Flexible packaging: old to new resin technologies and gateway to metallized barrier sealants based on polyethylene (Part 1 - Historical)

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This is a two part review paper which reviews resins from new and old technologies. There is a distinct difference in approach while creating barrier films from resins from new technologies. This paper highlights this difference.

Old generation resins partially fulfilled the challenges of replacing paper, glass and metal in food packaging. Barrier films from the old generation resins which enjoyed sizeable market were not enough for the modern day needs of the consumer. Changes in life style of the society world over, has brought in more foods in flexible packages which demand greater barrier properties. These requirements were met by new generation resins. New packages with various combinations of polymers emerged as a result of scientific progress that was achieved. The contribution of polymer producers, processors as well as packaging professionals has been phenomenous. This is an unending story as new structures are being created very often.

Film blowing was considered as an art 30/40 years back and has become science in today's time. The present approach of developing new structures is based on scientific principles which are highlighted as an example in Part Two of the review paper. The processing industry needs to upgrade the facilities to develop new structures and also develop the talent which can assimilate new information provided by various vendors to satisfy growing demands of consumers. In house knowledge development with operational expertise is the key to success. Innovation is more relevant and creative environment which nourishes new thoughts with scientific approach is necessary. The success will depend on the consistent quality of the produce to survive and grow in highly competitive field of flexible packaging. Source reduction, cost reduction and better barrier is key to this success and one successful commercial example has been quoted at the end of this review paper.

High density polyethylene

Preamble

DURING the decades of 80s and then 90s HDPE was predominantly considered as material for packaging of perishable foods. Three layer blown film was a common process to make barrier films. By this time resin manufacturers had educated most of technical persons working in the processing industry on relationship between melt flow index and density of polyethylenes. Every resin producer had created better or improved resins by improving the catalyst and then the reactor process parameters to create monopoly or edge over the competition.

Relationships between PE resin characteristics, film structure, processing conditions and permeation properties was well established. Utilizing this information, the barrier performance of multi-layer film structures can be optimized for their particular packaging application. It is worthwhile to understand this relation today so that we can still use the old options and build on this knowledge our business using new generation polyethylene resins made using single site metallocene resins.

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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. 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 packaged in 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.

Table 1 : Properties of different packaging materials

	Glass	Metal	Waxed Paper	HDPE Film
Weight	2.5 g/cc	2.5 g/cc	0.8 g/cc	0.95 g/cc
Sealability	Excellent	Excellent	Adeqate	Excellent
Barrier	Excellent	Excellent	Very Good/Moderate Good	
Packaging Speed	High	High	Slow	Moderate
Cost	High	High	Low	Low

PE packaging advantages/benefits

PE-based packaging materials offer numerous benefits compared to alternative types of packaging materials. *Table 1* lists a comparison of the various considerations for four types of packaging materials – glass, metal, waxed paper and HDPE-based films.

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) It's 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.

Today some of the states in India have banned plastics packaging for biscuits and then industry would be forced to use wax coated paper.

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

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.

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. 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.

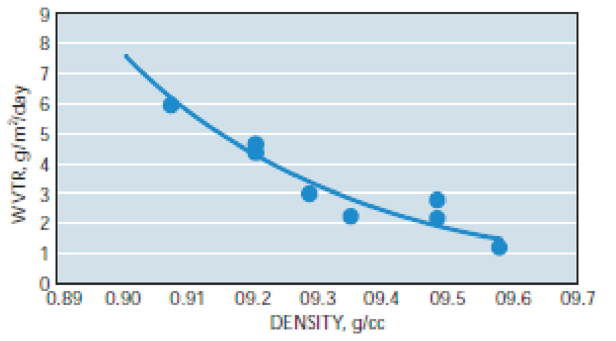

Fig.1: WVTR-density relationship

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.

4) 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.

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 effect 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.

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 2 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 3*

Table 2 : Effect of manufacturing technology on barrier

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

Table 2 summarizes the effect of these variables on barrier performance.

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 that can improve AO dispersion and effectiveness.

Removing catalyst residues can also improve the barrier performance of PE resins..

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

Barrier – Gauge relationship

Changes in film thickness can have significantly different effects on barrier properties depending upon the PE resin's properties.

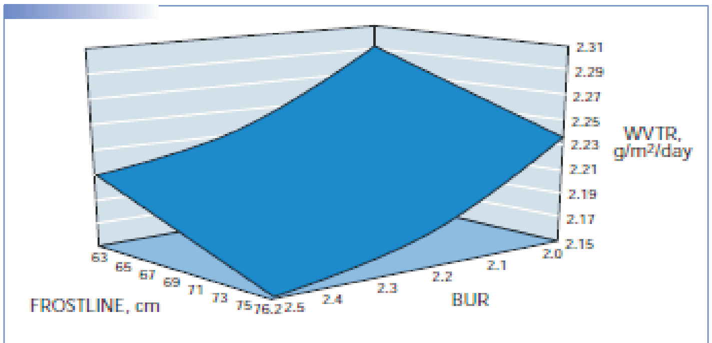

Fig. 3: Processing effects on WVTR

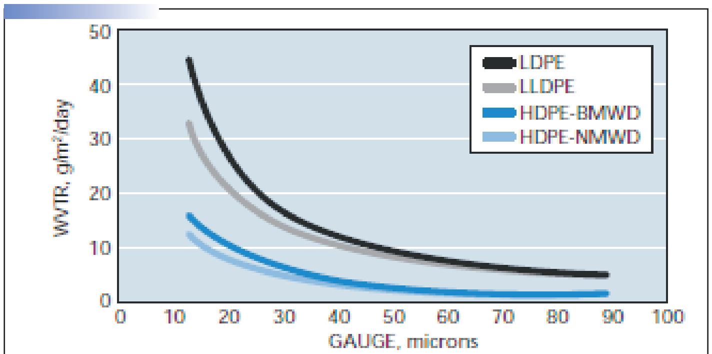

Fig. 2: Effect of gauge on barrier

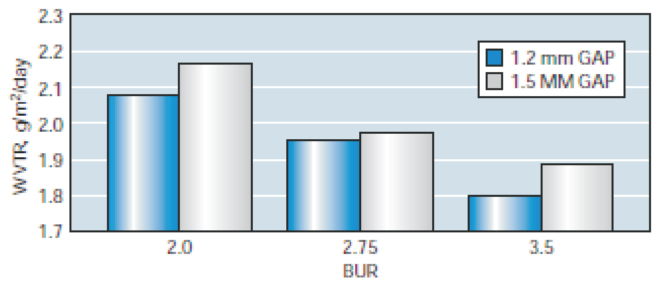

Fig. 4: Effect of die-gap and BUR on Barrier

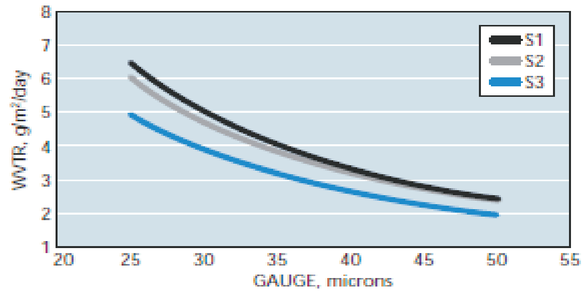

Fig. 5: Effect of layer positioning on barrier

illustrates the frost-line height and blow-up ratio effects on WVTR for a HDPE resin that has a broad MWD.

Permeation rates can also be affected by changing processing equipment. *Figure 4* 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

Barrier – Multi-layer film structure relationship

The barrier performance of multi-layer PE films can be affected by changing their layer configuration. *Figure 5* 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	HzD1/HD2/HD1	D2/HD1/HD1

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. Controlling one or more of the following permeation rates can maximize shelf life:
   - Water vapor
   - Oxygen
   - Aroma/odors
   - CO_2
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
   - Frost-line height
   - Layer position

References

Optimizing Barrier Performance of Multilayer Polyethylene Films by Equistar. ■