BARRIER PROPERTIES

A comparison of the oil, oxygen, and water-vapor permeation rates of various polyethylene blown films*

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ABSTRACT

The barrier properties of packaging materials determine the shelf life of many food products and provide other required packaging characteristics. While certain foods require moisture protection, others require low or minimal oxygen exposure to achieve longer shelf lives. In addition, many packaged foods contain natural oils, flavors, or aromas that can create handling, aesthetic, or odor problems.

Polyethylene resins are frequently included in single layer and multilayer film structures used for packaging products that require low water vapor, controlled oxygen, or low grease/oil permeation rates. High-density polyethylene films are known to provide excellent water vapor barrier properties; however, only limited information is available on the grease/oil and oxygen permeation rates of different polyethylene-based films.

Information is presented on the oil penetration and the oxygen and water-vapor transmission rates of various polyethylene blown films. Resins evaluated include high-density polyethylene, high-molecular-weight high-density polyethylene, linear low-density polyethylene, low-density polyethylene, and a metallocene-based polyethylene. Data presented include permeation rate vs. gauge for these resins. In addition, the effect of different processing conditions on permeation rate is investigated.

POLYETHYLENE-BASED PACKAGING materials have revolutionized the food industry. These materials range from high-density polyethylene (HDPE) blow- and injection-molded articles for packaging dairy products, to PE-based films for packaging dry food products and frozen or refrigerated meats and vegetables. PE-based packaging materials increase food shelf life, reduce spoilage, and increase the availability of different food products to the general public. An added benefit of this lightweight packaging is reduced food packaging, storage, and delivery costs. Some 3.5 billion lb/year of polyethylene is currently used in the food packaging industry, with approximately 45% used specifically in single layer or multilayer film structures *(1)*.

Food packaging films must have specific properties to provide acceptable product shelf life, product protection, and maximum consumer appeal. Film properties affecting product shelf life include water vapor transmission rate (WVTR) and oxygen transmission rate (O_2GTR). Low grease and oil penetration rates (OPRs) may also be required to maintain consumer appeal.

HDPE is well known for its excellent water vapor barrier properties, making HDPE-based films the material of choice for packaging moisture-sensitive dry foods such as cereals, crackers, and powdered (cake and pudding) mixes. HDPE-based films are also used for packaging oxygen-sensitive foods such as meat and poultry products. Many of these meat/poultry packaging films are coextruded structures, often incorporating one or more layers of linear low-density polyethylene (LLDPE) or ultra-low-density polyethylene (ULDPE) for puncture or tear protection.

Modified atmosphere packaging (MAP) of fresh fruits and vegetables is a growing application area for PE-based films *(2)*. MAP provides maximum product shelf life by controlling oxygen (and carbon dioxide) transmission rates *(2, 3)*. Fresh produce is commonly packaged in low-density polyethylene (LDPE) and, more recently, metallocene polyethylene (mPE)-based films.

Little data are available on the oil penetration and oxygen gas transmission rate of different polyethylene films. This paper presents information on the oil penetration, oxygen gas, and water vapor transmission rates of various PE blown films. Monolayer films made from conventional HDPE, high-molecular-weight HDPE (HMW-HDPE), LLDPE, LDPE, and an mPE resin were evaluated. The data show the effects of resin parameters, film gauge, and processing condition on OPR, O_2GTR, and WVTR.

EXPERIMENTAL PROCEDURES AND MATERIALS

Water vapor transmission rate testing

WVTR testing was performed using a MOCON® PERMATRAN- W®600 instrument, in accordance with ASTM F-1249, "Water vapor transmission rate through plastic film and sheeting using a modulated infrared sensor." This method involves placing a test film in a diffusion cell to create a "wet" and a "dry" chamber. Water vapor diffuses from the wet chamber through the film and is carried by the dry chamber purge gas to an infrared sensor. The sensor measures the concentration of water vapor in the purge gas, from which the film's WVTR is determined. The diffusion

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Property	ASTM procedure
Melt index	D-1238
Density	D-1505

I. ASTM resin/film test procedures

cell test area is 50 cm^2, and results are reported for 37.8°C (100°F) and 100% relative humidity test conditions.

Oxygen transmission rate testing

O_2GTR testing was performed using a MOCON OX TRAN® 2/20 ST instrument, in accordance with ASTM D-3985, "Oxygen gas transmission rate through plastic film and sheeting using a coulometric sensor." This method also involves placing a test film in a diffusion cell to form two chambers. Gas with a known oxygen content is passed through one chamber, while a nitrogen carrier gas purges the other chamber. Oxygen permeates the film and is transported by the nitrogen purge gas to a coulometric detector. The detector measures the amount of oxygen flowing to it per unit of time, from which the film's O_2GTR can be determined. The diffusion cell test area is 100 cm^2, and testing was performed at 23°C (73°F).

Oil penetration rate testing

OPR was determined in accordance with ASTM F-119, "Rate of grease penetration of flexible barrier materials." In this method, a test film is sandwiched between a grease- or oil-wetted cotton disc and a ground glass backing plate. The time required for the grease or oil to penetrate the test film is determined when the initial wetting of the glass plate is observed. Results are presented for testing at 49°C (120°F) using a mineral oil reagent.

Resin and film testing

Resin and film physical properties were measured in accordance with standard ASTM test procedures, as shown in **Table I**.

Resin	Material	I_2[a]	I_{20}[b]	Density, g/cm³
HD-1	Conventional HDPE	1.0	65	0.958
HD-2	Conventional HDPE	2.0	70	0.958
HMW-1	HMW-HDPE	0.03	5.4	0.949
HMW-2	HMW-HDPE	0.05	8.5	0.949
HMW-3	HMW-HDPE	0.07	11	0.949
LLDPE-1	Octene LLDPE	1.0	29	0.921
LLDPE-2	Butene LLDPE	1.1	27	0.920
LDPE	...	2.0	105	0.921
mPE	Metallocene PE	1.09	16.8	0.900

[a] I_2 is reported in grams of flow per 10 min (ASTM D-1238, 190/2.16)
[b] I_{20} is reported in grams of flow per 10 min (ASTM D-1238, 190/21.6)

II. Resin properties

Materials

The resins used in this study are listed in **Table II**.

Film production

All films were produced on a 65-mm grooved feed extruder with a 160-mm monolayer die equipped with a 1.5-mm (0.060-in.) die gap. HMW-HDPE films were produced in the typical high stalk configuration using a single-lip air ring. All other films were produced with a conventional bubble configuration using a dual-lip air ring.

Films were produced at nominal thicknesses of 12.7 µm (0.5 mil), 51 µm (2.0 mil), and 87 µm (3.5 mil) for each resin. (Note: No 0.5-mil LDPE film was produced due to drawdown limitations.) Films from the three HMW-HDPE resins were produced at a 4:1 blowup ratio (BUR), which is common for these resins. Likewise, the other, conventional resins were processed at a 2:1 BUR, which is typical for them. For all resins, additional 51-µm (2.0-mil) films were produced using a different BUR.

RESULTS

WVTR, OTR, and OPR results are shown in **Figs. 1–3**, respectively.

DISCUSSION

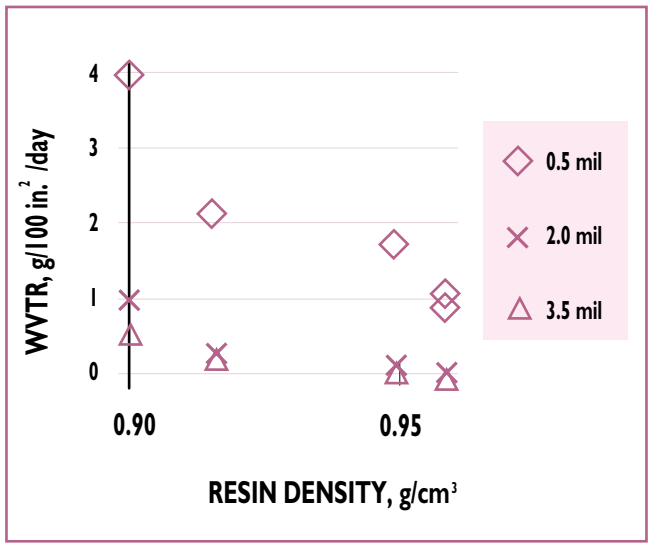
Permeation through polyethylene films involves three distinct physical steps *(4)*:

- Solution or sorption of the permeant material into one surface of the film
- Diffusion through the film to the opposite surface
- Desorption or re-evaporation of the permeant material.

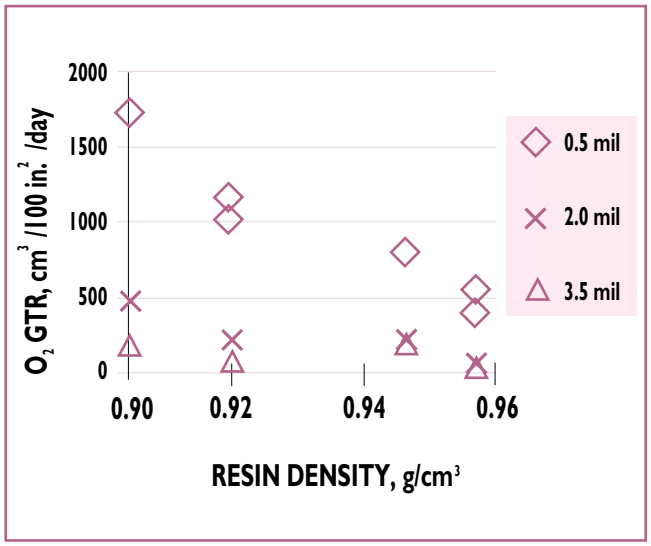
Polyethylene films are composed of crystalline and amorphous (non-crystalline) regions. Permeation through PE films occurs almost exclusively in the amorphous regions *(4)*. As a result, crystalline content (indicated by density) has a major effect on the permeability of PE films. As seen in Figs. 1–3, permeation rates increased dramatically as resin density decreased. Films produced from the 0.900-density metallocene resin had up to ten times the permeability of films produced with the 0.958-density HDPE resin.

Permeability–density relationship

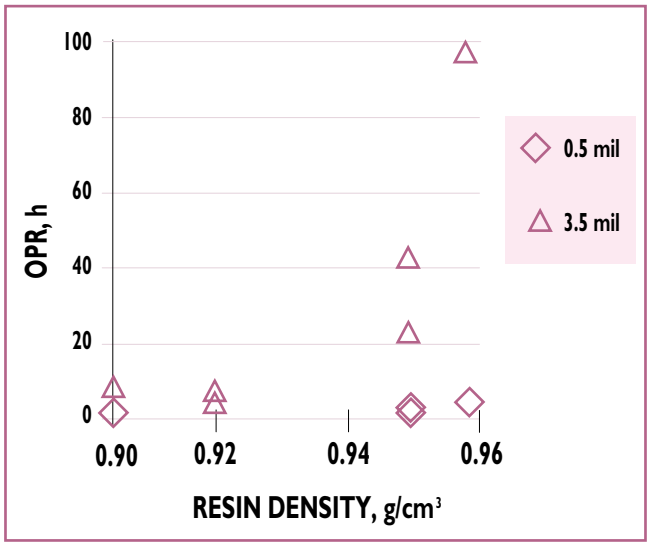
A variety of researchers have investigated and theorized on the relationship between permeability and polymer density *(5, 6)*. A number of these researchers predicted that permeability would vary with the square of the resin's amorphous fraction, or density. This squared relationship was derived using the fact that a permeant material would only be soluble (*S*) in, and only diffuse (*D*) through, the amorphous fraction. In



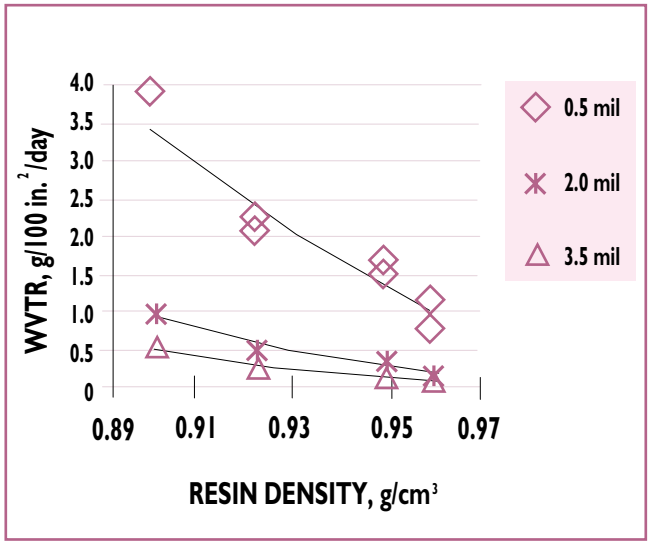
1. WVTR data



2. O_2GTR data



3. OPR data



4. WVTR-density correlation

fact, permeability (*P*) is mathematically related to solubility and diffusion through the following equation:

$$P = DS \qquad (1)$$

Alter *(6)* modeled the permeability–density relationship for PE films using the following equation:

$$P = K\,(1-\rho)n \qquad (2)$$

where ρ is density and *K* and *n* are constants.

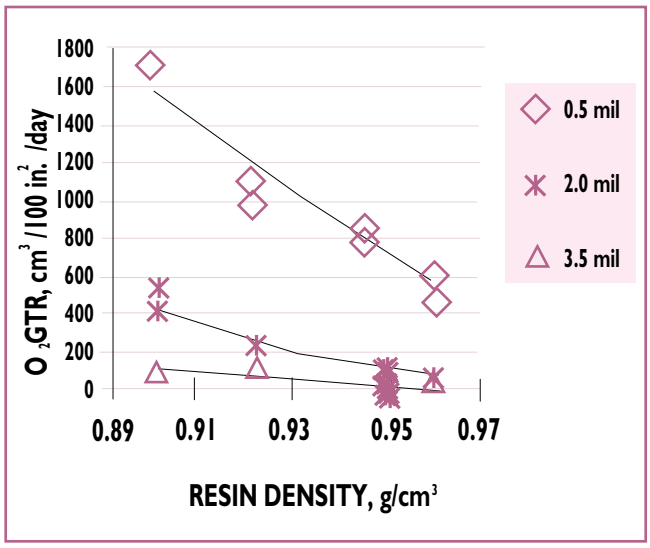
Film gauge, mils	WVTR			O_2GTR		
	n	*K*	r^2	*n*	*K*	r^2
3.5	1.868	34.9	0.974	2.021	22,700	0.937
2.0	1.777	54.0	0.826	1.836	29,000	0.804
0.5	1.309	67.9	0.879	1.193	24,200	0.884

III. Density model parameters

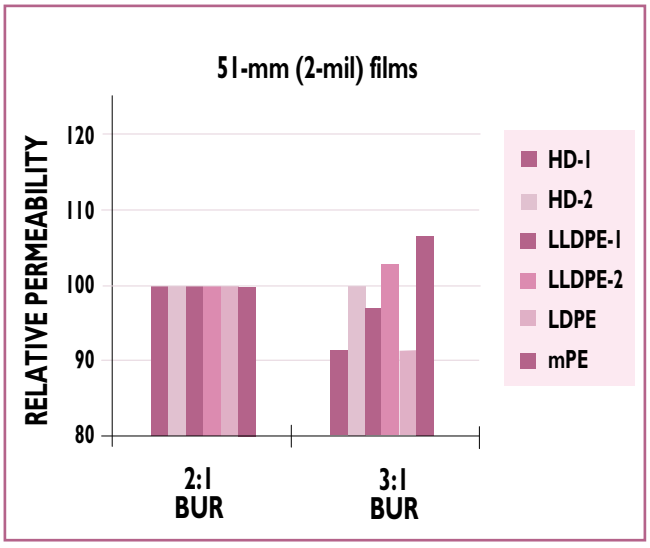
Alter obtained values for *n* of 2.160, 2.181, and 2.057 for nitrogen, oxygen, and carbon dioxide, respectively.

Alter's model (Eq. 2) was used to model the WVTR and O_2GTR data from this experiment. The values obtained for *n* and *K,* along with R^2 values, are shown in **Table III**.

Figures 4 and 5 show the fit of the experimental data to this model for WVTR and O_2GTR, respectively.



5. O_2GTR–density correlation



6. Effect of BUR on WVTR

Resin	MVTR, g-mil/100 in.²/day Low	High	% diff.	O_2GTR, cm³-mil/100 in.²/day Low	High	% diff.
HD-1	0.29	0.55	47	102	301	66
HD-2	0.24	0.43	44	102	215	53
HMW-1	0.58	0.82	29	277	399	31
HMW-2	0.49	0.77	36	203	376	46
HMW-3	0.46	0.76	39	186	370	50
LLDPE-1	1.03	1.05	2	452	520	13
LLDPE-2	1.01	1.11	9	434	565	23
LDPE	1.05	1.45	28	441	677	35
mPE	1.75	1.98	12	844	1018	17

IV. Range of film permeability coefficients

In general, this model provided a reasonably good fit of the data, especially for the thicker 3.5-mil film. The values for n were fairly close to 2 (a squared relationship) for the 3.5- and 2.0-mil films. However, a poorer fit of the data was obtained with the 2.0- and 0.5-mil films, as indicated by the lower r^2 values. This poorer fit is attributed to factors that are discussed later in this paper.

KEYWORDS
Absorption, addition polymers, air permeability, dimensions, evaluation, extrusion, gas permeability, high density polyethylene, linear low density polyethylene, low density polyethylene, oil absorption, permeability, physical properties, plastic films, polyethylene, polyhydrocarbons, polyolefins, thermoplastics, thickness, water permeability, water vapor permeability.

Permeability–gauge relationship

Permeability is often reported in terms of a permeability coefficient. Permeability coefficients are defined by the following equation:

Permeability coefficient = Permeability x Film gauge (3)

It is commonly assumed that permeability coefficients are independent of film thickness. However, data from this experiment, as well as from a number of other researchers *(7, 8)*, suggest that the permeability coefficients of many PE resins are not independent of film thickness. In fact, the permeability coefficient for many resins significantly increased as film gauge decreased.

Table IV lists the lowest and highest permeability coefficients for each of the resins evaluated in this study. This table shows the variation that occurred in the permeability coefficient for each resin. In general, coefficients were lowest for the 3.5-mil film and highest for the 0.5-mil films.

Talwar *(7)* modeled this phenomenon by proposing the concept of an "ineffective thickness." The ineffective thickness was the theoretical gauge at which the film's barrier property was zero. Talwar attributed the ineffective thickness to the rapid cooling occurring at the film's surface, which resulted in lower crystallinity and higher permeation rates. However, Talwar was unable to measure any film density differences that would have provided additional support for his model.

In this experiment, densities were measured on all 0.5- and 3.5-

mil films. Density differences between each set of films ranged from 0 to 0.0048 g/cm^3. Using Alter's permeability–density model (Eq. 2), a 0.0048-g/cm^3 density difference would only account for approximately an 11% difference in permeability; this is far less than the differences observed in most of the permeability coefficients. Other factor(s) must therefore be responsible for the increase in the permeability coefficients at lower gauges.

Four factors that may contribute to the variation in permeability coefficients are:

- Gauge variation/surface irregularities
- Pinholes
- Small gels
- Crystalline morphology/orientation.

Of these, crystalline morphology/orientation was identified as contributing to the variation in permeability observed in this experiment.

Permeability–orientation relationship

The permeability of PE films can be affected by changes in crystalline morphology and orientation *(9, 10).* Permeation differences of over 30% have been attributed to changes in orientation *(10).* In this experiment, permeation rates varied by more than 20% due to orientation differences.

Orientation is influenced by PE resin parameters and processing conditions. Two resin parameters affecting orientation are molecular weight (indicated by melt index) and molecular weight distribution (MWD). Resins having a narrower MWD exhibit less variation in permeation rates, as seen in Table IV. The two LLDPE and the metallocene resins have the narrowest MWD as well as the lowest variation in permeability coefficients.

PE film resins with a lower molecular weight (higher melt index) generally exhibit lower permeabilities *(10, 11).* This reduction in permeability is also attributed to orientation differences.

Processing conditions, such as frost-line height and blowup ratio, can influence orientation and permeability *(10, 11).* **Figure 6** compares the relative WVTR permeabilities for films produced at different BURs with the conventional resins (non-HMW). Permeation rates for the broadest molecular weight distribution resins (HD-1 and LDPE) were lower at the higher BUR. Similar trends were observed with the O_2GTR permeabilities for these two resins.

No consistent trends were observed when analyzing the effect of resin parameters or processing conditions on the permeabilities of the three HMW-HDPE resins. These inconsistencies are partially attributed to the unique high-stalk production process used to produce HMW-HDPE films. One other factor possibly contributing to the lack of clear trends is the presence of ultra-high-molecular-weight "microgels" that may be present in these films.

Oil penetration rate

The WVTR and O_2GTR test procedures use sophisticated instruments to accurately measure steady-state permeation rates. The OPR test, in comparison, is relatively primitive and involves determining the time it takes for the initial appearance of oil on an opposing film surface. Despite various modifications designed to refine the OPR test procedure, significantly higher standard deviations occurred with the OPR test results than with the other permeation tests.

As a result of the high standard deviation, only a few conclusions can be drawn from the OPR test results. As with the WVTR and O_2GTR results, OPR increased as density decreased. Likewise, OPR was significantly higher for the thinner films. It is also expected that a more discerning OPR test would reveal similar trends involving processing conditions and resin parameters, as was observed with the WVTR and O_2GTR data.

CONCLUSIONS AND RECOMMENDATIONS

The oil, oxygen, and water vapor permeation rates of PE blown films are affected by film thickness, PE resin parameters, and processing conditions. Thicker gauges, higher density and higher melt index resins, and a larger BUR generally result in films with lower permeation rates.

Permeability coefficients for a given resin can vary by more than 50%, depending on the resin's molecular weight distribution, film thickness, and process conditions under which the film is produced. Care must be exercised when using or comparing permeability coefficients because of this potential variation. **TJ**

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LITERATURE CITED

1. SPI Committee on Resin Statistics as compiled by Association Services Group, March 31, 1996.
2. Michiels, D. J., *Polyolefins IX Conference Proceedings,* Society of Plastics Engneers, Houston, TX, 1995, p. 553.
3. Young, G. L., *TAPPI 1995 Polymers, Laminations and Coatings Conference Proceedings,* TAPPI PRESS, Atlanta, p. 383.
4. Li, N. N. and Henley, E. J., *AIChE J.* 10: 666(1964).
5. Klute, C. H., *J. Polymer Sci.* 41: 307(1959).
6. Alter, H., *J. Polymer Sci.* 57: 925(1962).
7. Talwar, R., Ph.D. thesis, "The effect of liquid phase contact on the permeation of gases through polymeric film/liquid layer composites," Rutgers University, New Brunswick, NJ, 1973.
8. Aiba, S., Ohashi, M., and Huang, S., *I&EC Fund.* 7: 497(1968).
9. Schlotter, N. E. and Furlan, P. Y., *Polymer* 33: 3324(1992).
10. Culter, J. D., *J. Plast. Film & Sheet.* 1: 215(1985).
11. Tate, R. F., Alathon Technical Service Report, OxyChem, Alvin, TX, 1992.