OPTIMIZING BARRIER PERFORMANCE OF MULTI-LAYER POLYETHYLENE FILMS

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ABSTRACT

Multi-layer polyethylene (PE)-based films continue to capture numerous food packaging applications due to their performance and economic advantages. In the majority of these applications, the packaging film's permeation or barrier properties determine the shelf life of the packaged foods. Factors affecting these barrier properties are the specific PE resins or resin blends used, processing conditions, and the relative position of the resins in the multi-layer structure.

This paper reviews barrier requirements and shelf life consideration for various food products, and the advantages of polyethylene-based films versus other packaging materials. The paper shows relationships between PE resin characteristics, film structure, processing conditions, and permeation properties. Utilizing this information, the barrier performance of multi-layer film structures can be optimized for their particular packaging application.

INTRODUCTION

Polyethylene-based films have established a major position in the food packaging industry due to their excellent shelf life, product protection, product display and packaging/shipping costs. An estimated 1.6 billion pounds of polyethylene will be converted into films used in food packaging in 1998, with many of these films being multi-layer, coextruded structures [1]. Barrier performance of these multi-layer films depends on the resins used, fabrication conditions, and the resin positioning/placement in the various layers.

The characteristic of the packaged food product determines the optimal barrier performance for the packaging materials. Optimum barrier for some foods requires high-barrier packaging materials while others need low-barrier materials to maximize shelf life. For instance, dry foods, such as cereals, crackers, cookies and powdered (cake/pudding) mixes require a barrier to moisture/water vapor, while certain meat and poultry products call for minimum oxygen exposure. High density polyethylene (HDPE)-based multi-layer films are the material of choice for many of these packaging applications. Fresh produce and some meat packaging applications require a controlled oxygen (and carbon dioxide) exposure to maximize shelf life. These products can be packagedin low density polyethylene (LDPE), ultra low density polyethylene (ULDPE) and metallocene-catalyzed polyethylene (mPE) – based films.

This paper reviews the barrier requirements and shelf life considerations for various food products, and compares the advantages/benefits of polyethylene-based films versus other packaging materials. Also presented are the effects of PE resin properties, resin manufacturing technology, specific layer composition, and processing conditions on barrier performance. This information can help packaging engineers optimize multi-layer PE-based film barrier performance for their particular application.

DISCUSSION

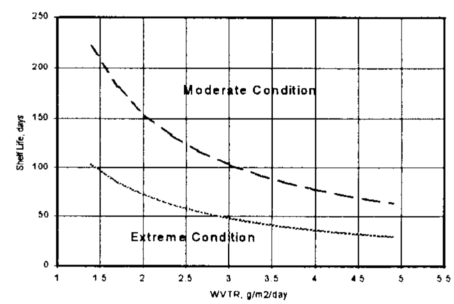
Shelf Life / Packaging Considerations for Various Food Products

The three major components determining food shelf life are: 1- health (chemical/microbial), 2 - appearance, and 3 - texture/taste/odor (sensory) - factors. For example, fungal growth is often the determining factor for the shelf life of strawberries, and can be moderated by CO2 exposure. Browning discoloration of fresh red meat and certain vegetables (e.g. lettuce) frequently limits their shelf life, and are affected by exposure to oxygen and/or CO2 [2,3]. Water pickup or loss can affect the texture and limit the shelf life for various foods, including cereals, crackers, snacks and frozen pizza.

Shelf life is also dependent on the shipping and storage environment. For example, the high humidity common in the Southeastern US presents a greater packaging/shelf life challenge for dry food products, such as breakfast cereals, crackers and chips. Figure 1 shows the effect of water vapor transmission rate (WVTR) on the estimated shelf life of a typical flaked cereal stored at the following two conditions [4]:

1) moderate condition - 70° F and 65% relative humidity (RH)
2) extreme condition - 85° F and 85% RH

Figure 1
Flaked Cereal Shelf Life Versus WVTR



In this example, a 100 day shelf life is obtained using a 1.4 and 3.0 g/m2/day barrier film for the moderate and extreme storage conditions, respectively. Compared to the moderate storage condition, the extreme condition requires more than double the barrier performance to achieve equivalent shelf life.

The shelf life or consumer appeal for certain breakfast foods and crackers can also be affected by the loss of flavors or odors into or through the packaging material. For example, fruit and chocolate flavored cereals require a good aroma barrier to achieve maximum shelf life. Multi-layer HDPE-based films, utilizing a layer of nylon to provide an aroma barrier, are commonly used for these packaging applications. On the other hand, some cereals require a low oxygen/aroma barrier to avoid the build-up of unpleasant odors in their packaging headspace, and these products should not be packaged in high aroma barrier films.

The shelf life of many other food products, such as red meat, poultry, and fresh produce are affected by their exposure to oxygen. Fresh red meat is an interesting case, and has dramatically different packaging requirements depending upon appearance and shelf life considerations [2]. For the longest shelf life (up to 21 days), primal cuts of red meat are usually packaged in a high oxygen barrier vacuum package, and have a purple appearance because of the absence of oxygen. On the other extreme, red-colored meat is achieved by high oxygen exposure (low oxygen barrier) but has a considerably shorter shelf life (<12 days). In the latter case, ULDPE and mPE-based films can provide the needed low oxygen barrier requirement as well as excellent puncture and tear resistance.

Fresh poultry products are commonly packaged in moderate oxygen barrier films (1100 – 1550 cc/m2/day) to extend shelf life, while minimizing the buildup of unpleasant or noxious gases/odors. HDPE-based multi-layer films readily meet these barrier requirements. One or more layers of a linear low density polyethylene (LLDPE) or ULDPE are often incorporated to provide enhanced puncture and tear resistance.

Numerous published articles have documented the increasing use of modified atmosphere packaging (MAP) to extend the shelf life of fresh produce [3,5,6]. Respiration rates and optimal package headspace characteristics (O2 and CO2 concentrations) can vary dramatically for different fresh fruits and vegetables, which in turn affect the barrier requirement of the packaging material. In general, packaging in low O2/CO2 and high water vapor barrier material maximizes fresh produce shelf life. Because of their favorable barrier, clarity and sealing characteristics, LDPE and mPE-based films are often used when packaging fresh produce.

PE Packaging Advantages/Benefits

PE-based packaging materials offer numerous benefits compared to alternative types of packaging materials. Table I lists a comparison of the various considerations for four types of packaging materials – glass, metal, wax paper and HDPE-based films.

Table 1. Properties of different packaging materials

	GLASS	METAL	WAX PAPER	HDPE FILM
Weight	2.5 g/cc	2.5 g/cc	0.8 g/cc	0.95 g/cc
Sealability	Excellent	Excellent	Adequate	excellent
Barrier	Excellent	Excellent	Very Good / Moderate	good
Packaging Speed	High	High	Slow	moderate
Cost	High	High	Low	low

The major benefits of PE-based packaging materials over metal and glass are lower weight and material cost. Compared to waxed paper, the main benefit of PE-based films is packaging speed. Two other negative issues for waxed paper are:

1) Its very good barrier in the flat form is greatly decreased when it is creased and wrinkled as it is in many packaging applications.

2) Breakfast cereals usually have a lower water activity than waxed paper, and will pull moisture from the paper. This moisture loss can cause brittleness in the finished package and can result in tearing during opening of the package.

Because of their advantages, PE-based films are selected over metal, glass and waxed paper for many packaging applications.

Resin Factors Affecting Barrier Performance

The physical properties most widely used to characterize PE resins are density, melt index (MI) and molecular weight distribution (MWD). Effects of these three properties on barrier performance are discussed below.

Barrier - Density Relationship

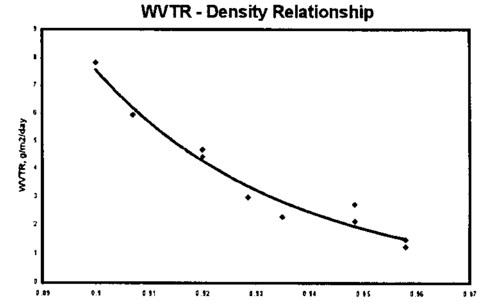
The relationship between permeation rate (P) and resin density has been modeled using an equation proposed by Alter [7];

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

Previous studies [7,8,9,] have shown that when all factors (such as orientation) are considered, n is approximately 2. Figure 2 shows that Alter's model provides a good fit for WVTR permeability–density relationship.

As seen in the chart, PE resins with higher density provide increased barrier levels. For foods 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.

Figure 2
WVTR - Density Relationship



Barrier – MI and MWD Relationship

Barrier properties generally increase using PE resins with a higher MI and/or a narrower MWD because of the influence of these properties on PE film crystalline structure [8,9]. Barrier properties of blown and cast PE films increase as crystalline orientation becomes more balanced. High MI and narrow MWD resins produce films with relatively balanced orientation, and are minimally affected by changes in processing conditions. On the other hand, processing conditions can have a significant effect on the barrier properties of lower MI and broader MWD resins. (This processing condition/crystalline orientation effect will be discussed in later sections.)

Barrier – Long Chain Branching Relationship

As with broad MWD resins, the barrier properties for long chained branching (LCB) -containing resins, such as LDPE, LDPE blends and certain HDPE resins, can vary dramatically depending on their processing conditions and will be later reviewed.

Resin Manufacturing Technology Factors Affecting Barrier Performance Relationship

Numerous factors in PE resin manufacturing technology can affect barrier performance. These factors include:

1) Reactor hold-up time (HUT) – Long hold up times can generate high molecular weight species (HMWS) which can cause gels and result in lower barrier performance.

2) Catalyst technology – Certain catalysts produce resins with LCB and/or HMWS. As discussed above, LCB changes a resin's sensitivity to processing conditions, which can affect crystalline orientation and barrier properties. Under certain processing conditions, some catalyst systems generate in-situ comonomer which depress homopolymer resin density.

3) Catalyst removal – Removing (versus deactivating and/or neutralizing) catalyst residues can lower a resin's crystallization rate and gel forming tendency, increasing its barrier performance.

4) Pelletization – Substantial work and heat input to pelletize a resin can affect numerous resin properties, including molecular weight, MWD, oxidation, LCB and gel content. These effects will generally lower a resin's barrier performance.

5) Antioxidant – Antioxidant (AO) dispersion can affect resin stability. Well dispersed antioxidants can increase stabilization at a given AO level, or allow a lower AO level to meet a given stabilization performance.

Table II summarizes the effect of these variables on barrier performance.

Table II. Effect of Manufacturing Technology on Barrier

Technology Factors	Lower WVTR	Higher WVTR
Reactor HUT	Short	Long
In-situ Comonomer Generation	No	Yes
HMWS/LCB	No	Yes
Catalyst Removed	Yes	No
Pelletizing – High Work and Heat	No	Yes
Anti-oxidant Dispersion	Good	Poor

The two technologies used commercially to produce PE resins are the solution process and the slurry process. In the solution process, polymer is produced in a single fluid phase, and is in molten form from the beginning. In contrast, slurry technology produces a solid form polymer in a carrier fluid (either gas or liquid).

The solution process technology has some inherent advantages over the slurry technology in high barrier packaging applications. Solution technology has short reactor holdup times and requires only minimal work input for pelletization, which can result in higher barrier performance. The solution process also offers alternative methods of AO incorporation, which can improve AO dispersion and effectiveness.

Removing catalyst residues can also improve the barrier performance of PE resins. However, due to the high cost of this step, only one domestic solution PE manufacturer currently uses this practice.

Process as well as catalyst technologies play a combined role in PE resin manufacturing. For example, LCB can be produced in the high pressure LDPE process, with slurry process chromium-based catalysts, as well as with certain solution process mPE catalysts. LCB content provides advantages in low barrier packaging applications, due to its affect on crystalline orientation. Blending in LDPE is a commonly used method for introducing LCB. However, this blending procedure may have certain drawbacks compared to in-reactor LCB production.

Processing Conditions Affecting Barrier Performance

Film processing conditions, such as film thickness, blow-up ratio (BUR), frost line height, die gap width and layer positioning, can all affect barrier performance. The effects of these processing conditions on barrier performance are discussed below.

Barrier - Gauge Relationship

Changes in film thickness can have significantly different effects on barrier properties, depending upon the PE resin's properties. Narrow MWD resins have relatively constant barrier properties per unit thickness (often reported as a permeability coefficient (PC) = permeation rate X gauge). In contrast, permeation rates for broad MWD resins or resins with LCB can be significantly higher than for narrow MWD resins at lower gauges (<50 microns). The higher permeation rates for resins with broad MWD and/or LCB is attributed to the more imbalanced crystalline orientation occurring in their thinner films.

Figure 3
Effect of Gauge on Barrier

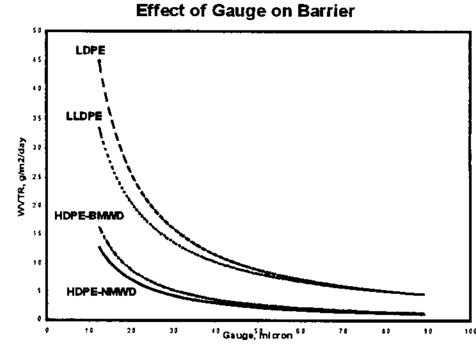


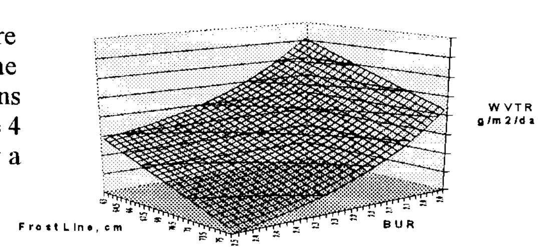
Figure 3 shows permeation rates versus gauge for two HDPE, a LDPE and a LLDPE resin.

While barrier properties for the 0.960 density broad MWD and narrow MWD 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.

Barrier - Processing Conditions Relationship

As previously noted, with narrow MWD resins, barrier properties are fairly insensitive to changes in processing conditions. However, the permeation rates of films produced from broad MWD resins and resins with LCB can be affected by changes in processing conditions. Figure 4 illustrates the frost line height and blow-up ratio effects on WVTR for a HDPE resin which has a broad MWD.

Figure 4
Processing Effects on WVTR



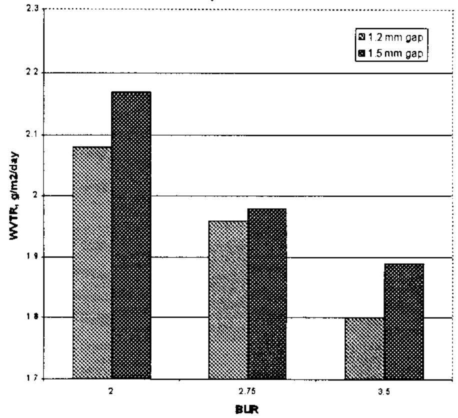
Permeation rates can also be affected by changing processing equipment. Figure 5 shows the effect of using different die gaps to produce blown HDPE films from a broad MWD resin.

At a given BUR, permeation rates are lower in films produced using a narrower die gap.

In order to maximize barrier properties (*minimize* permeation rate) of blown films produced from PE resins with a broad MWD and/or LCB, the following processing conditions are recommended:

1. Larger BUR
2. Higher frost line height
3. Narrower die gaps

Figure 5
Effect of Die Gap and BUR on Barrier



Barrier – Multi-layer Film Structure Relationship

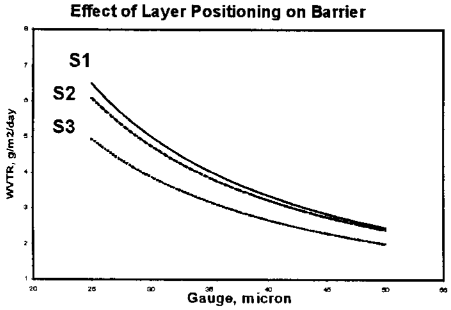
The barrier performance of multi-layer PE films can be affected by changing their layer configuration. Figure 6 shows the relative barrier performance for three different HDPE-based coextruded films made with two different homopolymer HDPE resins.

HD1	HD2
1.0 MI, broad MWD	2.0 MI, narrow MWD

The three different film structures are (all 33% layers)

Structure 1 (S1)	Structure 2 (S2)	Structure 3 (S3)
HD1/HD1/HD1	HD1/HD2/HD1	HD2/HD1/HD1

Figure 6
Effect of Layer Positioning on Barrier



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. Due to these more extreme shear and cooling forces, a material's barrier performance in a skin-layer will resemble its barrier property in a thin film. On the other hand, barrier performance for materials in the interior layers will be similar to their thick film property.

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

1. Optimum barrier performance for food packaging means many things and depends on the food being packaged! Shelf life can be maximized by controlling one or more of the following permeation rates:
   - Water vapor
   - Oxygen
   - Aroma/odors
   - CO2

2. PE resin density, MWD and LCB affect barrier performance.

3. Differences in PE resin manufacturing technologies influence barrier properties

4. For broad MWD and LCB-containing resins, the following processing conditions may affect barrier performance
   - Film thickness
   - BUR
   - Frostline height
   - Layer position

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