VARIABLES THAT AFFECT/CONTROL HIGH DENSITY POLYETHYLENE FILM OXYGEN/MOISTURE BARRIER

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ABSTRACT

Multiple layer polyolefin based films continue to be one of the preferred packages for both the food and medical industries. The technology of these films has advanced over the years from simple monolayer structures to multilayer hybrid structures. These affordable packages not only provide tamper proof evidence, but also protection from insects, bacteria, germs and dust and are very effective in providing moisture and oxygen barrier. This paper will discuss these latter two properties, moisture and oxygen barrier, when polyethylene is used as the primary film component.

Many variables affect high-density polyethylene (HDPE) film's oxygen transmission rates (OTR), and water vapor transmission rates (WVTR). These variables include film crystalline structure, relaxation rates of molten polyethylene, polyethylene manufacturing technology, polyethylene resin physical properties, atmospheric conditions, and film fabrication technology and structure. This paper will describe how permeation rates are measured and how each of the above variables affects the permeation rates.

KEY WORDS

HDPE, film processing, WVTR, O_2 transmission rate (OTR), crystalline structure, barrier film, melt relaxation, density, melt index, melt flow rates, frost line height, die gap, BUR, blown film, cast film, gauge effects, MWD

DISCUSSION

Permeation Rate

Permeation rate is typically determined experimentally by maintaining a constant permeant concentration on one side of a film sample and measuring the flow of permeant through the film sample after steady flux has been achieved. Typical permeation units are shown in table below.

WVTR (100 °F, 90 or 100% RH)	OTR (23 °C, 0 or 50% RH)
g/(100 in²-day)	cc/(100 in²-day)
g/(m²-day)	cc/(m²-day)
g-mil/(100 in²-day)	cc-mil/(100 in²-day)
g-mil/(m²-day)	cc-mil/(m²-day)

For medium molecular weight (MMW) HDPE, OTR and WVTR are directly related as shown in Figure 1. Please note that the units on the two permeation rates are different, mass versus volume. Figure 2 compares the rates on a mass equivalent basis.

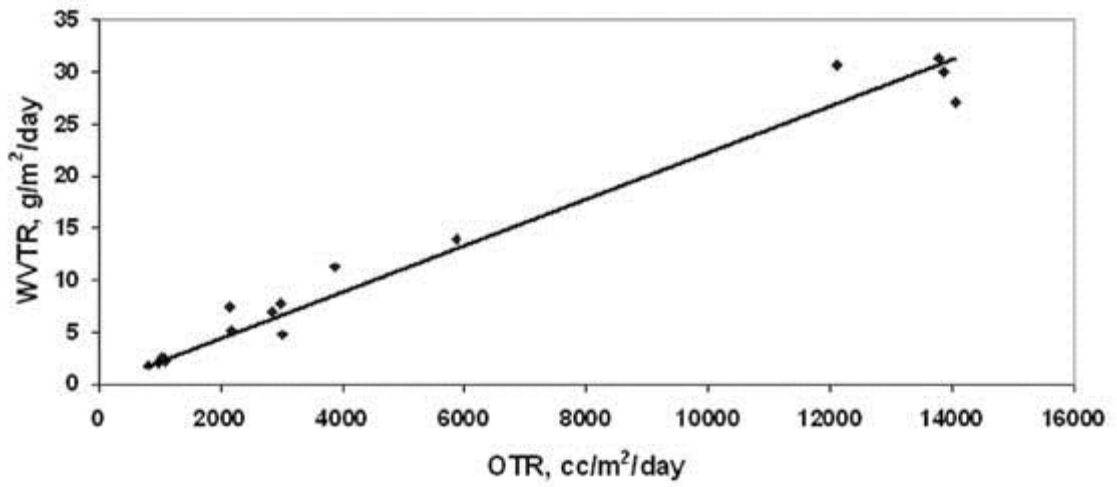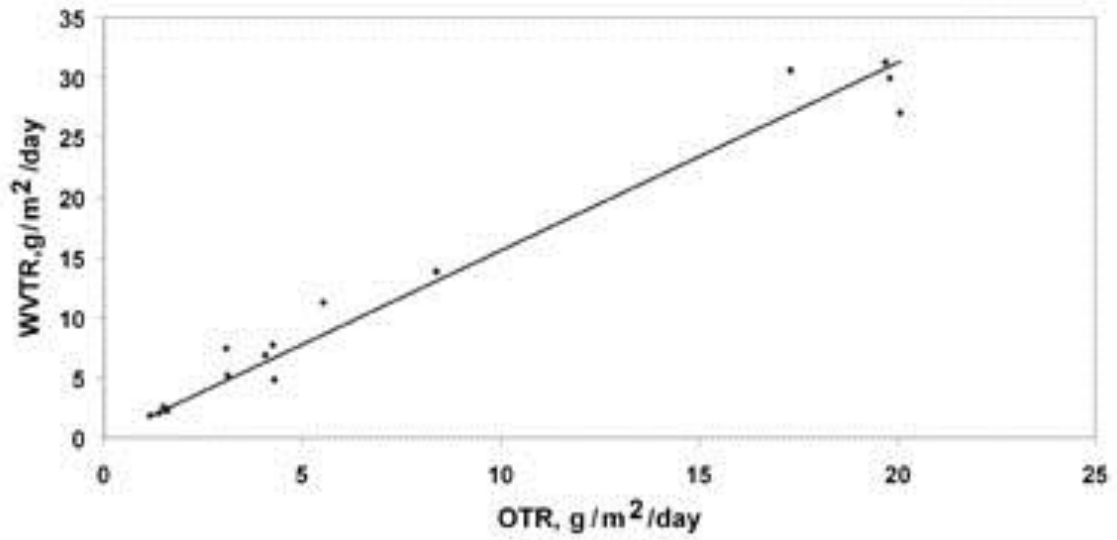**Figure 1. Water Versus Oxygen Transmission Rate**

Figure 2. Water Versus Oxygen Transmission Rate

The difference in permeation rates between water and oxygen is caused by differences in molecular weight, gas molecule size and polarity.

Film Crystalline Structure

Many textbooks can be found that describe the crystalline structure of blown HDPE films. In simple terms, there are two structural regions in the film; the crystal regions, which are impervious to water and oxygen transmission, and the amorphous regions through which water and oxygen molecules diffuse easily. A simple analogy would be a water molecule trying to diffuse through a glass of water full of crushed ice. The water molecule would have to work its way around all the pieces of ice, thus the more pieces of ice present, the slower the diffusion. Therefore, increasing the crystalline regions in blown films improve the barrier properties. The base resin density determines the amount of crystalline regions in the film. Resins with the highest density will yield the best barrier properties.

Polymer Melt Relaxation Rates

Shroff and Mavridis [1] have described the technical effect of polymer melt relaxation times on barrier properties. In layman's terms, as the polymer exits the die, it experiences excessive stress in the machine direction as the film is drawn down to its final gauge. The faster this stress can be relaxed, the more randomly orientated the crystalline regions will be, which maximizes the tortuous path for the water or oxygen molecule, thus improving the barrier. Many variables affect this relaxation; such as HDPE resin catalyst technology, film fabrication technology and film fabrication conditions. Each of these effects will be defined in the appropriate section below.

HDPE Resin Manufacturing Technology

One must understand the drawing below to grasp the effects of this section.
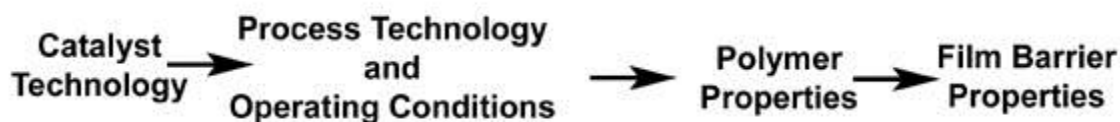
Simply put, the catalyst technology practiced and the process technology and operating conditions define the polymer physical properties. These polymer physical properties and the film processing equipment and conditions determine the film barrier properties!

Catalyst technology can affect long chain branching (LCB) and high molecular weight content (HMW). Increased LCB and/or HMW slow melt polymer relaxation rates, thus producing poorer barrier properties

Polymer Properties

As described above, the catalyst technology, process technology and operating conditions determine the polymer properties, which are typically characterized by molecular weight, molecular weight distribution, and crystallinity. Melt index (MI) which is the total flow of molten polymer measured in grams through an orifice in ten minutes under a 2.12 kg force, is used to reflect the molecular weight. Molecular weight distribution (MWD) can be represented by the ratio of two melt indexes measured at two different forces, 21.2 kg/2.12 kg, called the melt flow ratio, MFR. Density is used as a measurement of crystallinity.

Melt Index and Melt Flow Ratio

Figure 3a shows the effect of MI and MFR on WVTR [2,3]. As one can see, increasing MI and reducing MFR reduces the WVTR. These effects are the result of faster relaxation times. Higher MI and narrower MWD (NMWD) resins reduce the high molecular species, which increase relaxation rates.

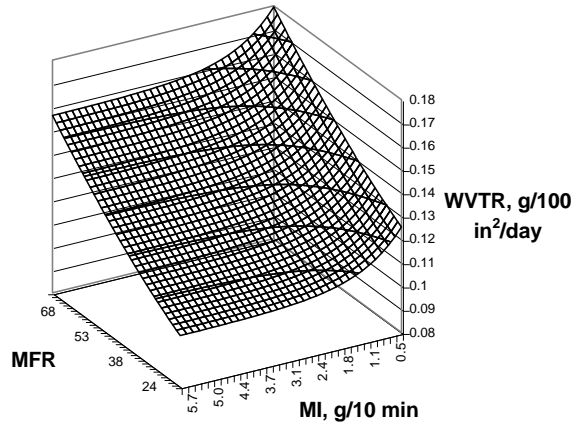**Figure 3a. WVTR as a Function of MI and MFR**

Figure 3b below is an alternate way to view the WVTR, MI and MFR relationships [4]. The figure has MFR plotted on the X axis, MI plotted on the Y axis and WVTR is plotted as constant isometric values. This chart clearly shows how two different combinations of MI and MFR can have the same WVTR. In fact, there is a continuum of MI and MFR combinations that will have the same WVTR. Picking the right combination has to be based on other film physical properties, such as bubble melt stability, MD and TD tear values, stiffness and many more.

Figure 3b. Isometric WVTR Chart as a Function of Melt Index and Melt Flow Ratio
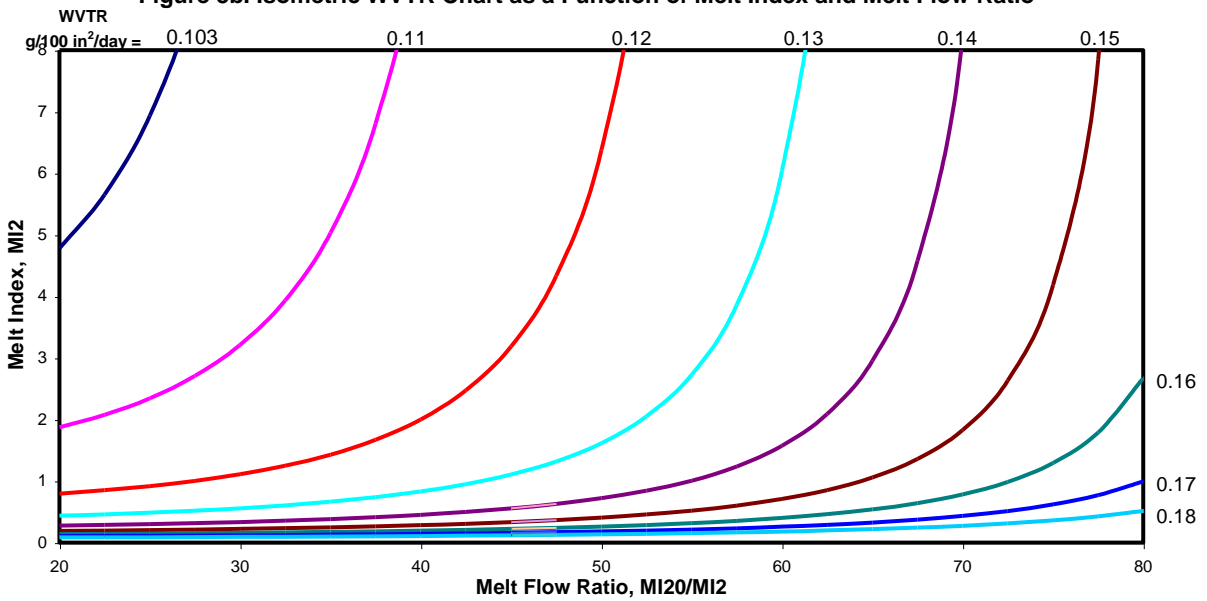

Density

Figure 4 shows the effect of density on WVTR [5]. As seen in the chart, PE resins with higher density provide improved barrier levels. For packaging requiring minimum moisture or oxygen exposure, optimum barrier performance would be achieved using the highest density PE resin. Conversely, lower density resins would be chosen for low barrier applications.

Atmospheric Conditions

For a given package size and contents, atmospheric conditions have a very strong effect on the product shelf life [6]. Figure 5 compares the relative shelf life of a given package for two different atmospheric conditions as a function of WVTR. Obviously, lower WVTR values improve shelf life. As can been seen from the figure, at a given WVTR, the shelf life can be reduced by fifty percent by changing atmospheric conditions

Figure 5. Flaked Cereal Shelf Life Versus WVTR as a Function of Atmospheric Conditions
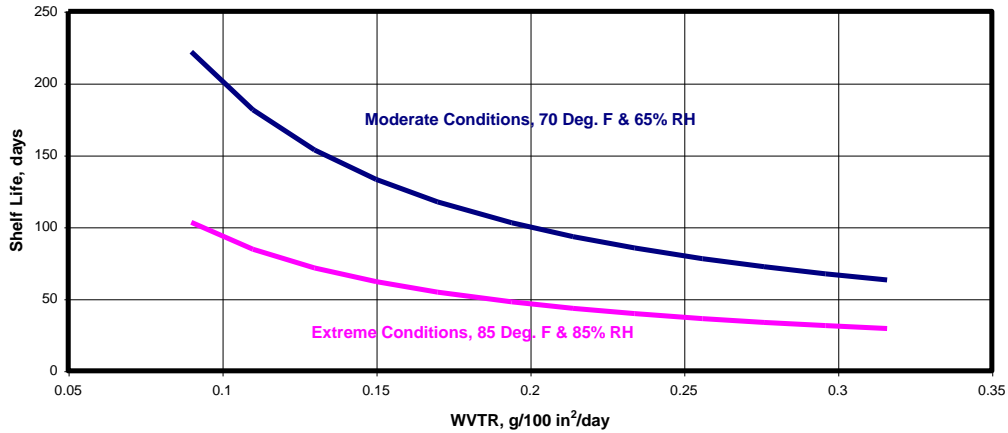
Film Fabrication Technology

The two major film fabrication technologies are cast and blown film. Cast film is extruded through a rectangular die and quenched very rapidly with either a cold water bath or a chilled roll. This fast quench allows very little melt relaxation. Blown film is extruded through a circular die and is slowly quenched by air, which allows longer relaxation time. In addition, the biaxial orientation obtained with the blown film process improves the barrier properties of film. The result is that blown films have better barrier properties (lower WVTR) than cast films made from the same resin to the same thickness as shown in Figure 6 [4].

Figure 6. Cast Film Versus Blown Film WVTR
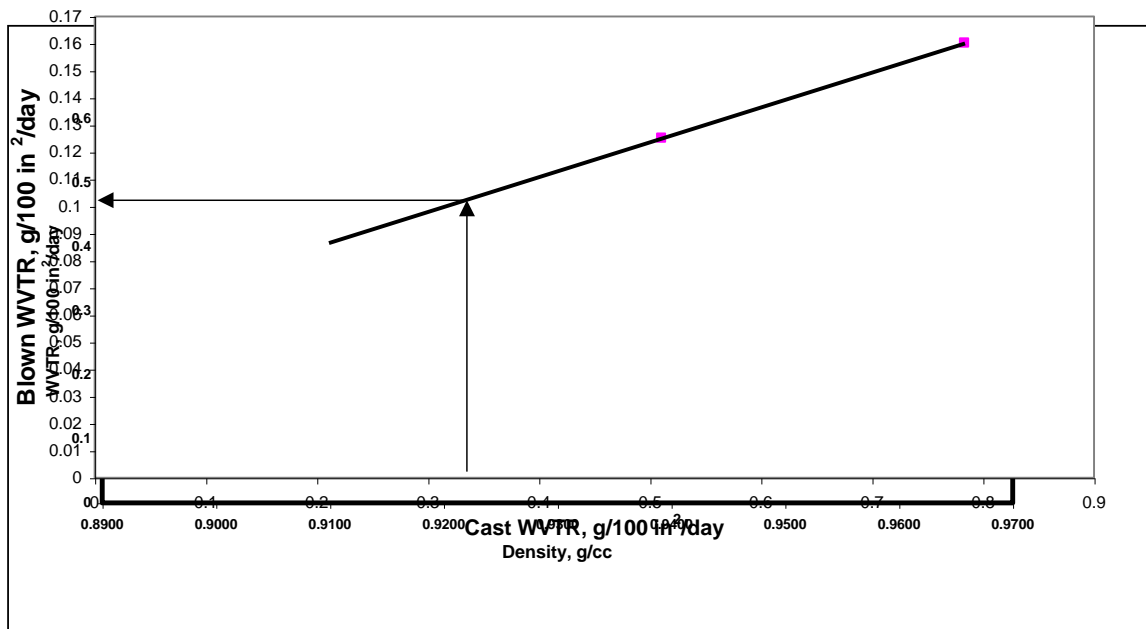
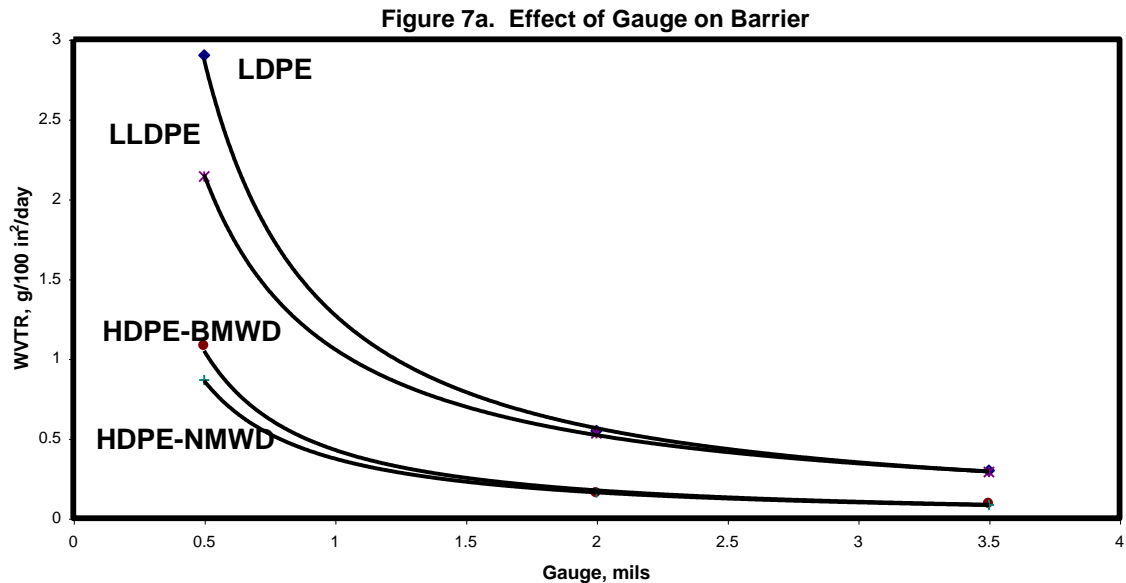## Blown Film Fabrication Conditions [7]

Film processing conditions, such as the following can all affect barrier performance.

- Film thickness
- Blow-up ratio (BUR)
- Frost line height
- Die gap width
- Layer positioning

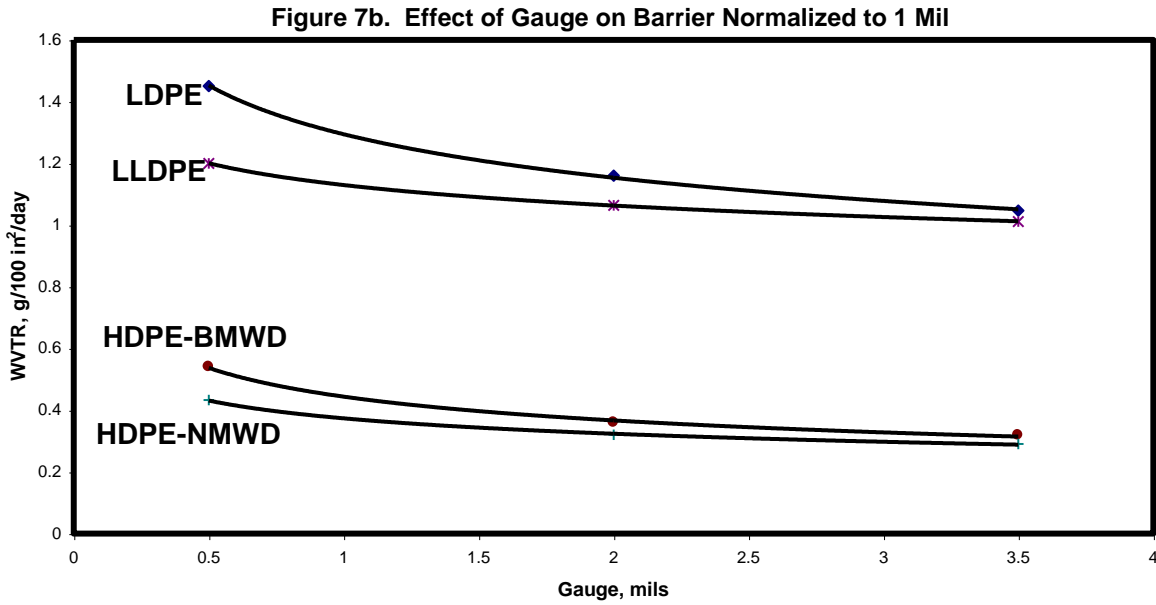The effects of these processing conditions on barrier performance are discussed below.

Barrier - Gauge Relationship

As one would suspect, increasing film thickness improves barrier properties. Figure 7a shows WVTR rate versus gauge for two HDPEs, a low density polyethylene (LDPE), and a linear LDPE (LLDPE), resins. All four resins show significant reduction in WVTR with increasing thickness at the thinner gauges. At thicker gauges, the reduction is much less. As predicted above, the NMWD HDPE film has better barrier than the broad molecular weight distribution (BMWD).

Figure 7a. Effect of Gauge on Barrier

WVTR, g/100 in^2/day vs Gauge, mils

Curves labeled: LDPE, LLDPE, HDPE-BMWD, HDPE-NMWD

While barrier properties for the 0.960 density BMWD and NMWD HDPE resins are similar at thicker gauges, the narrow MWD resin has nearly 20% higher barrier at the lower gauge. Likewise, the 0.920 density LDPE and LLDPE resins have nearly identical barrier properties at thicker gauges, but the LLDPE exhibits over 25% higher barrier at the thinner gauges.

Another way to examine the effect of gauge on barrier is look at the WVTR by normalizing to a thickness of one mil as shown in Figure 7b.

Figure 7b. Effect of Gauge on Barrier Normalized to 1 Mil

LDPE

LLDPE

HDPE-BMWD

HDPE-NMWD

Y-axis: WVTR, g/100 in^2/day

X-axis: Gauge, mils

Again, the WVTR is nonlinear with gauge. It has been theorized [8, 9] that the increase in permeability with decreasing gauge is caused by a non-effective skin layer, which has infinite permeability. Another probable explanation is that the thinner gauges crystallize much faster than the thicker gauges and thus have much greater stresses/less random orientation of the crystalline lamella in the film.

Barrier - Processing Conditions Relationship

Frost Line Height and BUR

Figure 8 illustrates the frost line height and blow-up ratio effects on WVTR for a HDPE resin. The improvement in barrier with increasing frost line height is due to the longer time the film is in the molten state, which gives it more time to relax the stresses induced by the die and the draw down ratio. Increasing the BUR ratio increases the stress in the transverse direction (TD), which helps balance the machine direction (MD) stresses and thus imparts more random orientation of the crystals.

Figure 8. WVTR as a Function of Frostline Height and Blowup Ratio

WVTR, g/100 in^2/day

Blowup Ratio

Frostline Height, in
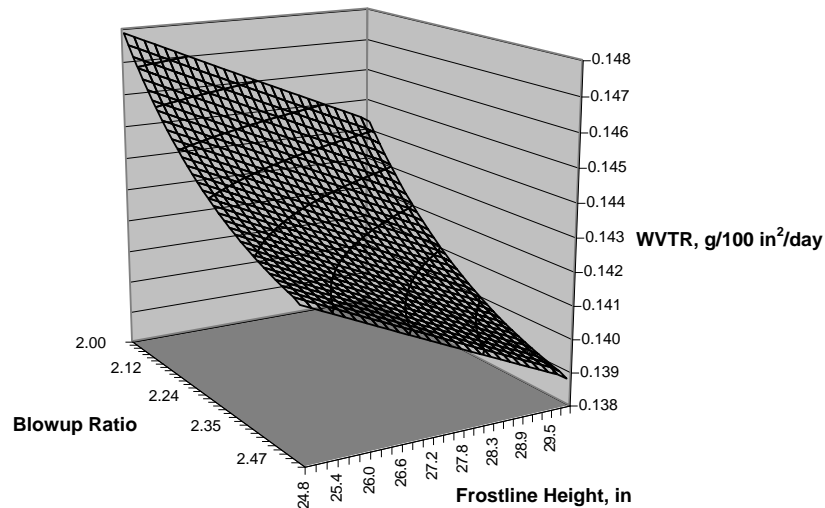
Die Gap Width

Permeation rates can also be affected by changing processing equipment. Figure 9 [7] shows the effect of using different die gaps to produce blown HDPE films from a medium molecular weight (MWD) resin. A smaller die gap reduces the MD draw down ratio, which in turns reduces the stress in the film as it crystallizes.

Figure 9. Effect of Die Gap and BUR on Barrier
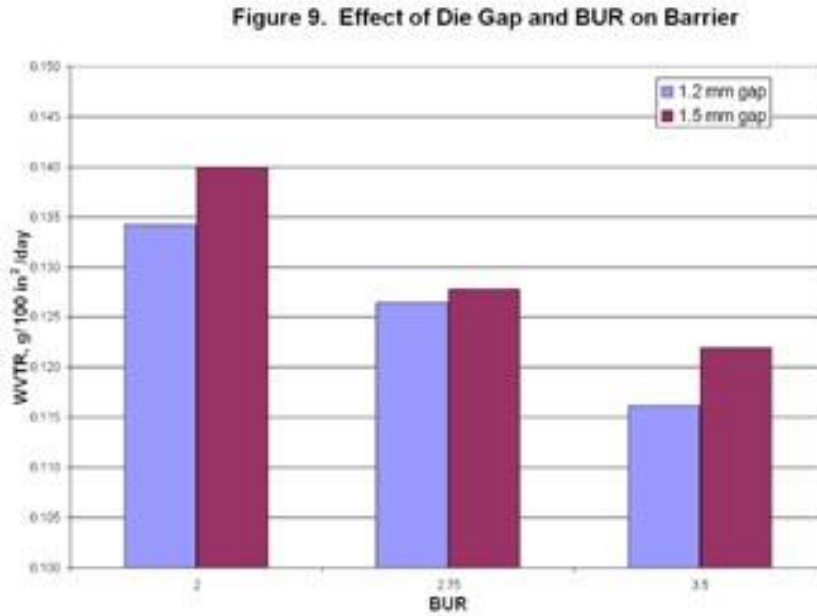
At a given BUR, permeation rates are lower in films produced using a narrower die gap.

Barrier – Multi-layer Film Structure Relationship

The barrier performance of multi-layer PE films can be affected by changing their layer configuration [7]. Figure 10 shows the relative barrier performance for three different HDPE-based coextruded films made with two different homopolymer HDPE resins, 1.0 MI, BMWD and 2.0 MI with a NMWD. The three different film structures had equal layer thickness (33.3% each).

Figure 10. Effect of Resin Positioning In Three Layer Barrier Film
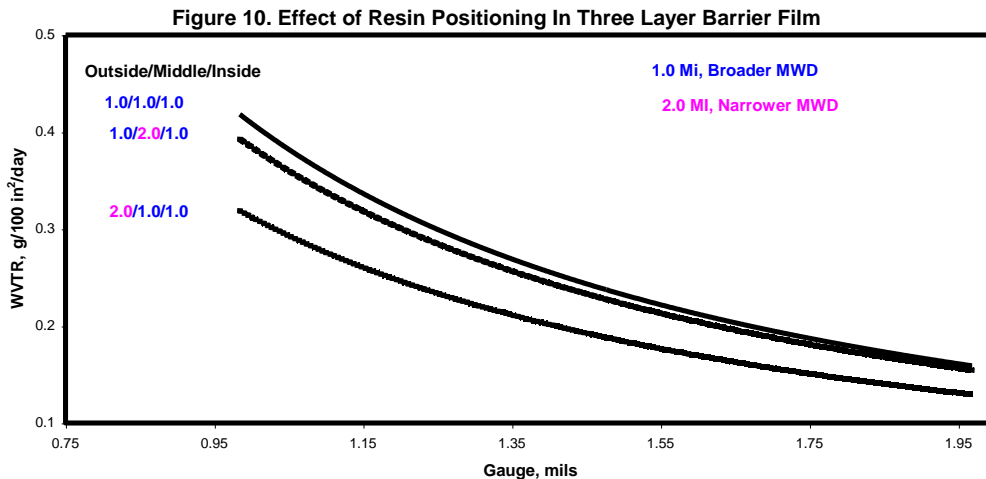
Structure 3 has better barrier (lower permeation rate) than structures 1 and 2, and its barrier advantage increases as film gauge is reduced. This layer position effect is due to the different conditions each layer experiences during the film manufacturing process. For example, a film's outer most (skin) layers are subjected to more intensive shear and cooling forces than the interior layers. Therefore having a higher melt index resin with a faster melt relaxation rate in this outside layer improves the barrier performance of the structure. This type of hybrid structure is widely utilized commercially.

Combined with information previously covered, the layer effect can assist in optimizing the barrier properties of multi-layer PE-based films. For high barrier applications, skin-layer resins should have a narrow MWD and minimal LCB. Conversely, barrier properties can be minimized by using broad MWD resins and/or resins with LCB in the skin layer.

CONCLUSIONS

Maximum WVTR/OTR barrier in blown HDPE film is achieved by maximizing the crystalline regions and the random orientation of the crystalline lamella. Using resins with the highest density will maximize the crystalline regions. Random orientation of the lamella can be maximized by:

1. Reduce melt relaxation times / increased high relaxation rates by:
    - Reducing molecular weight / increasing MI
    - Reducing molecular weight distribution / reducing MFR
    - Minimize LCB and HMW species
    - Increase frost line height
2. Minimize MD stress in the melt bubble by:
    - Increasing the BUR
    - Reducing the die gap
3. Utilize hybrid film structures

ACKNOWLEDGEMENTS

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