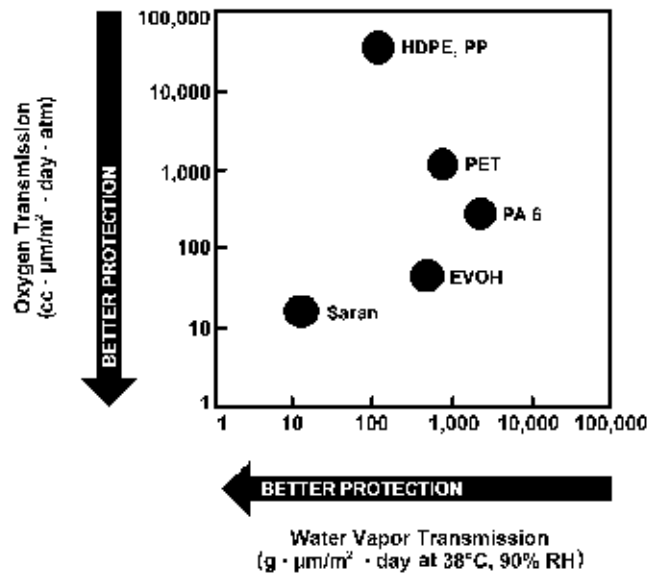


Figure 4. Oxygen.^[1050]

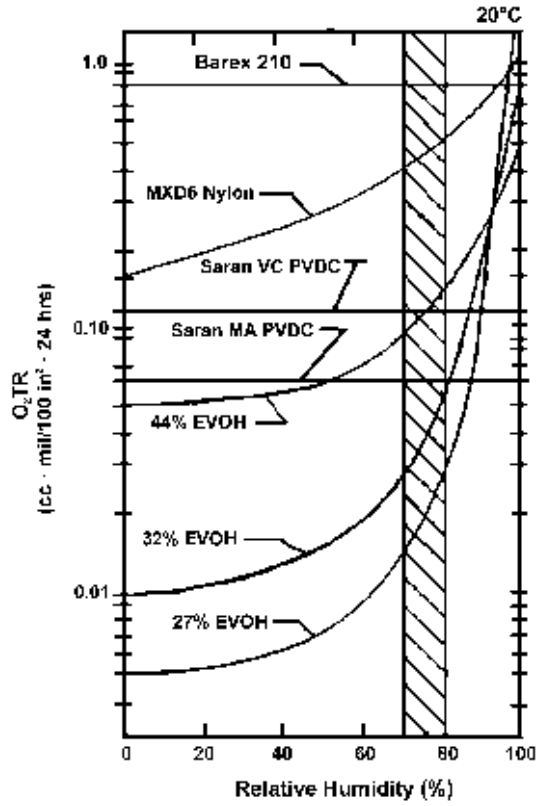


Figure 5. Oxygen vs. relative humidity.^[1020]

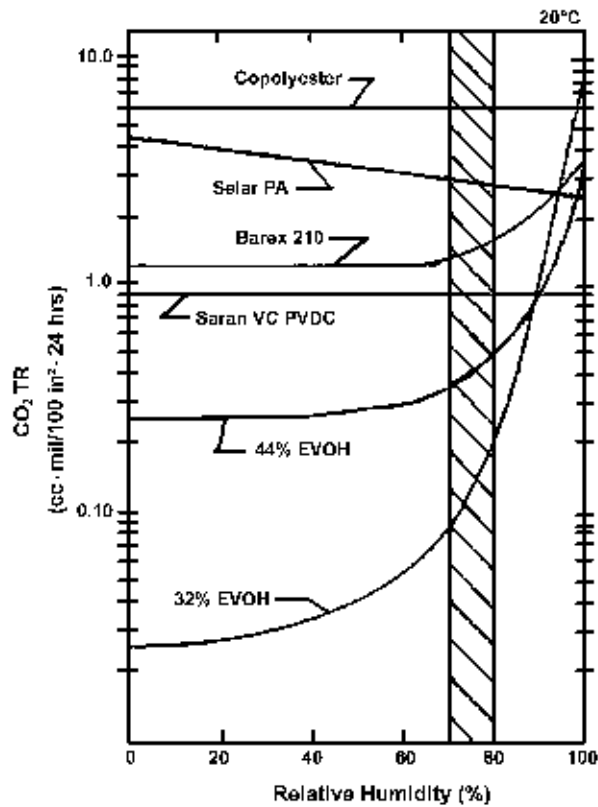


Figure 6. Carbon dioxide vs. relative humidity.^[1020]

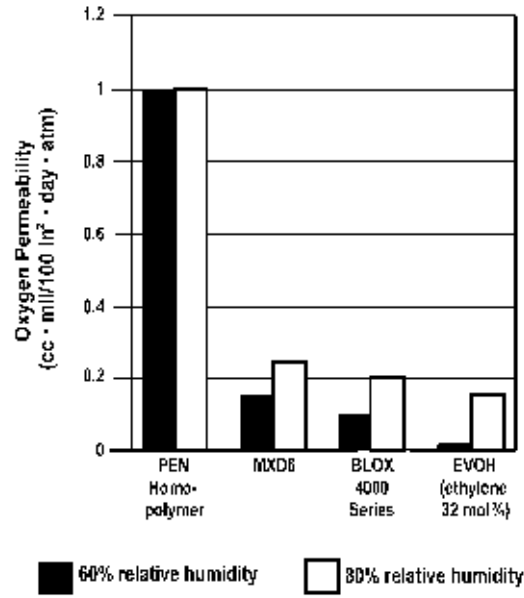


Figure 7. Oxygen as a function of humidity.^[1075]

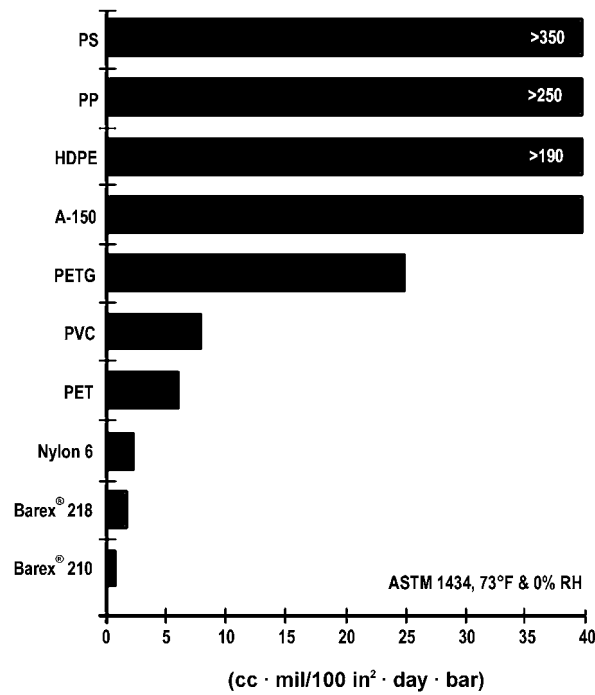


Figure 8. Oxygen transmission rate.^[2003]

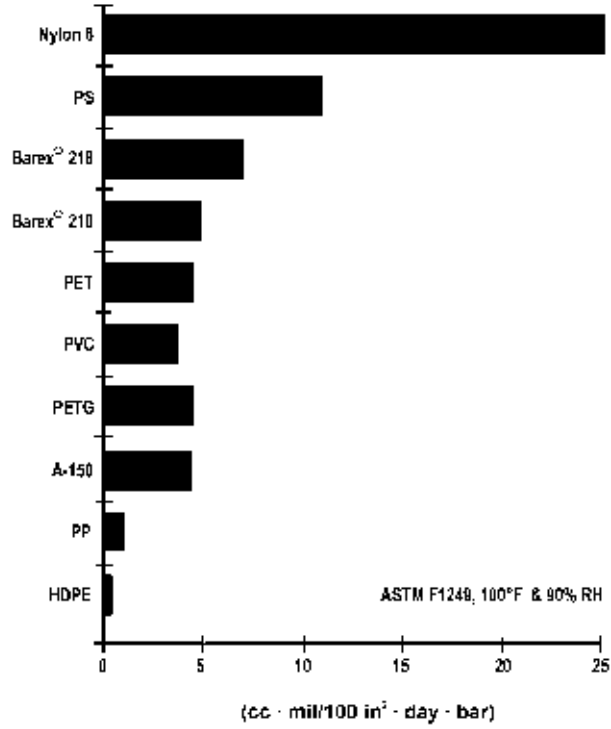


Figure 9. Water vapor.^[2003]

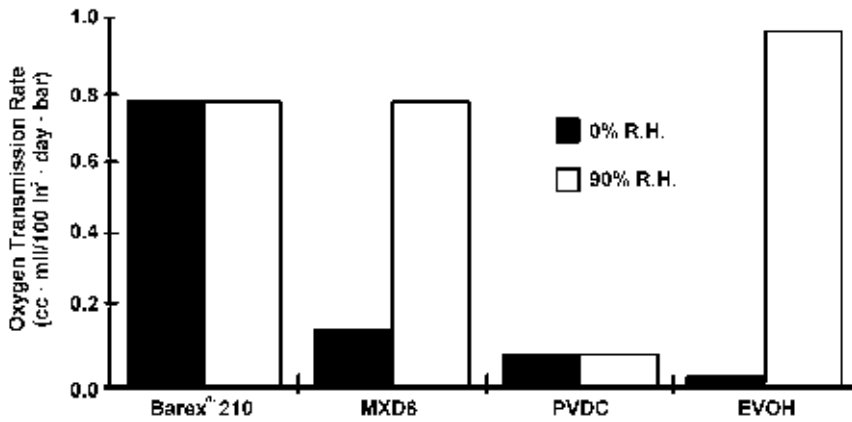
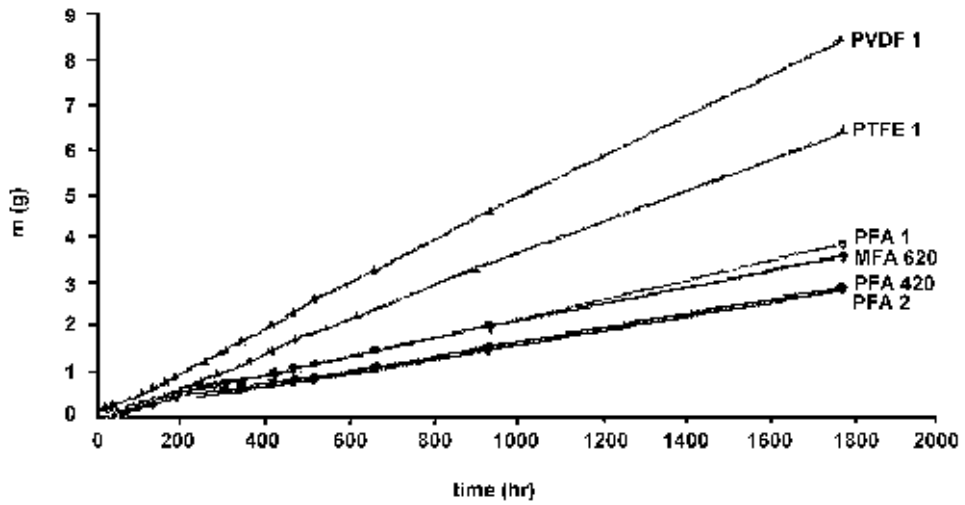


Figure 10. Effect of moisture on oxygen permeability.^[2003]

Mass of permeant leaving outer surface of tube wall (m) vs. time
for the tubes exposed to toluene at 80°C.



*Values for PFA 1 coincide with those of PFA 2

Figure 11. Toluene at 80°C.^[2004]

Mass of permeant leaving outer surface of tube wall (m) vs. time
for the tubes exposed to 65% nitric acid at 80°C.

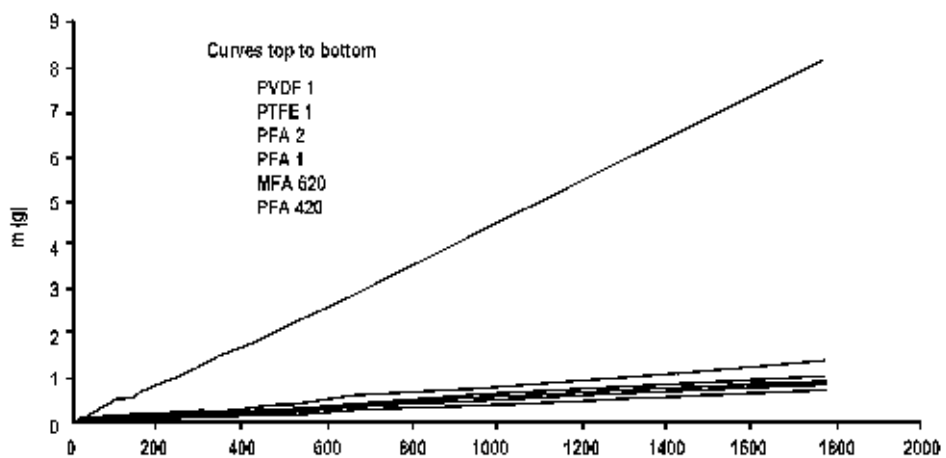


Figure 12. Nitric acid at 80°C.^[2004]

Mass of permeant leaving outer surface of tube wall (m) vs. time for the tubes exposed to deionized water at 80°C.

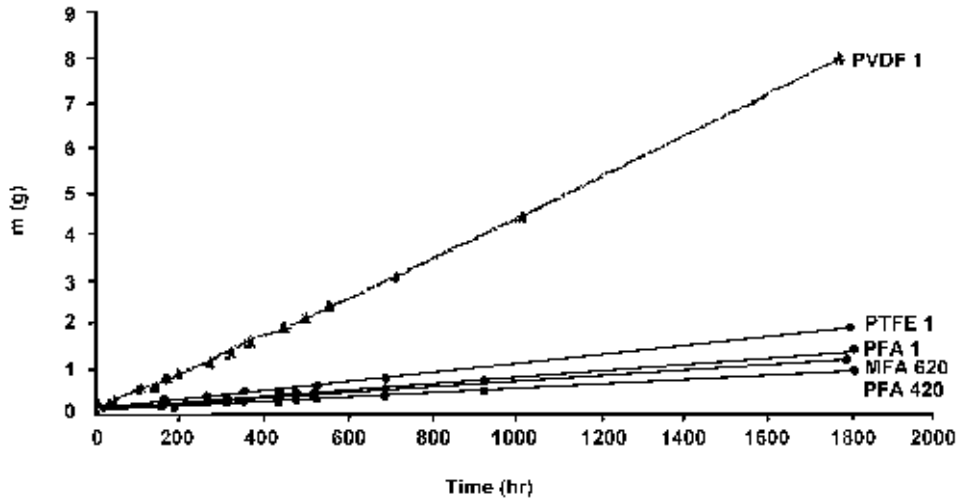


Figure 13. DI water at 80°C.^[2004]

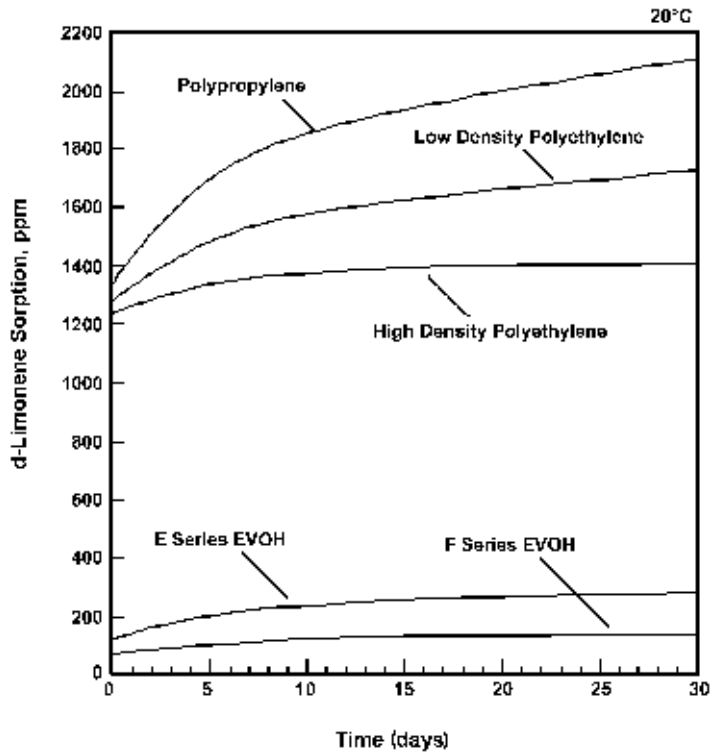
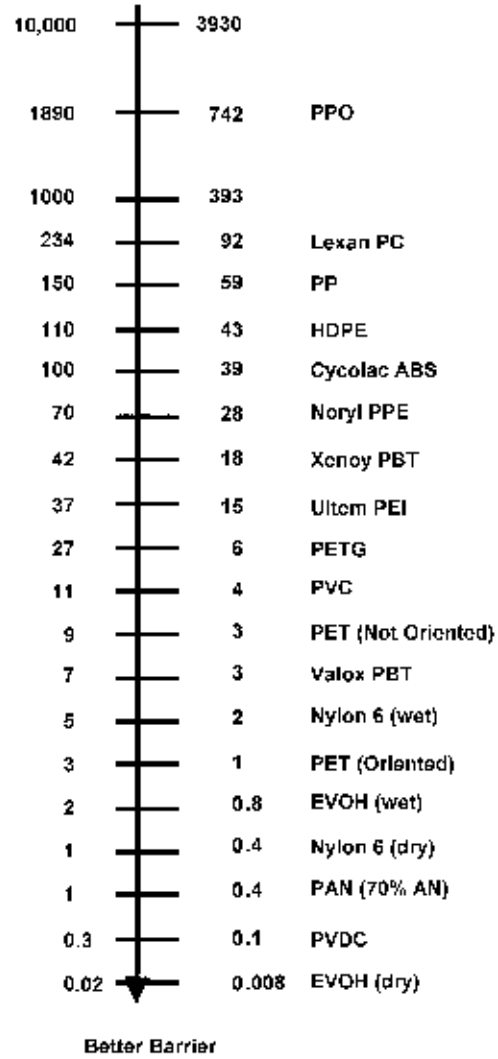


Figure 14. d-Limonene sorption, 20°C.^[1021]

Units

cc · mil/24 hr · 100 in² · atm

Units

cm³ · mm/m² · day · atmFigure 15. Oxygen.^[1033]

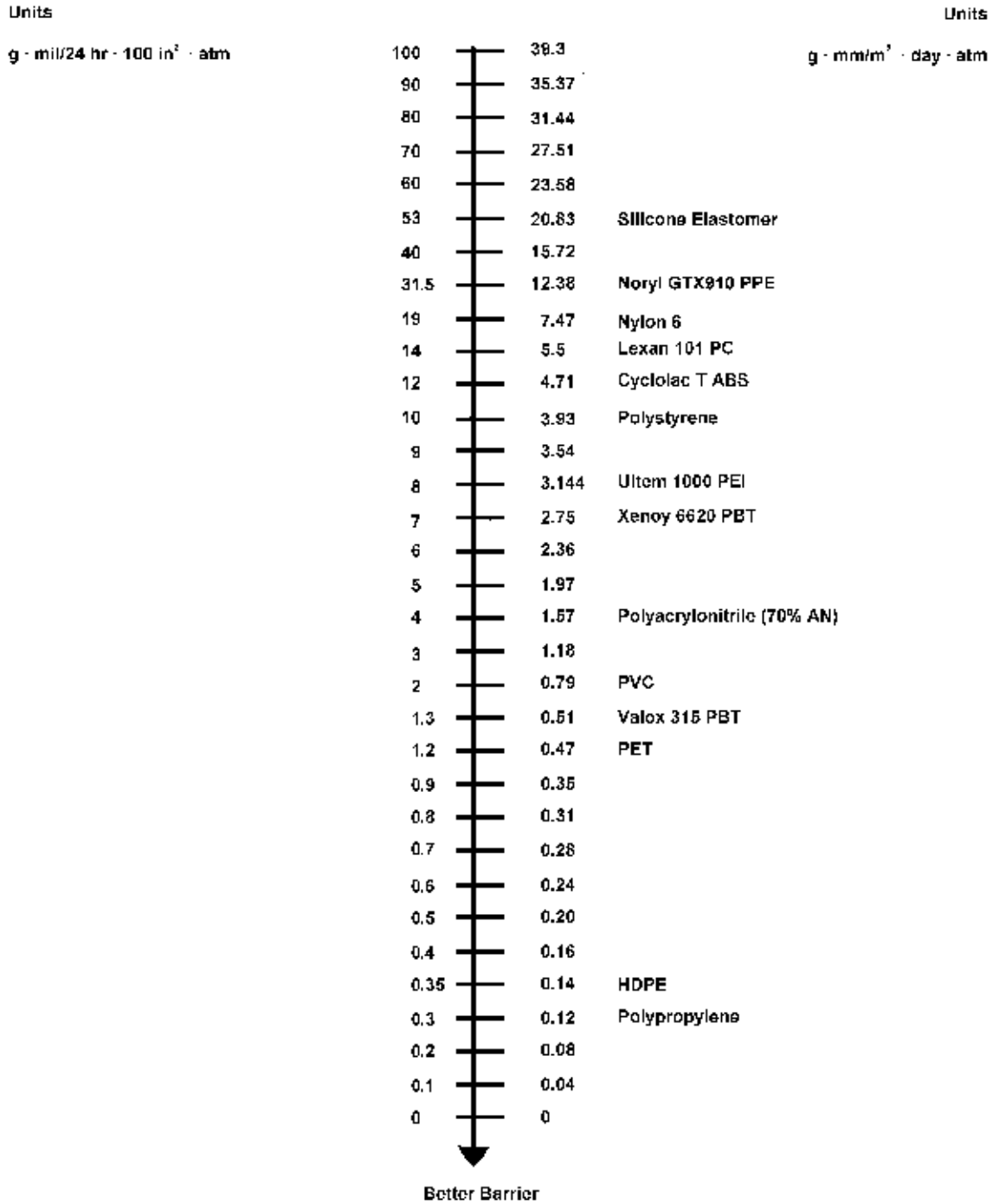


Figure 16. Water vapor.^[1033]

3.0 Processing

Blown Film. Blown film is one of two prime processes used to fabricate film products. Films are typically defined as less than 0.254 mm (10 mils) in thickness, although blown film can be produced as high as 0.5 mm (20 mils). The blown film process is used to produce a wide variety of products, ranging from simple monolayer films for bags to very complex multilayer structures used in food packaging. Co-extrusion is also a growing process technology, which can provide additional functional, protective, and decorative properties.^[1022] See Fig. 17 for the blown film process.

The material feed system combines virgin polymer with recycled material from edge trim or scrap film. The virgin material can be a single component or blends of two or more polymers. Various additives such as slip, antiblock, or pigments can also be blended into the feed to the extruder.

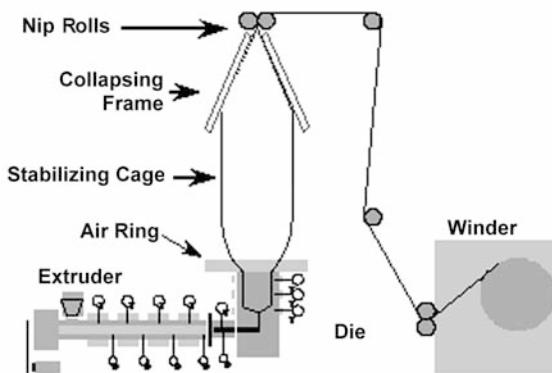


Figure 17. Blown film process.^[1022]

The extruder is the heart of the blown film process, this mechanism conveys the polymer into the extruder, melts the polymer, and then creates enough pressure to push the molten polymer through the die.

The blown film die forms molten polymer from the extruder into an annular shape. After the molten

polymer exits the die, it is formed into its final dimensions and cooled. Stretching the molten polymer is achieved by expanding the bubble using air pressure trapped inside the bubble. The web is drawn down with the nip rolls, reducing the film to the target thickness.

After collapsing into a flat web, any of several auxiliary processes can be performed, such as treating, slitting, sealing, or printing. The finished film can be made into rolls using a winder for later processing, or fed to an in-line bag machine and converted into bags.^[1022]

Biaxial Orientation.^[1055] *Co-Extrusion.* Co-extrusion combines two or more molten polymer layers into a composite extruded web or tube which provides functional, protective, or decorative properties. The advances in co-extrusion equipment technology, the new polymers introduced, and the market application development have made co-extruded films attractive. Figure 18 illustrates the process for producing bi-axially oriented film.

The co-extrusion process for the manufacture of bottles and containers in multilayer technology opens up new markets. An increasing demand for blow molded containers with barrier layers is making itself felt around the world, not only for packaged food, but also for cosmetics, chemicals, agro-chemicals, and pharmaceuticals. Multilayer technology produces precise wall thickness for all layers. Figure 19 shows a cross section of multilayer bottles produced through co-extrusion.^[1054]

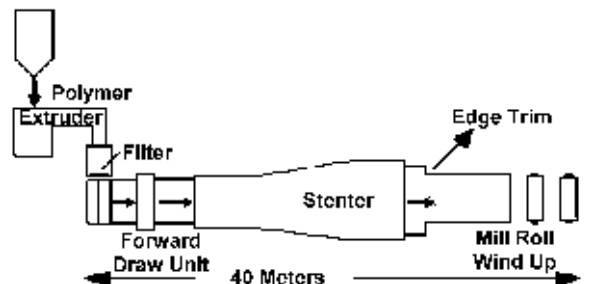


Figure 18. Process for producing biaxially oriented film.^[1055]

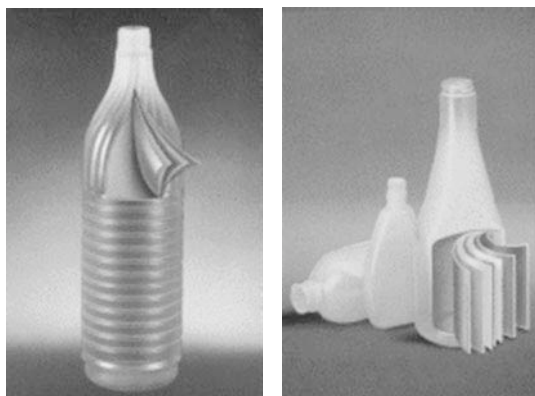


Figure 19. Cross-section of multilayer bottles produced through co-extrusion.^[1054]

In recent years, there has been an increase in the number of polymers available for extrusion. There are several types of polymers to choose from, with attributes such as high barriers, selected permeation rates, adhesion, high-strength sealants, easy opening (peelable) sealants, low temperature sealants, high hot tack sealants, high-tensile strength, high-impact strength, high-tear strength, high modulus, high temperature resistance, low temperature impact, high clarity, abrasion resistant, chemical resistant, low taste and odor, high cling, low slip, stabilized, degradable, antistatic, antifog, pigmented, thermoformable, and the list goes on. The performance attributes of polymers will continue to grow as application needs are identified.

When the requirement for specific performance properties cannot be met by a single polymer, or even with blends of different polymer types extruded in a monolayer film, co-extrusion with a high strength polymer can allow significant down-gauging while maintaining or improving key properties. Heat-seal polymers can be incorporated into a film structure to improve packaging line efficiency or speed. Co-extrusion can:

- lower the cost to produce many films by reducing the amount of expensive polymer used, increasing the amount of less costly polymers, using recycled material, or reducing film thickness
- reduce the number of process operations required when several polymers are needed to obtain the desired properties and allows scrap or trim material to be recycled into the core of the structure.

Calendering. Calendering consists of a series of counter-rotating and temperature controlled metallic rolls that convert softened polymer or rubber blends to a very uniform flat sheet or film at relatively high production rates. The polymer is softened or compounded using Banbury batch mixers, planetary extruders, twin screw compounding extruders, or continuous mixing devices. Softened polymer batches may be dropped into large two roll mills that condition the rubber and allow continuous material flow to a short barreled extruder/strainer which filters out contaminants. The filtered feedstock may then be conveyed in a rope form to the calender where it is formed to its final thickness, finished or embossed, cooled, slit, and packaged. Finished product thickness is primarily a function of the gap between two calender rolls. The calendering process is generally used to process highly amorphous elastomeric polymers such as plasticized PVC and other rubbery materials.^[1063]

Cast Film. A typical cast film line uses single-screw extruders to convert a variety of thermoplastics into continuous melt streams that are formed by the dies into the film structure. The cast film process involves the extrusion of polymer melt through a slot or flat die to form a thin molten sheet, or film. This film is “pinned” to the surface of a chill roll (typically water-cooled and chrome-plated) by a blast of air from an air knife or vacuum box. The film quenches immediately and then has its edges slit prior to winding.

Because of the fast quench capabilities, a cast film generally has much better optics than a blown film and can be produced at higher line speeds. However, it has the disadvantage of higher scrap due to edge-trip, and very little film orientation in the cross-direction.

Cast films are used in a variety of applications, including stretch/cling films, personal care films, bakery films, and high clarity films.^[1022]

Extrusion Coating and Lamination. In extrusion coating and lamination, resin is melted and formed into thin hot film, which is coated onto a moving, flat substrate such as paper, paperboard, metal foil, or plastic film. The coated substrate then passes between a set of counter-rotating rolls, which press the coating onto the substrate to ensure complete contact and adhesion.

Extrusion laminating, also called sandwich laminating, is a process related to extrusion coating. However, in this case, the extrusion coated layer is used as an adhesive layer between two or more substrates. A second layer is applied to the extrusion coating while

it is still hot and then the sandwich is pressed together by pressure rolls. The extrusion coated layer may also serve as a moisture barrier.

Substrates that can be coated with polyolefins include paper, paperboard, bi-axially-oriented polypropylene (BOPP), bi-axially-oriented nylon (BON), polyester and other plastic films, metal foil, fabrics, and glass fiber mats.^[1022]

Injection Molding. Injection molding has been one of the most important fabrication tools for the plastics industry since the reciprocating screw machine was patented in 1956. Today, it is almost impossible to do anything without using injection molded parts. Approximately 32% of all plastics are converted using the injection molding process, which provides the capability to mass-produce intricate parts in a precise manner. They are used in automotive interior parts, electronic housings, housewares, medical equipment, compact discs, pallets, toys, crates, pails, thin-wall food containers, promotional drink cups, lids, and milk bottle caps.

The injection molding process involves melting the plastic in an extruder and using the extruder screw to inject the plastic into a mold, where it is cooled. Speed and consistency are vital keys to running a successful injection molding operation, since profit margins are normally below 10%.^[1022]

Plasma Polymerization. Plasma polymerization is a process of depositing high quality permeation barrier coatings on plastic substrates. The process allows for several layers to be “stacked” forming multilayer coatings. The arrangement of the layers has an effect on the permeation properties. Figure 20 shows a principle sketch of the processing equipment used for the coating of flat samples.

After the chamber is evacuated to a pressure of approximately 2–10 Pa, suitable gas mixtures are fed into the back of the quartz tube—the plasma reactor. The gas molecules cross the area of high microwave intensity and are enhanced to a plasma state, in which the gas molecules are fragmented and activated. These particles from the plasma start to react and definitely cross-link on the substrate surface to form a thin layer. The layer formed in this way can display marked differences from conventional polymers due to the high energy plasma reactions and can supply completely new surface properties. All coatings show fundamental properties, such as a high degree of cross-linking, high density, good thermal and chemical resistance, freedom from micropores, and good adhesion to the substrate, even to non-polar surfaces. These typical properties predestine plasma polymerized coatings for the use as permeation barriers on plastic substrates.

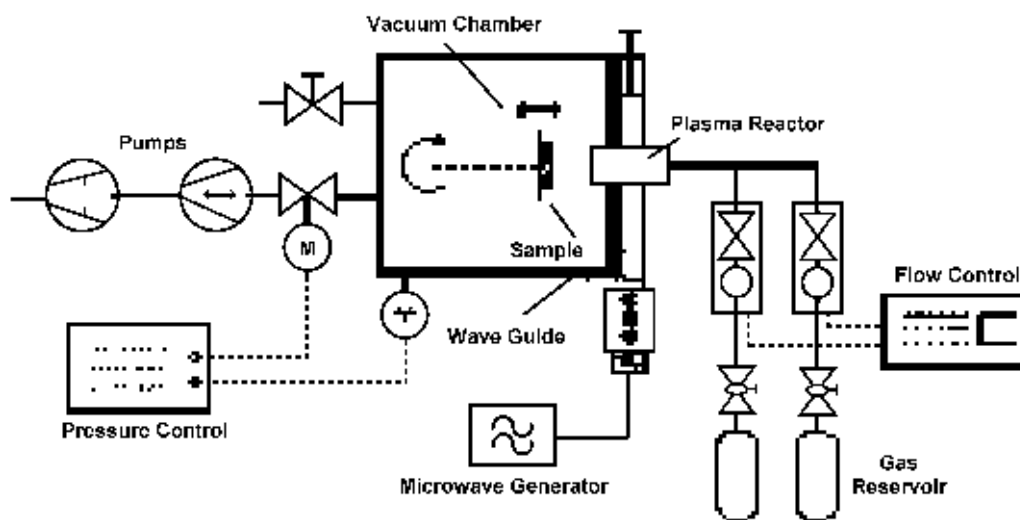


Figure 20. Sketch of the plant for microwave plasma polymerization.^[1074]

In general, gas permeation barrier coatings consist of SiO_x or AlO_x structures. Barrier coatings are most often deposited onto polyethylene terephthalate, polypropylene and polyethylene films.^[1074]

Rotomolding. Rotomolding resins can be molded in complex shapes and provide good physical properties and surface finish. Many are UV stabilized, available in granule or powder form. Rotomolding applications include toys, large tanks, road barriers and other similar applications.

Rubber. Rubber is compounded, basic ingredients added to make the desired set of properties in a final rubber product, mixed, and cured to make the final product; several different methods can be used to combine the ingredients.

There are many different classes of ingredients and each class has many different types of materials. Some rubber products are relatively simple, others, such as tires are quite complicated. After compounding, the rubber must be mixed. There are different ways to combine all the different ingredients that go into making a complete rubber compound.

In order to make something useful out of a rubber compound, the compound has to be “cured.” Unlike plastic, which is melted and then forced into a cold mold to be formed into a part, rubber needs to be heated to a high enough temperature and for a time long enough to cause the chemical reaction called curing to take place. Among the methods of forming a rubber part are molding, extruding, and calendering.^[1114]

4.0 Markets and Applications for Packaging: Overview

Three categories of materials are generally included in the term “packaging;” flexible, semirigid and sealants or adhesives. Flexible materials whose application may be lidding, pouches, or bags, include films of a thickness equal to or less than 0.127 mm (5 mils). Semirigid materials are thicker than 0.127 mm. They are usually formed as sheets from a variety of materials including PVC, PS, acrylics, polyesters, HIPS, HDPE, PP, PAN, and many others. Sealants or adhesives are used to adhere multiple layers together, typically requiring heat and/or pressure.^[1061]

4.1 Packaging Materials

Polymeric packaging materials are used to surround a package completely, securing contents from gases and vapors, moisture, and biological effects of the outside environment, while providing a pleasing and often decorative appearance. Water vapor and atmospheric gases if allowed to permeate in or out of a package can alter the taste, color, and nutritional content of the packaged good. The effects of gas and vapors on food are complex and comprise a major branch of food science. Consequentially, the following is a brief overview for introductory purpose.

Water Vapor. Many products need to be protected against the gain or loss of moisture. Materials such as coated cellophane, polyethylene, polypropylene, polyvinylidene chloride, and polyester films are excellent barriers to water vapor and are used to block the transmission of water vapor through film. These materials are often used on the outside (and inside) layers of multilayer films. It should be noted however, that even the most impermeable of these films has a measurable permeability.

Other products such as fresh vegetables need to breathe so as to avoid condensation of water or the growth of mold. Materials such as polyolefin plastomers and certain grades of cellophane are suited for these applications.

The rate of water vapor transmission will depend upon the vapor pressure gradient across the film. Dry contents in a humid environment would absorb moisture, wet contents in a dry environment would lose moisture, and if the relative humidity inside and outside the package are equal, there will be no transmission even through the most permeable of films.

Atmospheric Gases. Oxygen, carbon dioxide, and nitrogen within a package often must be controlled. If oxygen is allowed into a package, it will break down organic materials initiating or accelerating the decay process. Uncontrolled, this will promote staleness and loss of nutritive value.

In the case of fresh meat, a high rate of oxygen transmission is required to maintain the bright red color of meat. To meet this special requirement, special grades of cellophane, polyethylenes, and nitriles have been developed to provide the low water vapor transmission needed to avoid drying the meat while providing high oxygen transmission to maintain the color.

This phenomenon of high transmission for oxygen combined with low transmission of water seems paradoxical but is very critical to these specialized needs. The reverse characteristics apply to nylon and other films that have a relatively high permeability to water vapor but a low permeability to oxygen, nitrogen and carbon dioxide. Other films have high (or low) transmission rates for all gases, as well as water vapor.

Odors and Flavors. Packaging films are also used to control the permeation of many organic compounds that impart flavor and odor. This protects the package contents from either the absorption of unwanted odors or the loss of volatile flavoring ingredients. Two common flavoring ingredients are d-limonene, a component in lemon and other citrus flavors, and methyl salicylate, used in breath fresheners, wintergreen, and food flavors. Aromas include: allyl sulfid (garlic), acetic acid (vinegar), ethyl phenyl acetate (soaps and floral fragrances), β -pinene (household cleaners), ethyl acetate (food flavorings: citrus, berry, coconut, coffee, chocolate, and honey), and menthol (chewing gum and peppermint).

The permeation of flavors and odors is difficult to measure quantitatively because they contain many components. Many times, only a simple component of a flavor is measured if a quantitative value must be determined. Another important flavor consideration is commonly called “flavor scalping.” Flavor scalping is the selective absorption of certain flavor constituents from the product. Polyolefins are known flavor scalpers.

Among good barriers to organic vapors are cellophane, saran, and vinyl. Cellulose acetate and polyethylene are poor odor and flavor barriers unless coated with a good barrier material.

4.2 Markets and Applications

Agricultural Chemicals. Fertilizers, insecticides, and herbicides are a few of the chemicals packaged in high density polyethylene (HDPE) containers. Multi-layer structures—up to 7—are used to provide reinforcement as well as additional protection against “pinholing” which often can occur in monolayer structures.

Fluorination, coating the inner surface of the container with fluorine gas which reacts with the HDPE, provides a chemical resistant and tough inner coating. Fluorination is also applied to the outer skin of an HDPE container to provide additional shelf life.

Nylon co-extrusions are recommended as a cost effective alternative to fluorine gas treatment.^[1085]

Agricultural Films. Advances in polyethylene technology for agricultural films have reduced the need for chemical fertilizers, pesticides, and herbicides.

The most common types of agricultural films are greenhouse films, mulch films, and silage films. Greenhouse films are generally made at very high layflats, as high as 20 meters. As a result, bubble stability is very important during production. A typical film might be made of a blend of LLDPE and LDPE, with additives. A low MI LDPE (0.2) provides the best stability, but the least favorable clarity. Adding a high MI LDPE (2.0) will give better clarity, but less bubble stability. The choice of LLDPE and LDPE also depends on equipment capabilities.

Mulch films are used to cover land in preparation for planting. They are used to reduce water consumption from evaporation, reduce weed growth, and improve herbicide retention.

Silage films help to maintain the nutritional value of forage plants such as corn, vegetables, and grasses that continue to respire after cutting. Silage film helps to exclude the air so lactic acid fermentation can take place, leaving a feed rich in vitamins and carotene. When silage film is used, the feed can keep its nutrients for several months, depending on the amount of air left (the less air, the better). Thus, feed is available for use in periods when forage is not available in sufficient quantities.^[1022]

Bag and IBC Liner Film - Polypropylene. Large polypropylene (PP) woven bags and intermediate bulk containers (IBC) are widely used to pack all types of material, from powders to granules to liquids. Often, they are equipped with an inner liner to prevent leakage and/or to protect their contents (for example, against moisture).^[1062]

Polypropylene-based blown film is rapidly finding its way as inner liners for woven bags, wooden big boxes, carton octabins, and more. This is because a PP liner offers exceptional performance at reduced thickness as compared to conventional, polyethylene (PE) solutions. Typically, a PP liner can be up to 30% thinner than its PE counterpart while offering comparable mechanical properties.^[1062]

Bakery, Convenience Food Items. Oriented polystyrene (OPS) is present in bakery and other food products which require transparent, resistant, but flexible packaging. The food contact agreement of PS is also an important aspect of the development of the material in this segment. A low amount of monomers

is an absolute requirement, because of the special nature of the processing and its use in contact with food.^[1043]

Caps and Closures. A closure is an access-and-seal device, which attaches to glass, plastic, and metal containers. These include tubes, vials, bottles, cans, jars, tumblers, jugs, pails, and drums. The closure works in conjunction with the container to fulfill two primary functions: to provide protection containment through a positive seal, and to provide access and resealability according to varying requirements.



Figure 21. Access and seal devices.^[1043]

Molded plastic closures are divided into two groups, thermosets and thermoplastics. Thermoset materials cannot be recycled once they are molded. Thermoplastic materials can be softened or recycled by heat.^[1022]

Chemical Products. Household cleaning supplies including liquid and solid laundry and dishwashing detergents and similar products for the industrial workplace are the primary chemical products packaged in high density polyethylene, HDPE, containers. These containers usually do not require further barrier protection.^[1085]

Compression Film - Polypropylene. Film used for packaging of compressed products such as glass, wool, and baby diapers is called compression film. Its most important requirement is resistance to elongation under stress, otherwise known as creep resistance.^[1062]



Figure 22. Compression film is used for consumer bags and wraps.

Condiments. Squeeze bottles containing condiments, ketchup and mustard in particular, have long been a major application for HDPE blow molded bottles. The bottles have an inner layer of barrier material, primarily EVOH, but also include nylon to protect the flavor in a shelf-stable, non-refrigerated environment.^[1085]

Consumer Bags and Wraps. Consumer bags and wraps protect products from contamination and damage during shipment. Overwraps must offer clarity, to reveal the visual quality of the product, and they must be printable.^[1022]

Dairy Form Fill Seal (FFS). Extruded polystyrene sheets with a thickness ranging from 0.7 mm to 1.8 mm are used to package a variety of products on Form Fill Seal (FFS) machines. The FFS forms the container, fills the product, and seals the lids on the container in one processing step. Polystyrene is the choice material for the FFS sheet, because it can be broken when twisted. Form fill and seal packaging is more common in Europe but is also used in North America.^[1043]

Dairy Containers, Food and Non-food Items, Drop Fill Seal (DFS). Thermoformed PS containers are present in many forms: yogurt and cream pots, ice cream containers, sour cream and cottage cheese containers, and coffee creamer portions. Thermoformed PS items are generally made by blending polystyrene to obtain flexible and ductile products. This two-step process involves the production of a sheet with a thickness ranging from 0.3 mm to 2.5 mm. This means that at the end of the extrusion line a winding station will produce a roll. This roll will then be fed to a

thermoforming station. In some cases, the sheet is made in one factory and the container is thermoformed in another. In other cases, the extrusion and thermoforming can take place in the same factory. But at the end of the day preformed pots, ready to fill and seal, are delivered for filling.^[1043]

Easy-Peel Film. Blending polybutene (PB1) in polyethylene (PE) results in an immiscible blend which forms the basis of a peelable seal formulation. An easy-open heat seal base allows for easy access to contents, and enhances the package appearance before and after opening. With this system, the consumer can peel the sealed package surfaces apart with a steady even force. The strength required to start peeling action (initiation peel strength) is similar to that required throughout the peeling process (propagation peel strength).

Polybutene-1 (PB-1) can be blended with either polyethylene homopolymer or copolymers to form an easy-open system. High density (HDPE), low density (LDPE), and linear low density (LLDPE) can be components of the system. Additionally, the new metallocene polyethylenes (mPE) may also be used. These mPE systems offer enhanced performance (improved hot tack, better seal through contaminants, and low odor) and processing flexibility. The most commonly used PE copolymer is ethylene vinyl acetate (EVA); however, ethylene acrylic acid (EAA), ethylene methyl acrylate (EMA), and ethylene ethyl acrylate (EEA) may also be used. Minor amounts of a third polyolefin may also be added to modify the performance properties. Processing aids such as slip and antiblock additives may be used as needed.^[1062]

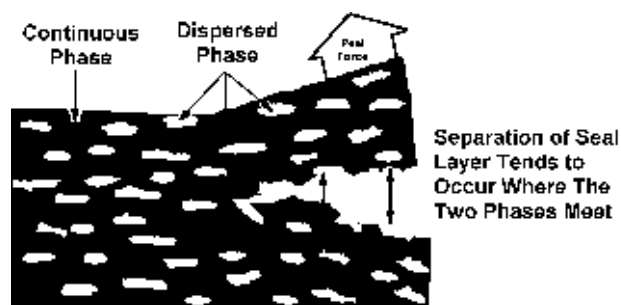


Figure 23. Microscopic dispersion of two phases.

Egg Cartons, Meat/Poultry/Veggie/Fruit Trays.

Light but strong, the expanded foam PS trays are a mainstay of fresh food packaging in the retail market. Meat and poultry are presented on foam polystyrene trays either packaged in the store or pre-packaged in a central location. Fresh products and vegetables are sold on trays and eggs are displayed in foam polystyrene cartons.

Foam sheet is made with crystal polystyrene on large specially equipped extrusion lines. The sheet is then thermoformed into the various trays and cartons to package all sizes and varieties of fresh food. The material choice depends on the required thickness, density, and rigidity.^[1043]

Extrusion Sheet for Consumer Packaging - Polystyrene. The processing units are producing sheets with a width ranging from 200 mm up to 850 mm and with a thickness ranging typically from 0.5 mm up to 2 mm. This kind of production is made on large capacity extrusion lines (more than 1T/h) in order to decrease variable costs.

Such lines require a careful setup in order to adjust winding correctly, stress level, orientation, gloss, etc. If some barrier properties are required, a co-extrusion material must be adopted.^[1043]

Extrusion Thermoforming for Disposables - Polystyrene. The disposables market in polystyrene is mostly processed through the inline thermoforming technology, because the latter is used in the case of huge production size, which is mostly the case of this market. This inline process consists of extruding a sheet of polystyrene through a flat die and then some variations take place concerning technology:

- Either the sheet is pulled by a mini calender in order not to cool it down too much, and then directly fed to a forming station with off-mold cutting.
- Or the sheet is calendered, sometimes the edges are cut, and then this same sheet is fed to a standard thermoforming unit with heaters.

The first process is widely used to produce cups and the second is more widespread for lids and plates.

The inline extrusion thermoforming process is the only solution to produce objects made out of pure crystal polystyrene, as this product cannot be wound up in a roll.^[1043]

Fabric Film Laminates. The absorbent products sector, including disposable baby diapers, feminine hygiene products, and adult incontinence materials, along with the medical laminates segment are very important parts of the nonwovens industry. Films used for the diaper backsheet have evolved from monolayer polyethylene film to blends of polyethylene and polypropylene, to multilayer films. In the 1990s, breathable films were adopted as backsheet materials, allowing higher water vapor to pass through the film.^[1062]

Foam Extrusion Thermoforming for Consumer Packaging - Polystyrene. Two main technologies are used today in order to produce thin foamed sheets. This sheet can be either immediately thermoformed (molten phase thermoforming) or stored in huge rolls for some days and fed into a thermoforming unit specially designed to heat foamed sheets. In the second case, there is a post expansion phenomenon, due to the fact that the sheet is reheated in the oven, causing gas trapped inside polystyrene to expand.

The gases which are used are usually explosive like butane or pentane, which need special storing and handling solutions.

Food Wrap Film. A co-extruded film with tacky skin layers and a polypropylene core layer offers all the desired properties for this application. Food wrap film needs good puncture resistance as well as good elastic recovery. A co-extruded film based on polyolefin resin has excellent puncture resistance and good elastic recovery.

A food wrap film also requires a good degree of oxygen and water vapor permeability. The co-extruded solution combines a good oxygen and water vapor transmission rate which most likely means a longer shelf life for products such as fresh meat.^[1062]

Geomembranes. Geomembranes are sheet-like structures, which are commonly used in environmental and water protection applications. These membranes are used to prevent the release of gas or odors into buildings or into the environment, and also help to protect groundwater against spoilage with contaminated water.

Geomembranes are essential in waterproofing applications, helping to protect new construction against corrosion or water erosion. They are also used in containment, collection, and conveyance of drinking water, helping to prevent water loss.^[1022]

Heat Resistant Film. Autoclavable Biohazard Waste Disposal Bags and Auto Paint Masking Films. Films manufactured into bags for autoclavable bio-

hazard waste disposal are part of the overall industrial trash can liner market used to collect and dispose all types of waste. Autoclavable bags are used for infectious and regulated waste, also known as biohazard waste. Biohazard waste products are primarily generated by the medical industry (hospitals, nursing homes, clinics, doctors' offices, medical labs, etc.).^[1062]

Polypropylene based polymers are used to manufacture masking films and bags, which are used to cover various sections of an automobile during an automotive body repainting process. These masking films act as a paint and temperature shield during a process that requires the painted part to pass through a series of baking ovens.^[1062]

Heavy Duty Shipping Sacks. Heavy duty shipping sack producers manufacture a broad range of custom bags and films that must provide moisture and barrier protection, reinforced strength properties, uniform gauge control, and impact resistance. As a result, the resins used to produce the bags and films must be very robust, providing outstanding performance over a broad range of conditions.^[1022]

Heat-Shrinkable PP Film. Thin, bi-oriented PP shrink films produced using the Double-Bubble technology are widely used as display films for books, videos, toys, sweets, fruits, etc., as monolayer and co-extruded film structures, and skin and core layers.^[1062]

Heat Seal Resins. Heat seal resins are key to the production of heat sealable co-extruded films. They are used extensively in the BOPP market for sealable films, lacquered films, and metallized films. These resins have been designed to form a seal at a specific temperature, called the Seal Initiation Temperature (SIT).^[1062]

High Clarity LLDPE Film. High clarity polyethylene films are often used to package products for retail sale, where the clarity and gloss of the film provide a better display and presentation for the enclosed product. These high clarity polyethylene (PE) films are predominantly produced from either specialty clarity low density PE (LDPE) grades, or metallocene linear low density PEs (LLDPEs).^[1062]

High Performance Food and Specialty Films. High performance films are typically used in food and specialty packaging. Most are composed of a multilayer structure, and include barrier materials such as ethylene vinyl alcohol copolymer (EVOH), nylon, foil, HDPE, or oriented polypropylene (OPP). All polyethylene structures may include combinations such as ULDPE/LLDPE/ULDPE used in liquid packaging. Polyethylene resins are typically incorporated into the

sealant portion of the structure, or used as a toughening layer buried in the structure.

High performance films are often used to package fresh produce, meat and cheese, liquids, dry foods, and frozen foods. Most of these are packaged utilizing form/fill/seal equipment. Other applications include pre-made pouches for bag-in-box applications, clarity films for bread bags, and lamination films. High performance films are also used in medical packaging.

High performance films are fabricated via a variety of processes, including blown and cast film co-extrusion, or adhesive and/or extrusion lamination of monolayer and co-extruded films to barrier substrates.^[1022]

Industrial Films. When used in industrial films, polyethylene resins can provide desirable moisture barrier properties, tear strength, and puncture resistance. Industrial films made from polyethylene are used in industrial sheet, wrap, and tubing, as well as fabricated industrial liners for shipping containers, steel drums, boxes, cans, tote bins, and truck beds.

The vast majority of industrial films are between one and six mils. Because industrial films are custom-made, each product has its own specifications.^[1022]

LLDPE/LDPE blends dominate industrial films. LDPE resins with a fractional melt index are the most commonly used resins in industrial films, providing the bubble stability required to make thick films. A commodity-grade LLDPE resin is added to provide the proper bag toughness.^[1022]

Injection Molding for Medical. Injection molding allows for production of high tolerance parts in short cycle times. Small objects can be produced with very precise geometry to meet the needs of automatic diagnostic testing. Multi-cavity molds are used on high speed injection molding machines to produce these petri dishes and assay trays. Hot runners are used to ensure precise molding and eliminate scrap. Robots are used because of very short cycle time and the need for hygiene. White rooms are often required to achieve the cleanliness required.^[1043]

Juice Packaging. High density polyethylene (HDPE) containers are used with and without barrier layer. The typical barrier layer when used, is nylon, approximately 0.001 inches co-extruded with the HDPE outer wall of the container.

Gable-top paperboard cartons use EVOH almost exclusively for the barrier required for the packaging of fruit juices.^[1085]

MAP (Modified Atmosphere Packaging). Modified atmosphere packaging (MAP) of fresh cut produce is one of the fastest-growing food packaging segments. MAP film controls transmission of oxygen, carbon dioxide, and water vapor.

Medical Packaging. Most flexible packages for medical devices contain at least one part that is plastic film. This film provides a number of functions in a pouch: product visibility, puncture resistance, sealability, and peelability.



Figure 24. Medical packaging.^[1084]

The most common material used in device packaging is a lamination of polyester and polyethylene, typically 0.0127 mm oriented polyester film, adhesively laminated to low-to-medium density polyethylene (0.038–0.051 mm) usually modified with EVA for better sealability. These films may be sealed to plain or coated DuPont Tyvek®, plain or coated papers, or other films.

A primary requirement of any sterile packaging material is that it provide a bacterial barrier. That is, any film or nonfibrous material must be pin-hole free, and fibrous or porous material must have pores below a specified size to prevent passage of microorganisms through the material.

A barrier to gases or liquids is required for packages containing liquid or volatile substances, or materials that need protection from the environment. The degree of barrier required depends upon shelf life requirements, and conditions to which the package will be subjected.

Porosity is required for packages that are used in EtO sterilization or autoclaving to allow the sterilizing gases to enter and leave the package easily. Porosity is not essential for radiation sterilization.^[1073]

Pharmaceutical blister packs are another plastics application in the medical marketplace. The use of thermoformed blisters for the packaging of pharmaceutical products is a rapidly growing area, displacing traditional packaging media such as glass or plastic bottles. The ICH (International Conference on Harmonisation of Technical Requirements for Registration of Pharmaceuticals for Human Use) extended stability testing requirements for the pharmaceutical industry. Testing after a six month storage at ambient conditions, 40°C and 75% RH, is required at a minimum, and for full validation, three years of testing at ambient conditions is required. The chemical stability of the contents can be very sensitive to moisture, thus, it is important that moisture penetration be as low as possible for several years.^[2028]

PVC has traditionally been used in this market for products requiring little protection from moisture vapor, and PVC/PVDC (Polyvinylidene chloride) or PVC/ACLAR (Polychlorotrifluoroethylene) for products requiring medium or high barrier. These products have been selected for their moisture vapor barrier, on the flat sheet prior to thermoforming. Cyclic olefin copolymer (COC), a new potential packaging material, has been developed for this market.^[2028]

Milk Packaging. The largest food application for high density polyethylene (HDPE) containers is milk packaging produced from homopolymer in a hazy color. Milk jugs are valued for their ability to be recycled. No barrier protection is required in this application.^[1085]

Non-Fusion Shrink Film. Polyethylene (PE) shrink film is often used for the covering of stacked pallets, particularly when pallet stability is crucial. Frequently, however, the heat used to shrink the film causes the hood to stick to the contents encased within. When the hood is removed, the packaging can be damaged and contents may spill. To prevent this problem, a thin non-fusion layer is often co-extruded to the inside of the shrink film.

Polypropylene (PP) film is an alternative. Polypropylene sealing resins are modified to ensure that the film sticks to itself (at low seal initiation temperatures) but does not adhere to the PE film (bags, labels, etc.) due to the presence of the polypropylene backbone.

To insure that no delamination occurs between the PP (non-fusion) and the PE (shrinkage) layer one inserts a tie layer that contains a blend of the supersoft PP grade and a linear low density PE.^[1062]

Oriented Polystyrene (OPS) for Consumer Packaging. Bi-oriented Polystyrene is used mainly in the consumer packaging area, bakery and other food products which require transparent, resistant but flexible packaging. Sheets are produced with an orientation ratio ranging from 2×2 to 3×3 . Most often these sheets (colored or natural) are thermoformed by another processor. The sheets can be colored by way of masterbatch, and the formulation includes mainly a GPPS of high molecular weight, mixed with a small amount of elastomer, sometimes blended with an even smaller amount of HIPS in order to improve toughness, and not to decrease clarity.^[1043]

Polyethylene Terephthalate, PET, Containers. For carbonated soft drinks, the major application of PET, as well as edible oils, peanut butter, juices, and isotonic sports drinks, no barrier materials are used. With some other food products, condiments, salad dressings, and dessert toppings, PET does not provide adequate oxygen barrier for a stable shelf life. For these applications, multilayer structures with an EVOH barrier layer have been developed.

Beer packaging in PET has generated significant interest. The single most important limiting factor is the cost of the PET bottle with the appropriate barrier properties to prevent flavor scalping, and to provide a 3–4 month shelf life for O₂ and CO₂ barrier.^[1085]

Shrink Bundling Film. The shrink bundling film market is dominated by LDPE films, typically blends of fractional-melt index LDPE and LLDPEs. The most common blends run in the 25% to 50% LLDPE range. Adding more than 50% LLDPE typically results in a dramatic reduction in transverse direction (TD) shrinkage, to the point where shrink performance becomes unacceptable.^[1062]

Stationery Films. Stationery films include applications such as photo albums, sheet protectors, book covers, and binders. In recent years, cast polypropylene films have made significant inroads into this application, in particular, sheet protectors which had been dominated by PVC.^[1062]

Stretch/Industrial Collation. Stretch film is an effective and inexpensive solution for protecting palletized products through storage and distribution.^[1022]

Sugar Drinks. Single-serve sugar-based drinks in HDPE bottles are shelf-stable and require no refrigeration. No barrier materials are used in the sugar-based drink market.^[1085]

5.0 Automotive Fuels

Plastics and elastomers are used extensively by the automotive industry, over 30% of the weight of most cars is now polymeric.^[1187] Applications include interior, exterior and under the hood. Due to the excellent performance of polymeric materials in areas such as mechanical strength, weight, flexibility, ease of processing and cost, just to name a few, the use of these materials is expected to continue to increase.

However, on the environmental front, the regulations involving hydrocarbon emissions are becoming more stringent. The SHED (Sealed House for Evaporation) test sets as a target 2 grams of hydrocarbon emissions from the whole car during a 24 hour period. Components of the fuel circuit are the greatest source of emissions,^[1090] and the fuel circuit consists primarily of polymeric components. The use of oxygen containing fuels and blends of fuels make the situation more complex since many blends can be more aggressive than unleaded fuel alone on polymers.^[1091] Methanol content of the fuel influences permeability since methanol contributes to swelling of the polymer.^[1090]

Nylon 12, polyamide (PA12), is used for most fuel line systems and the continued use of nylon 12 will not meet the SHED requirements. Other plastic materials have improved barrier properties but are often more expensive. Thus, multilayer tubes are often the solution to mechanical as well as barrier needs. Multilayer tubes generally consist of a primary inner barrier layer to decrease diffusion of the fuel with an outer layer of nylon 12 to provide mechanical properties such as toughness, flexibility, and impact strength. These layers are often joined with a “tie” layer adhesive to prevent delamination.^[1093]

Plastics are also used as containers for fuels, primarily blow molded containers. The Japanese and European standards set weight loss of gasoline containers at less than 20 g/24 hrs at 40°C and will be reduced to a standard requirement of 5 g/24 hrs in the future.^[1094]

The development of new materials and the improved permeability of existing materials is a focus of today’s automotive industry and those manufacturers and researchers who support the industry. The following data is an overview of the permeability of several materials to automotive fuels designed to show trends between polymeric families. This chapter is not designed to be a comprehensive resource for polymers in automotive applications, rather a supporting chapter to present general permeability trends of polymers used in automotive fuel applications. Society of Automotive Engineers (SAE) and the manufacturers of the materials continue to remain the best source for specific needs.

High-Density Polyethylene Fuel Tanks. High-density polyethylene with a high molecular mass has been widely accepted as a material for fuel tanks. It permits substantial rationalization on automotive production lines because of the great scope it allows in styling, the savings in weight that it achieves over its steel counterparts, the ease with which it can be produced by extrusion blow molding, and assembled in the vehicle. As compared to steel, polyethylene is not completely impermeable to gasoline, but it does not rust.

The permeability to gasoline can be reduced by more than 90% by fluorinating or sulfonating the fuel tanks. Since the thickness of the impermeable fluorinated or sulfonated layer is of the order of only a few micrometers, the fuel tanks retain their high level of mechanical properties.

Other potential methods of reducing the permeability to engine fuels include special surface coatings, dispersions, films, modification of the material, and the co-extrusion of composite fuel tanks.

Selected Elastomers, Nylon 12 and Fluoropolymers. Table 10 shows permeability to standard ASTM fuels for general purpose and specialty types of Viton Fluoroelastomer and several other materials.

Tables 11 and 12 represent permeability on two grades from over fifty Dyneon fluoroelastomers. These grades were chosen as they are commonly found in automotive applications. For additional information on test methods, reproducibility and accuracy see Society of Automotive Engineers, SAE, papers 2000-01-1096 and 2001-01-1126.

Table 10. Selected Elastomers, Nylon 12, and Fluoropolymers^[1110]

Material	Fuel C	Average Permeation Rate for ASTM Standard Fuels, (g · mm/m ² · days)		
		90% Fuel C,		
		10% Ethanol	15% Methanol	85% Methanol
NBR (33% ACN)	669	1028	1188	264
HNBR (44% ACN)	230	553	828	211
Fluorosilicone	455	584	635	261
Nylon 12	5.5	24	83	90
Viton GLT	2.6	14	60	149
Viton B70	0.8	7.5	36	55
Viton GFLT	1.8	6.5	14	11
Viton B200	0.7	4.1	12	7.4
Viton GF	0.7	1.1	3.0	0.9
Tefzel ETFE	0.03	0.05	0.20	0.20
Teflon PFA	0.05	0.03	0.13	0.05
Teflon FEP	0.03	0.03	0.03	0.03

* Mathematically normalized to 1 mm thickness using data from test described in ASTM E96-53T

Table 11. Fuel CE10 and CM15 Through Dyneon FE 5640Q Fluoroelastomer (FKM)

Material Family	FKM	
Material Supplier/Grade	DYNEON FE 5640Q, 66% FLUORINE	
Reference Number	1128	

TEST CONDITIONS

Penetrant	Fuel CE10	Fuel CM15
Temperature (°C)	23	40
Test Note	45% toluene + 45% isooctane + 10% ethanol	42.5% toluene + 42.5% isooctane + 15% methanol

PERMEABILITY (normalized units)

Vapor Permeability (g · mm/m ² · day)	6	43	125
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Table 12. Fuel CE10 and CM15 Through Dyneon FE 5840Q Fluoroelastomer (FKM)

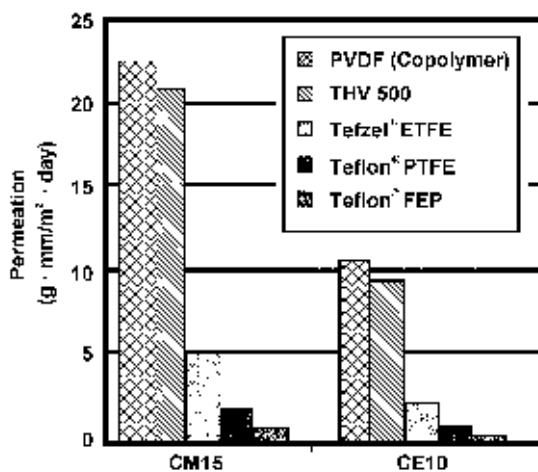
Material Family	FKM	
Material Supplier/Grade	DYNEON FE 5840Q, 70.2% FLUORINE	
Reference Number	1128	

TEST CONDITIONS

Penetrant	Fuel CE10	Fuel CM15
Temperature (°C)	23	40
Test Note	45% toluene + 45% isooctane + 10% ethanol	42.5% toluene + 42.5% isooctane + 15% methanol

PERMEABILITY (normalized units)

Vapor Permeability (g · mm/m ² · day)	4	12	46
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Figure 25. Fuel CE10 and CM15 through various fluoropolymers at 60°C.^[1091]

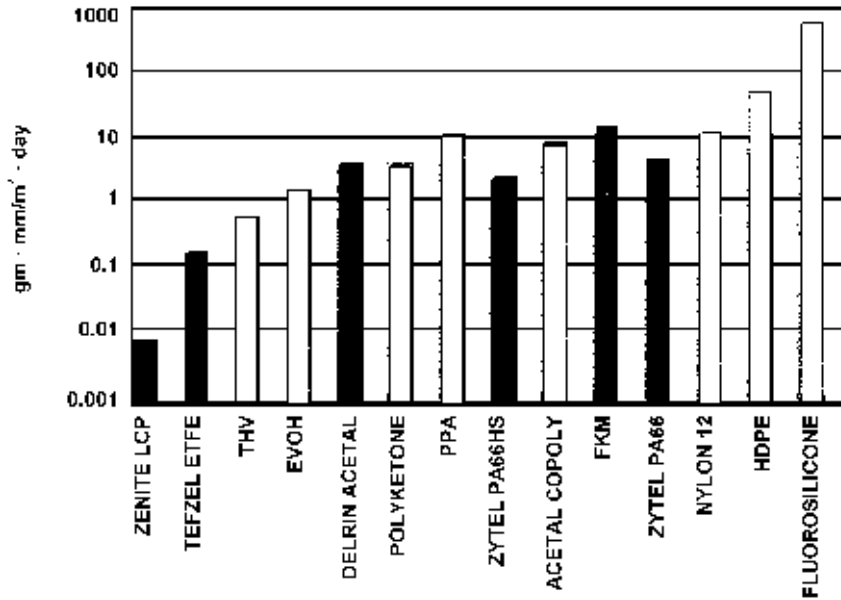


Figure 26. Fuel CE10 through various materials at 40°C.^[1091]

- *Fluoropolymers.* Fluoropolymer resins provide excellent barriers to permeation for automotive fuels. Typical data indicated that fluoropolymers permeate 80–90% less fuel than the equivalent nylon 12 hose.^[1092]

- *Note on Data Interpretation.* The following tables list peak permeation rate and average “equilibrium” rate. The peak rate is based on one data point whereas the average rate is based on multiple readings averaged over time.^[1091]

- *Standard Test Fuels.*^[1091]

Fuel C 50% Isooctane/50%
Toluene

Oxygenated 90% Fuel C/10%
Ethanol

Fuels 90% Fuel C/10%
Methyl-t-Butyl Ether

Flex Fuels 85% Fuel C/15%
Methanol

50% Fuel C/50%
Methanol

15% Fuel C/85%
Methanol

- *Materials.* When possible, common industry designations are used such as FKM for fluoroelastomers, FEP and PFA for fluorocarbon resins, etc.

Table 13.

Industry Designation	Material Name
NBR	nitrile rubber
HNBR	hydrogenated nitrile
FPM	fluororubber
Nylon 12	GM Fuel hose grade, plasticized
FVMQ	fluorosilicone
FKM A200	dipolymer A200, 66% fluorine
FKM B70	terpolymer B70, 66% fluorine
FKM GLT	tetrapolymer GLT, 65% fluorine
FKM B200	terpolymer B200, 68% fluorine
FKM GF	tetrapolymer GF, 70% fluorine
FKM GFLT	tetrapolymer GFLT, 67% fluorine
FEP 1000L	fluorocarbon resin FEP 100
PFA 1000LP	fluorocarbon resin PFA 340
ETFE 1000LZ	E-TFE 200
PA	polyamide

Table 14. Permeation Rate Summary—As Tested^[1091]

Average Permeation Rate (g/m ² · day) ASTM E96					
Material	Fuel C	90% Fuel C 10% Ethanol	85% Fuel C 15% Methanol	15% Fuel C 85% Methanol	Sample Thickness (mm)
NBR (33% ACN)	352	541	625	139	1.9
HNBR (44% CAN)	121	291	436	111	1.9
FVMQ (fluorosilicone)	599	769	836	343	0.76
FKM A200 (66% fluorine)	1.0	9.9	48	73	0.76
FKM B70 (66% fluorine)	1.0	8.8	42	125	0.76
FKM GLT (65% fluorine)	3.4	18	79	196	0.76
FKM B200 (68% fluorine)	0.9	5.4	16	9.7	0.76
FKM GF (70% fluorine)	0.9	1.4	3.9	1.2	0.76
FKM GFLT (67% fluorine)	2.4	8.5	19	14	0.76
FEP 1000L	0.1	0.1	0.1	0.1	0.25
PFA 1000LP	0.2	0.1	0.5	0.2	0.25
ETFE 1000 LZ	0.1	0.2	0.8	0.8	0.25
Nylon 12	4.3	19	65	71	1.27

Table 15. Permeation Rate Summary—Mathematically Normalized to 1 mm Thickness^[1091]

Average Permeation Rate (g · mm/m ² · day) ASTM E96				
Material	Fuel C	90% Fuel C 10% Ethanol	85% Fuel C 15% Methanol	15% Fuel C 85% Methanol
NBR (33% ACN)	669	1028	1188	264
HNBR (44% CAN)	230	553	828	211
FVMQ (fluorosilicone)	455	584	635	261
FKM A200 (66% fluorine)	0.8	7.5	36	55
FKM B70 (66% fluorine)	0.8	6.7	32	95
FKM GLT (65% fluorine)	2.6	14	12	7.4
FKM B200 (68% fluorine)	0.7	4.1	12	7.4
FKM GF (70% fluorine)	0.7	1.1	3.0	0.9
FKM GFLT (67% fluorine)	1.8	6.5	14	11
FEP 1000L	0.03	0.03	0.03	0.03
PFA 1000LP	0.05	0.03	0.13	0.05
ETFE 1000LZ	0.03	0.05	0.20	0.20
Nylon 12	5.5	24	83	90

Table 16. Peak Permeation Rate Summary—As Tested^[1091]

Peak Permeation Rate (g/m ² · day) ASTM E96					
Material	Fuel C	90% Fuel C 10% Ethanol	85% Fuel C 15% Methanol	15% Fuel C 85% Methanol	Sample Thickness (mm)
NBR (33% ACN)	638	1072	1273	109	1.9
HNBR (44% CAN)	194	527	748	168	1.9
FVMQ (fluorosilicone)	59785	1128	1404	470	0.76
FKM A200 (66% fluorine)	2.9	13	66	161	0.76
FKM B70 (66% fluorine)	2.8	14	66	329	0.76
FKM GLT (65% fluorine)	6.6	26	127	606	0.76
FKM B200 (68% fluorine)	2.5	7.8	27	17	0.76
FKM GF (70% fluorine)	2.3	2.9	7.9	2.3	0.76
FKM GFLT (67% fluorine)	4.2	11	31	22	0.76
FEP 1000L	0.7	0.5	1	1.1	0.25
PFA 1000LP	0.7	0.6	1.5	1.4	0.25
ETFE 1000LZ	0.7	0.6	1.7	1.5	0.25
Nylon 12	6.9	26	79	80	1.27

Table 17. Peak Permeation Rate Summary—Mathematically Normalized to 1 mm Thickness^[1091]

Peak Permeation Rate (g · mm/m ² · day) ASTM E96				
Material	Fuel C	90% Fuel C 10% Ethanol	85% Fuel C 15% Methanol	15% Fuel C 85% Methanol
NBR (33% ACN)	1212	2037	2419	361
HNBR (44% CAN)	369	1001	1421	319
FVMQ (fluorosilicone)	597	857	1067	357
FKM A200 (66% fluorine)	2.2	10	50	122
FKM B70 (66% fluorine)	2.1	11	50	250
FKM GLT (65% fluorine)	5.0	20	97	461
FKM B200 (68% fluorine)	1.9	5.9	21	13
FKM GF (70% fluorine)	1.7	2.2	6.0	1.7
FKM GFLT (67% fluorine)	3.2	8.4	24	17
FEP 1000L	0.18	0.13	0.25	0.28
PFA 1000LP	0.18	0.15	0.38	0.35
ETFE 1000LZ	0.18	0.15	0.43	0.38
Nylon 12	8.8	33	100	102

The permeation rate can be influenced by many factors. Temperature and fuel content are two of the factors whose influences can be noted from the following data. Permeability could not be “normalized” in this circumstance due to the lack of thickness information. Permeability units for this group are g/100 cm² · day. Total hydrocarbon permeation rate refers to permeation through inside diameter (barrier layer).

- *Fuel Tube Construction.* 3-layer elastomeric fuel tubes.^[1090]
- *NBR.* Having acrylonitrile rubber barrier layer.
- *FPM1.* Having fluororubber barrier layer, fluororubbers are copolymers whose properties depend upon fluorine content. With increasing fluorine content the resistance to fuel increases and the permeation rate decreases.
- *FPM2.* Having fluororubber with chlorinated polyethylene barrier layer.

- *PA.* Having a thin polyamide barrier layer.

- *Fuel Composition.*^[1090]

FAM A: 50 vol% toluene, 5 vol% ethanol, 30 vol% isooctane, 15 vol% diisobutylene.

FAM B: 84.5 vol% FAM A, 0.5 vol% water, 15 vol% methanol.

Total permeation can vary depending upon fuel composition. The higher the methanol content, the higher the total permeability for the following conditions.

Fuel permeability is temperature dependent as seen in Table 16. Results show an increase in permeability across all barrier layers with an increase in temperature.

The composition of the permeant is barrier layer dependent.

Table 18. Permeation Rate of Tested Fuels^[1090]

Permeability (g/100 · cm ² · day)		
Barrier Layer	FAM A	FAM A + 10 vol% methanol
FPM1	0.3	1.4
FPM2	0.7	0.8
NBR	7.5	11.4

Table 19. Permeation Rate at Three Different Temperatures^[1090]

Tube Construction					
Fuel	Temperature	FPM 1	FPM 2	NBR	PA
		(average value)	Permeability (g/100 · cm ² · day)		
FAM B	40°C	0.9	0.6	11.8	0.5
FAM B	60°C	2.2	2.0	16.0	0.7
FAM B	80°C	5.1	5.1	21.0	2.9

Table 20. Composition of Permeant^[1090]

FAM B % of Permeant					
Barrier Layer	Diisobutylene	Ethanol	Isooctane	Methanol	Toluene
FPM1	5	5	5	24	61
FPM2	4	4	9	22	61
NBR	5	3	9	16	67
PA	--	13	--	62	25

Blow Molded Containers. The barrier performance of blow molded containers for methanol/gasoline made from polyethylene (PE) can be enhanced through the incorporation of polyamide (PA), modified polyamides (MPA), polyvinyl alcohol (PVA), and compatibilizer precursor (CP).^[1094]

The barrier properties of MPA or PAPVA blends with PE are better than those unmodified blends or homopolymer PE.

The permeation rate decreases with increased methanol vol%. The barrier properties for methanol are best with PE alone, because the polar methanol molecules are hard for non-polar PE to absorb. In addition, the polar MPA and MPAPVA absorb methanol easier than PE. When gasoline is added to the methanol, the permeation of the non-polar gasoline through non-polar PE amorphous regions is easier than permeation through polar MPA or MPAPVA crystalline regions.^[1094]

Barrier properties improve as the PVA content increases. As the content of CP increases, the degree of crystallinity decreases as the lamellar structure improves. Adding 30% CP into MPAPVA blends results in the best barrier properties.

In all the different compositions of PE/MPAPVA blends, the weight loss of the fuel is within 2 g/24 hrs in the 40°C environment, well below the 5 g/24 hrs at 40°C requirement for Japan and Europe.

Acetal. Ticona Celcon® acetal copolymer is an excellent material for fuel handling applications, including oxygenated (reformulated) fuels and gasohols.

The fuel permeation rate for an ASTM Fuel C through Celcon acetal standard unfilled grade was less than 0.07 gm · mm/hr · m² over the temperature range of 45–80°C.^[2002]

Table 21. Composition of MPA, MPAPVA, and UMPAPVA Blends^[1094]

Materials	PA	PVA	CP
MPA ₁₀	90		10
MPA ₃ PVA _{a10}	67.5	22.5	10
MPA ₇ PVA _{a10}	78.75	11.25	10
MPA ₁₅ PVA _{a10}	84.375	5.625	10
MPA ₂₀	80		20
UMPA ₃ PVA _{f10}	67.5	22.5	10
MPA ₃ PVA _{f10}	67.5	22.5	10
MPA ₇ PVA _{f10}	78.75	11.25	10
MPA ₁₅ PVA _{f10}	84.375	5.625	10
UMPA ₃ PVA _{a20}	60	20	20
MPA ₃ PVA _{a20}	60	20	20
MPA ₇ PVA _{a20}	70	10	20
MPA ₁₅ PVA _{a20}	75	5	20
MPA ₃₀	70		30
UMPA ₃ PVA _{a30}	67.5	22.5	20
MPA ₃ PVA _{a30}	52.5	17.5	30
MPA ₇ PVA _{a30}	61.25	8.75	30
MPA ₁₅ PVA _{a30}	65.625	4.375	30

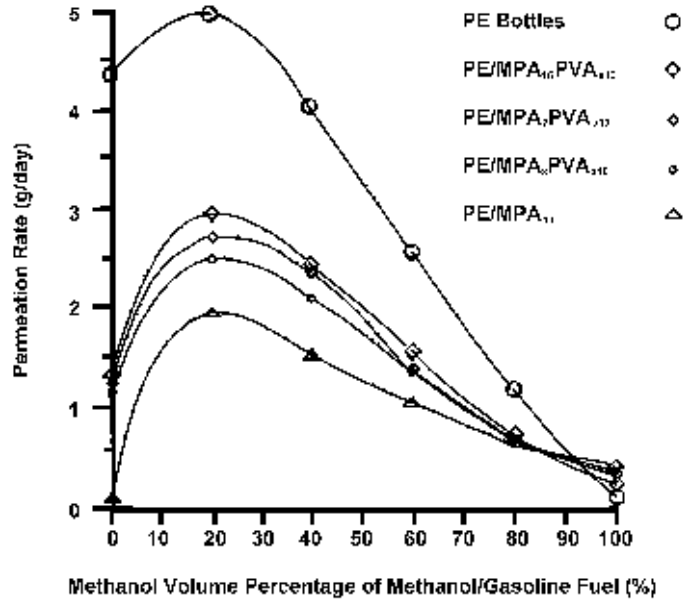


Figure 27. Methanol permeation rate with PVA_{a10}^[1094]

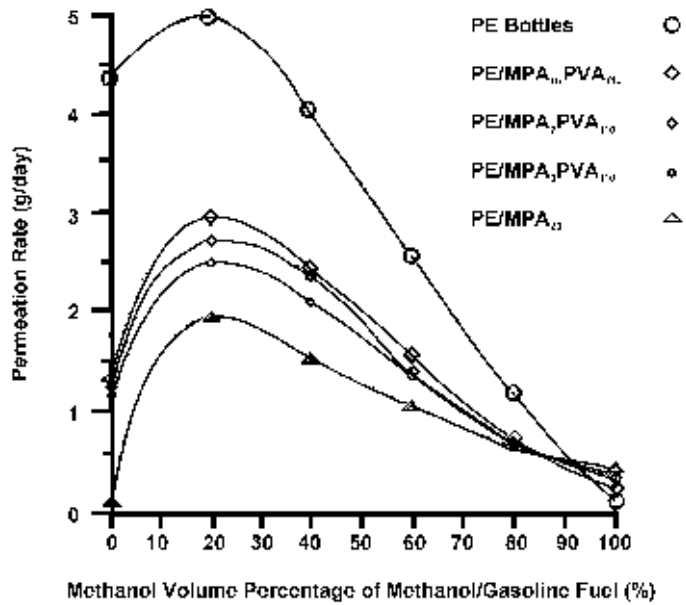


Figure 28. Methanol permeation rate with PVA_{f10}^[1094]

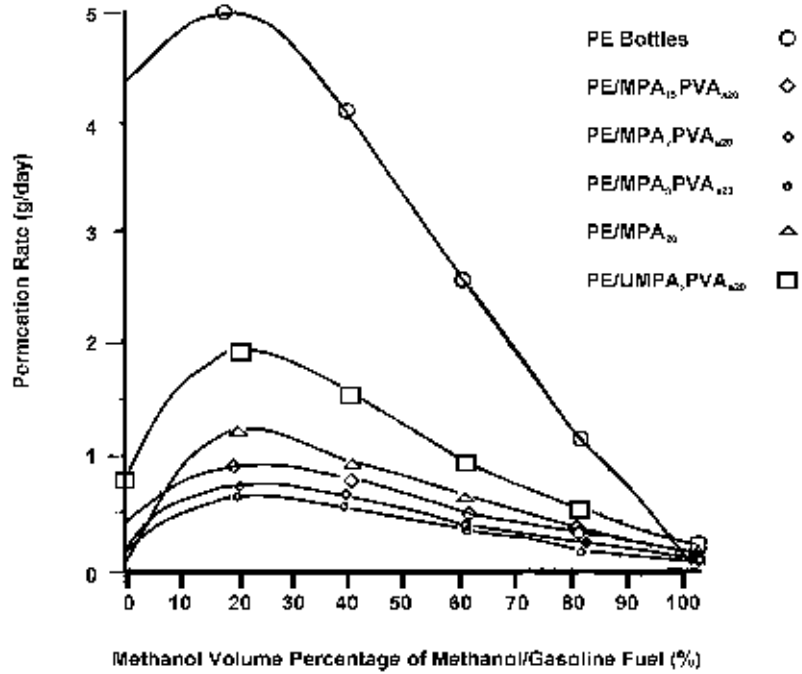


Figure 29. Methanol permeation rate with PVA_{a20}^[1094]

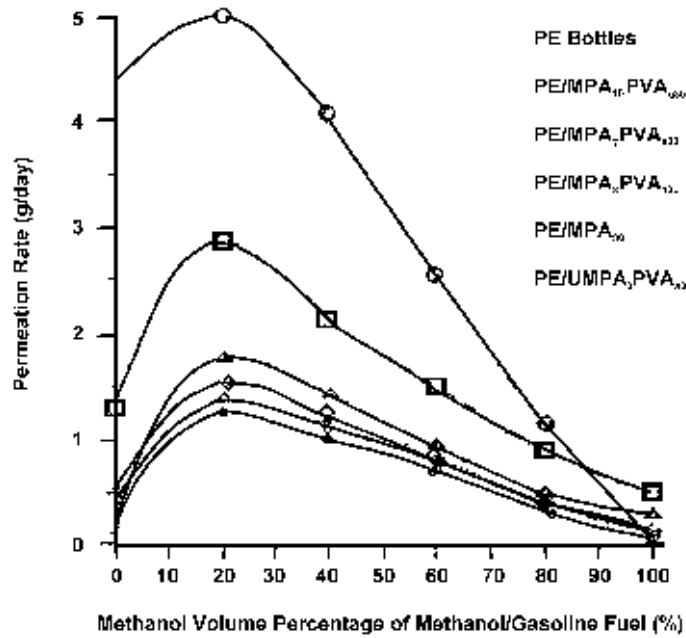


Figure 30. Methanol permeation rate with PVA_{a30}^[1094]