High Gas Barrier Materials with Multilayer Morphology for Packaging Applications

Guojun Zhang
guojun.zhang@aschulman.com
A. Schulman, Inc.
1183 Home Ave, Akron, OH 44310, USA

Abstract

Multilayer films are widely used in packaging industry to fulfill different applications. It is well known that multilayer structure is essential for high gas barrier packaging using EVOH, because moisture has negative effects on EVOH’s barrier properties [1, 2]. In order to effectively use EVOH in barrier applications, usually a moisture barrier layer and a tie layer are required [3, 4]. In this study, specially prepared polymeric compounds based on EVOH and polyolefin with good dispersion, proper compatibility/incompatibility and viscosity match are prepared. These special materials all yield a morphology that is similar to multilayered structure after the resins are extruded into thin film. Different from some previous researches [5, 6, 7], our technique involves with a pre-compound process, which ensure the multilayer morphology to form after resins are extruded into thin films.

With multilayer-like morphology inside, EVOH phase is extended and protected. Therefore, good gas barrier (both OTR and WVTR) properties agreeing with series model calculation are reported for all film samples. These materials with multilayer-like morphology have also shown decent adhesion with different PE reins, so 3-layer instead of 5-layer films are successfully fabricated, which are applicable in barrier packaging applications in terms of barrier and optical properties. It is expected that these special materials with multilayer-like morphology inside can be used as monolayer films or a layer in multilayer structures to enhance the barrier performance as well as process flexibility of EVOH resins.

Introduction

Ethylene vinyl alcohol (EVOH), as the barrier layer widely used in packaging industry has drawn a lot interests in the past decade because of its excellent oxygen barrier property [1, 2]. Although it owns extraordinary oxygen barrier, it is very sensitive to moisture, as water molecules are known to increase EVOH’s molecular chain mobility [1]. Therefore, EVOH, as the oxygen barrier layer, is usually embedded in multilayered structures [3, 4]. However, the process for fabricating multilayer structure is expensive and complex [1]. In the contrast, polymer blends are easy to produce. It would be valuable, if people can simply use polymer blends to replace or reduce the number of layers in multilayered structures. It is actually a traditional method for improving gas barrier property of a polymer by blending it with another higher barrier polymer.

The key concern is: whether polymer blends can yield the maximum barrier for given compositions.

![Figure 1](image1.png)

**Figure 1.** Comparison of series model calculation and miscible blend model calculation, with assumption of each polymer component having the same barrier property as its bulk control.

According to Fig. 1, assuming polymer A and B has OTR permeability of 1 and 0.01 (barrer) respectively, the layered morphology always shows better barrier property than miscible blend morphology for a given composition. This gives a reason why people generally prefer layer structure for barrier applications regardless of the cost and complexity.

![Figure 2](image2.png)

**Figure 2.** Different morphologies of polymer blends.

Based on Fig. 2, it is clear that when polymer blends have different morphologies, they can yield distinctive barrier properties. It is well known that polymer blends can form various morphologies as a result of different
compositions and process techniques [8-15], and therefore are suitable for different applications. For a polymer blend film, under certain conditions, a layer-like morphology can be achieved. This means polymer domains are extended to their maximum degree. In this case, a polymer blend shows characteristics of a multilayered film, which could be beneficial for gas barrier applications.

A specially prepared LLDPE and EVOH blend with specific composition and good dispersion but without any compatibilizer was first prepared and studied. Due to the reasonable compatibility and proper immiscibility between LLDPE and EVOH, extended and layer-like morphology appears after this pre-compound resin is extruded to fabricate thin films. Because of the morphology, the extruded thin film shows good barrier properties following the series model calculation. Given the barrier property, the blend of LLDPE-EVOH can be possibly used to replace multilayered structure or reduce the number of layers in a multilayer film. The LLDPE domains behave similar to moisture barrier layers, which are protecting EVOH from affecting from moisture. Moreover, the LLDPE domains in the blend film also provide us with enough adhesion to some other polymers. Thus, three-layer films without tie-layers are successfully fabricated.

The LLDPE-EVOH blend was named as EXP BAR2400 available in A. Schulman’s portfolio. Based on these fundamental findings, a series of materials containing similar internal multilayer-like morphology as EXP BAR2400 were developed as well. With the balance of excellent oxygen barrier and good WVTR (water vapor transport rate) barrier, these EXP BAR materials are expected to be suitable for food packaging applications.

**Materials and Experiments**

Linear low density polyethylene (LLDPE,) and Ethylene vinyl alcohol (EVOH with 44% of ethylene) were used to fabricate EXP BAR2400. Resin and sample information is listed in Table 1.

Generic names were used throughout this paper to label samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>ASI internal name</th>
<th>T₁/₅°C</th>
<th>T₂/₅°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>LLDPE</td>
<td>LLDPE</td>
<td>124</td>
<td>115</td>
</tr>
<tr>
<td>EVOH</td>
<td>EVOH</td>
<td>159</td>
<td>140</td>
</tr>
<tr>
<td>B24</td>
<td>EXP BAR2400</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Compound of LLDPE and EVOH</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B25</td>
<td>EXP BAR2500</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>PE cast film</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B26</td>
<td>EXP BAR2600</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>PE blown film</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

All compound resins were prepared by a twin-screw extrusion system at A. Schulman Inc., Akron, OH, USA. Sample B24 from the table was first investigated.

Before extrusion process, B24 resin was dried in a vacuum oven for overnight at 80 °C. A single-screw cast film line was utilized to fabricate monolayer thin films with final film thickness of ~25 µm. The process is demonstrated in a diagram shown in Figure 3.

The same 3-layer cast film line was also employed to fabricate 3-layer films with sample B24 in the core.

Figure 3. Melt process for sample B24.

Figure 4. Melt process for making 3-layer film containing B24 in the core.

Atomic force microscopy (AFM) was employed to investigate the morphology of the extruded thin films. Small pieces of specimen were embedded in epoxy (5 Minute Epoxy, Devcon, Rivera Beach, FL) and cured for 24 hours at room temperature. Cross sections were prepared by microtoming at both extrusion direction (ED) and transverse direction (TD) after cooling the samples to -120 °C in liquid
As a result of layer-like morphology, good barrier property is expected for B24 extruded thin film. The OTR barrier data is listed in Table 2.

### Table 2. Oxygen permeability for films.

<table>
<thead>
<tr>
<th>Extruded blend film</th>
<th>P O2/ Barrer</th>
<th>P O2/ Barrer based on blends model</th>
<th>Improve ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>LLDPE control</td>
<td>3.7±0.1</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>EVOH control</td>
<td>0.0015±0.0001</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>B24</td>
<td>0.0034±0.0001</td>
<td>0.07</td>
<td>21</td>
</tr>
<tr>
<td>33-layer LLDPE-EVOH multilayer film</td>
<td>0.0030±0.0001</td>
<td>/</td>
<td>/</td>
</tr>
</tbody>
</table>

\[
\ln P_{blend} = \phi_1 \ln P_1 + \phi_2 \ln P_2 \tag{1}
\]

\[
\frac{1}{P_{Film}} = \frac{\phi_1}{P_1} + \frac{\phi_2}{P_2} \tag{2}
\]

Where \( P_1 \) and \( P_2 \) are the oxygen permeability of LLDPE control and EVOH control respectively; \( \phi_1 \) and \( \phi_2 \) are the volume fraction of LLDPE control and EVOH control respectively. Equation (1) is miscible blend model. Equation (2) is series model that is used to predict permeability for layered films.

B24 shows good OTR barrier, which is in the same scale of EVOH control. The improve ratio is 21 times when compared to the miscible blend model (the improve ratio is: calculated value/measured value). Obviously, although B24 is a compound product, it actually shows oxygen permeability close to multilayered film, which agrees with series model. This morphology is very meaningful, as it offers an opportunity for those who would like to enter the barrier application but without a capability of producing more than 3 layers.

B24’s OTR performance is also studied under different RHs, which is shown in Fig. 6.

![AFM images of partial cross section of extruded B24 and 33-layer multilayer film of LLDPE and EVOH](image)

**Figure 5.** AFM images of partial cross section of extruded B24 (left) and 33-layer multilayer film of LLDPE and EVOH (right).

**Figure 6.** OTR of extruded B24 under different RHs.
When RHs increases, B24’s oxygen permeability also increases. This is because EVOH phase is still more or less affected by moisture. However, compared to EVOH control, the water sensitivity has been reduced [2]. This is again because LLDPE domains are protecting EVOH domains.

\[
\text{Capillary Rheology}
\]

![Capillary Rheology](image)

**Figure 7.** Capillary rheology result of B24 at 210 °C.

The viscosity of B24 is comparable to a homopolypropylene with MFI of 3.0. This suggests B24 can be easily co-extruded with many other polymers.

### Three - layer structure of B24.

B24 is proved to have layer-like morphology and can yield good gas barrier properties. In order to practically use this material for packaging applications, 3-layer structures with different PE skins have been fabricated as well. The skin layers are expected to further protect B24 and provide us with other functions, like printability, sealability et al. The 3-layer structures are illustrated below:

![3-layer structure of B24](image)

**Figure 8.** B24 with 3 types of PE skins.

All three films have shown decent adhesions between layers, which can be felt by peeling layers manually. Oxygen and water vapor permeability were then tested for the 3-layer films.

**Table 3. Permeability of BAR2400 in 3-layer structures.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>WVTR (g.mil/100cn2.day)</td>
<td>1.58 ± 0.07</td>
<td>1.35 ± 0.06</td>
<td>0.70 ± 0.01</td>
</tr>
<tr>
<td>O2 (0% RH) Barrer</td>
<td>TBD</td>
<td>0.0041</td>
<td>0.0041</td>
</tr>
<tr>
<td>O2 (50% RH) Barrer</td>
<td>TBD</td>
<td>0.0026</td>
<td>0.0019</td>
</tr>
</tbody>
</table>

Based on the data from Table 3, it appears that with HDPE skins, the 3-layer film yields the best moisture barrier, while it still keeps very good oxygen barrier.

Besides the barrier property, haze of these three films are also investigated under the standard of ASTM D1003.

**Table 4. Haze of BAR2400 in 3-layer structures.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Haze %</td>
<td>4.9 ± 0.5</td>
<td>9.2 ± 0.2</td>
<td>25.7 ± 1.2</td>
</tr>
</tbody>
</table>

As expected, HDPE skin increases the overall haze of 3-layer film.

### Other BAR materials.

While LLDPE is not the best material for WVTR barrier application, sample B25 and sample B26 were developed accordingly with enhanced WVTR barrier. B25 and B26 were designed based on the fundamental findings of B24, but are targeted for different processing. B25 is appropriate for cast extrusion, and B26 is good for blown extrusion.

![Comparison of oxygen barrier for BAR series materials](image)

**Figure 9.** Comparison of oxygen barrier for BAR series materials. (All samples are cast films, except B26 is blown film)

In terms of oxygen permeability, B24, B25 and B26 films are all comparable to EVOH (44% ethylene grade) and Barex resin. As the RH increases from 0% to 90%, oxygen permeability does not increase dramatically. This suggests that oxygen barrier performance remains at higher RHs for BAR series materials, especially for sample B25 and B26.
More interestingly, when looking at WVTR barrier performance, B24, B25 and B26 all have shown lower permeability than EVOH and Barex resins. Especially, B25 and B26 have shown comparable WVTR barrier performance as HDPE barrier resins.

Data from Fig. 9 and Fig. 10 suggest that B24, B25 and B26 yield both excellent oxygen barrier property as well as WVTR barrier property, which is not always true for all barrier resin. This is again because all samples yield multilayer morphology. While the higher WVTR barrier phase offers the moisture barrier, EVOH phase is supplying the oxygen barrier. B26’s morphology is checked by AFM as well, since it was blown extruded, which is different from B24 and B25.

Both B25 and B26 show moderate haze values and relatively low gloss values. Their light transmission rate is typically higher than 90% for most of the visible light wavelength range.

Conclusions

Extruded blend films sample B24 are successfully fabricated. Due to the good dispersion and appropriate processing, elongated and layer-like morphology is observed. This layer-like morphology enables B24 to yield similar barrier properties as actual multilayered films. LLDPE domains within B24 provide protection for EVOH from moisture as well as adhesion between skin layers. Therefore, B24 can be easily embedded in a 3-layer structure.

Besides B24, based on the same principles, B25 and B26 with enhanced WVTR barrier properties were also developed. Balanced with both good oxygen and WVTR barrier, these materials are suitable for packaging applications. This technique offers an opportunity for those who would like to enter the barrier applications but without a capability of producing more than 3 layers. At the same time, due to the barrier properties and processability, BAR series materials can also be used in 5-layer or 9-layer structures.

References