FACTORS AFFECTING THE PERMEABILITY OF PE BLOWN FILMS

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ABSTRACT

The vast majority of packaged foods require a barrier to gases, flavors or odors to maintain product quality and provide acceptable shelf life. For example, baked foods often require moisture protection, while fresh meats and vegetables require low or controlled oxygen exposure to maximize shelf-life and consumer appeal.

Single and multi-layer polyethylene-based films are being used to package many different food products. The specific permeation properties of these films determine the shelf life of the packaged food products that they contain.

Information is presented on the factors affecting the permeation rates of polyethylene blown films. Models correlating permeation rates with the major effects of density, film gauge and crystalline orientation are shown. In addition, the impacts of processing conditions and resin molecular weight distribution are discussed.

INTRODUCTION

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 pounds/year of polyethylene is currently used in the food packaging industry, with approximately 45 percent used specifically in single and multi-layer film structures [1].

Food packaging films must have specific properties in order 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 gas transmission rate (O_2GTR).

This report presents information on the factors affecting the water vapor and oxygen gas transmission rate of polyethylene blown films. These two permeation rates are directly related, and the major factors affecting permeability are shown to be density, film gauge and crystalline orientation. The impacts of processing conditions and resin molecular weight distribution are also presented.

EXPERIMENTAL PROCEDURES & 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*. Results are reported in grams/meter^2/day for testing at 37.8°C (100°F) and 100% relative humidity.

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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*. Results are reported in cc (@ STP)/meter^2/day for testing performed at 23°C (73°F).

Elmendorf Tear Testing

Tear testing was conducted in accordance with ASTM D-1922, *Propagation Tear Resistance of Plastic Film and Thin Sheeting by Pendulum Method*. The test is performed in the film's machine direction (MD) and transverse direction (TD). Directional tear strengths are reported in grams, while the tear ratio, (TD/MD) is unitless.

Materials

Data from numerous experiments, covering a broad spectrum of PE resins, were compiled for this report. The PE resins ranged in density from 0.900 to 0.958, in melt index (MI2) from 0.03 to 2.0, and had melt flow ratios (MFR (MI20/MI2)) ranging from 15.4 to 180.

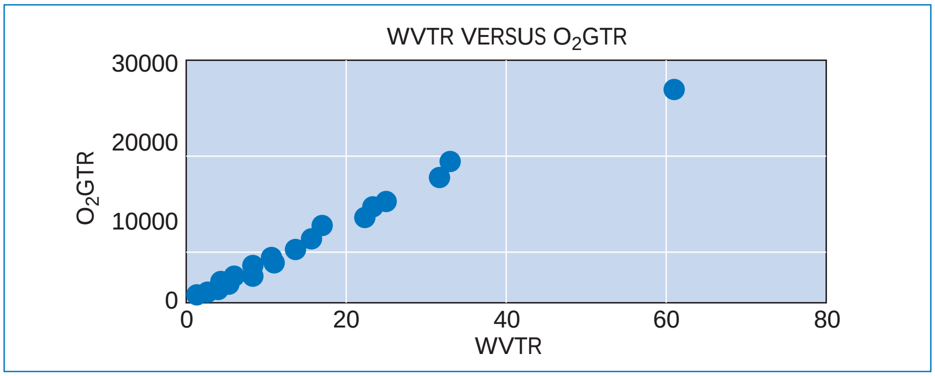
Monolayer films from these resins were produced using a 65mm grooved feed extruder coupled with a 160mm blown film die. Films tested ranged in thickness from 12.7 micron (0.5 mil) to 89 micron (3.5 mil).

DISCUSSION

WVTR versus O_2GTR

WVTR testing was conducted on all films, whereas O_2GTR testing was performed on a selected set of films. Figure 1 is a plot of the WVTR and O_2GTR results for films where both tests were performed.

Figure 1. WVTR/ O_2GTR data



This charts show that for PE blown films, WVTR and O_2GTR results are related and can be modeled with the following equation:

$$O_2GTR = 470 \times WVTR \qquad (1)$$

This relationship means that only one of these permeation tests need be performed, that WVTR measurements can be used to accurately predict O_2GTR results, and visa versa.

Permeation – Density Relationship

A variety of researchers have investigated and theorized on the relationship between permeability and polymer density [2,3]. Alter [3] modeled the permeability-density relationship for PE films using the following equation:

$$P = K\,(1 - \text{density})^n \text{, where K and n are constants} \qquad (2)$$

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

Alter's model (equation (2)) was utilized to model WVTR data spanning the density range from 0.900 to 0.958. Figure 2 shows Alter's model provides a reasonably good fit for 89-micron (3.5 mil) WVTR data.

Figure 2. WVTR – density plot for 89 micron films

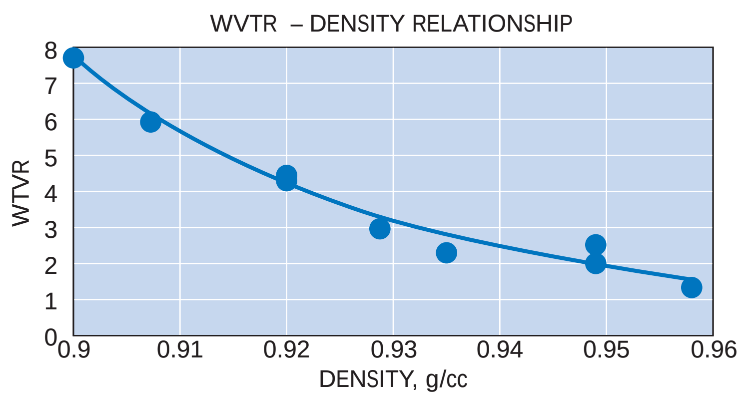


Table 1 lists the n, K and R-squared values for the 89-micron (3.5 mil), 51-micron (2 mil) and 12.7-micron (0.5 mil) films.

Table 1. WVTR – density model parameters

Film Gauge	n	K	R-squared
89 micron	1.81	431	0.93
51 micron	1.71	617	0.77
12.7 micron	1.31	1050	0.88

The model did not fit the thinner film data as well, as indicated by the lower R-squared values. This poorer fit is attributed to crystalline orientation changes that will be discussed later in this report.

Permeation – Gauge Relationship

Permeation results are often reported in terms of a Permeability Coefficient. Permeability Coefficients (PC) are defined by the following equation:

$$PC = \text{Permeation Rate} \times \text{Film Thickness} \quad (3)$$

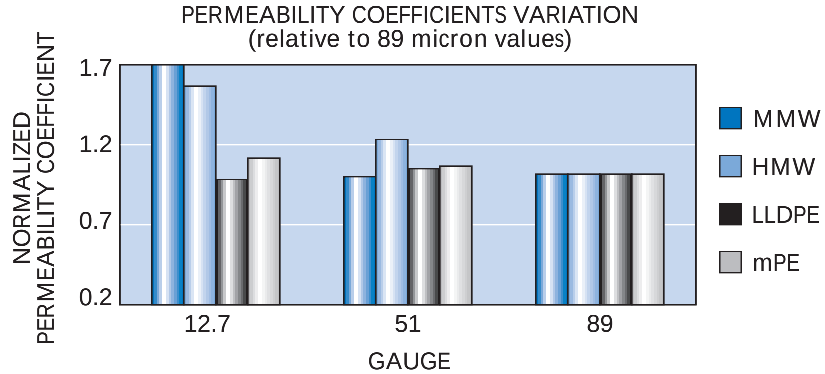
It is commonly assumed that Permeability Coefficients are independent of film thickness. However, data from our experiments, as well as from a number of other researchers [4,5] clearly showed that Permeability Coefficients for many PE resins are not independent of film thickness, and can increase significantly as film thickness is reduced. Furthermore, permeation rates for certain PE resins will vary with changes in processing conditions, without any change in film thickness.

Figure 3 is a plot of WVTR Permeability Coefficients for four resins.

The variability in Permeability Coefficients can be related to the resin's molecular architecture. Resins having a narrow molecular weight distribution (MWD – as indicated by low MFR) exhibit low Permeability Coefficient variability. For example, the linear low density polyethylene resin (LLDPE) and metallocene polyethylene resins (mPE) have relatively narrow MWD and exhibit little variation in their Permeability Coefficients.

On the other hand, the Permeability Coefficients of broad MWD resins can vary by 50% or more [6]. This variability is observed in films produced from the conventional high density PE resin (MMW) and the high molecular weight high density PE resin (HMW). This variability is attributed to changes in crystalline orientation, and will be discussed in the following section.

Figure 3. Graph of WVTR Permeability Coefficients

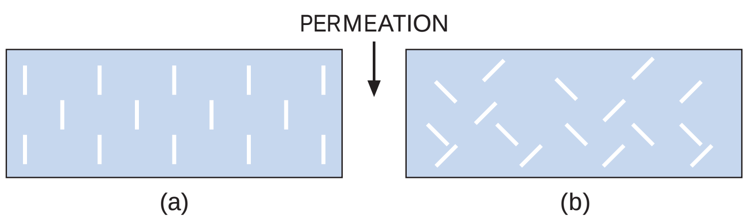


Permeation – Orientation Relationship

Permeation through PE film occurs almost exclusively in the polymer's non-crystalline region. This accounts for the relationship between permeation rates and crystalline content (indicated by density) – the higher the crystalline content, the lower the permeability.

A film's crystalline alignment/orientation can also alter its permeability by affecting the pathways available for diffusion. Various papers have considered this principle, often referring to it as a tortuosity factor. This "tortuous path" concept is represented in Figure 4.

Figure 4. Tortuous path concept



Permeability would be lower in films having a crystalline orientation that creates a more tortuous pathway, such as in Figure 4 (b).

Sophisticated analytical methods, such as small angle or wide angle X-ray scattering (SAXS or WAXS), birefringence, Raman spectroscopy and various, high-resolution microscopic techniques have been used to characterize the crystalline structure of polymers. Numerous studies have utilized these analytical methods to define the crystalline structure of PE [7,8,9], and some have attempted to correlate crystalline structure and permeation properties [8,9]. However, these test methods are not commonly available and most studies have yet to successfully correlate permeability and crystalline structure properties using these methods.

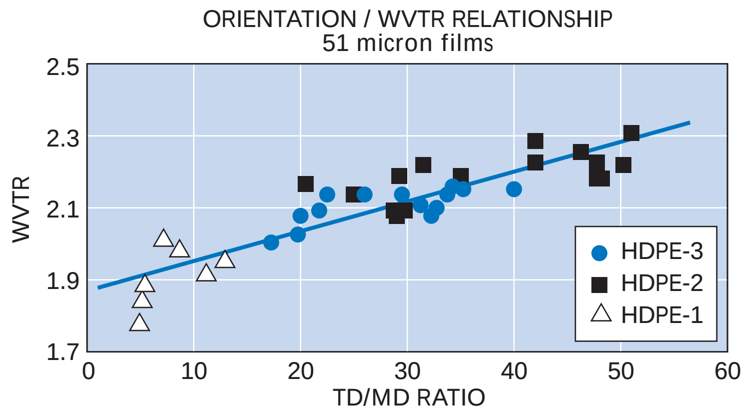
One common analytical method that has shown promise in correlating permeation rate is tear strength. Rohn [10] correlated O_2GTR with the tear strength of various PE films. Our studies have also shown a correlation between permeation rates and tear strength, or more specifically tear balance (TD/MD).

For example, a number of our studies were conducted to evaluate the effect of processing conditions on the permeation rate of HDPE blown films. In one designed experiment, the effects of the following processing conditions were evaluated on three different HDPE resins:

1. Blow-up ratio (BUR)
2. Frost line height (FLH)
3. Output rate
4. Cooling air temperature

WVTR versus tear balance (TD/MD ratio) data from this experiment are plotted in Figure 5.

Figure 5. Permeation rate versus TD/MD ratio for three HDPE resins



Permeation rates are generally higher in films having a larger TD/MD ratio. Test results from various other studies have also shown a similar trend.

WAXS was used to investigate the correlation between permeation rate and TD/MD ratio. Films having a lower TD/MD ratio displayed a more random crystalline orientation than those with a larger TD/MD ratio did. Films with a large TD/MD most likely have high machine-direction crystalline alignment, creating a less tortuous pathway than in films with a more random crystalline orientation.

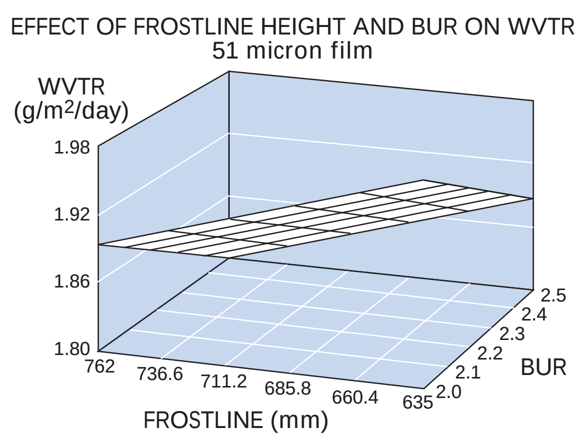
Changes in orientation are also responsible for the variation seen in Permeability Coefficients. Narrow MWD resins, such as the LLDPE and mPE resin, have almost constant TD/MD ratios and Permeability Coefficients throughout the gauge range. TD/MD ratios for the broad MWD resins were higher at thinner gauges, contributing to their increased Permeability Coefficients.

Permeation – Processing Conditions Relationship

The TD/MD ratio can help in understanding the relationship between permeation rates and blown film processing conditions. For example, the permeation rates (and TD/MD ratios) for narrow MWD resins are fairly insensitive to changes in processing conditions.

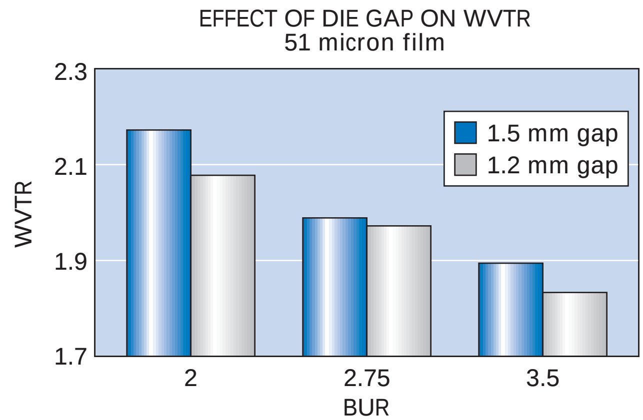
However, the permeation rates of films produced from broad MWD resins can be affected by changes in processing conditions. Figure 6 illustrates the frostline height and blow-up ratio effects on WVTR of a HDPE resin having a broad MWD.

Figure 6. Processing effects on WVTR



Permeation rates can also be affected by changing processing equipment. Figure 7 shows the effect of using different die gaps to produce blown HDPE films from a broad MWD resin.

Figure 7. Effect of different die gap on WVTR



At a given BUR, permeation rates (and TD/MD ratios) are slightly lower in films produced using a narrower die gap.

In order to *minimize* the permeation rate of blown films produced from broad MWD PE resins, the following processing conditions are recommended:

1. Larger blow-up ratio
2. Higher frost line height
3. Narrower die gaps

CONCLUSIONS

1. The oxygen gas and water vapor transmission rates of blown PE films are directly related.
2. The major factors affecting PE film permeation rates are density, film gauge and crystalline orientation.
3. Permeability Coefficients for narrow molecular weight distribution resins are relatively insensitive to changes in processing conditions.
4. Permeability Coefficients for PE resins with a broad molecular weight distribution can vary by 50% or more. This variation is due to changes in crystalline orientation brought about by changes in processing conditions.
5. PE film tear strength ratio (TD/MD ratio) is an indication of relative crystalline orientation, and permeability and TD/MD ratio follow similar trends.
6. Producing film with a large blow-up ratio, high frost line height and a narrow die gap can minimize permeation rates for resins with a broad molecular weight distribution.

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