Modifying LDPE For Improved Adhesion To Aluminum Foil

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ABSTRACT

A modifier was developed to enhance the adhesion of LDPE to aluminum foil in extrusion coating/lamination. Statistically designed experiments identified four factors that most influence the adhesion: % of modifier blended with LDPE, temperature, thickness and time in the air gap. The results show that the modifier offers several benefits to flexible packaging applications, including greater consistency in meeting adhesion specifications and the ability to run at faster line speed or at lower temperatures without sacrificing adhesion. These are demonstrated using statistical modeling and analysis.

INTRODUCTION

Aluminum foil (Al) is often used in food packaging for its moisture and oxygen barrier properties. Because of its poor flex crack resistance, inability to form a hermetic seal and cost, it is typically combined with other materials such as paper, OPET, OPP and PE. Some common structures include:

- Paper/LDPE/Al/LDPE
- OPP/primer/LDPE/Al/LDPE
- OPET/primer/LDPE/Al/LDPE.

Here the paper, OPP or OPET provide stiffness and a surface for printing. The first LDPE layer imparts adhesion to the foil, and the second acts as the sealing layer. Applications include many dry food packages such as powdered drink mix pouches.

Extrusion coating/lamination processes are used commercially to assemble these structures. LDPE is the most commonly used resin for bonding to aluminum foil. It processes well and is low in cost. About 900 million pounds of LDPE are used by the extrusion coating industry in the U. S. each year.

LDPE, however, has several deficiencies. Because it is nonpolar, it does not naturally bond to the basic groups on the aluminum surface. High processing temperatures are required to partially oxidize the surface of the LDPE, creating acid, aldehydes and ketones. These species then provide adhesion to the foil. This mechanism only provides moderate levels of adhesion that are often inconsistent. Furthermore, the polar species formed during oxidation cause odor and taste issues in some applications. High temperatures can also create excessive smoking, gel formation and other problems. Considerable time in the air gap is required for oxidation to take place, putting limitations on line speed.

Options to improve the performance of LDPE include the use of ozone treatment, primers and acid copolymers. Ozone treatment helps create polar species at a lower temperature, but it still has many of the same drawbacks as LDPE alone. Primers add cost and possible environmental issues to the lamination process. Acid copolymer resins (ACRs) are copolymers of ethylene and acrylic or methacrylic acid. The acid groups provide adhesion to the basic aluminum oxides on the foil surface without the need for oxidation and the limitations associated with LDPE. ACRs provide strong durable bonds and have been widely adopted in demanding applications such as structures for orange juice, toothpaste and condiments. They, however, are overengineered for some applications.

The goal of the present work is to develop an adhesion enhancing (AE) modifier for LDPE that can be pellet blended with LDPE during the extrusion coating/lamination process to modestly improve its adhesion to aluminum foil. The cost and performance of the modifier system will fall between that of LDPE and acid copolymers.

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1 For a review of LDPE adhesion mechanisms see reference 1.
EXPERIMENTAL

All of the experiments except the converter trial were carried out on an Egan Davis Standard extrusion coating line with an ERWEPA feed block and Cloeren edge bead reduction die. We coated 50-µm foil with either a coex coating or monolayer coating. The extruders were 63 and 113 mm in diameter. The resins tested are given in Table I. Blends of the AE modifier with LDPE were made by mixing the pellets just prior to feeding them into the hopper of the extruder.

<table>
<thead>
<tr>
<th>Resin</th>
<th>Characteristics</th>
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<tbody>
<tr>
<td>LDPE</td>
<td>7 MI, 0.918 g/cc</td>
</tr>
<tr>
<td>ACR1</td>
<td>Acid copolymer with 14 MI, 12% acid</td>
</tr>
<tr>
<td>ACR2</td>
<td>Acid copolymer with 11 MI, 4% acid</td>
</tr>
<tr>
<td>AE</td>
<td>Adhesion enhancing modifier</td>
</tr>
</tbody>
</table>

Adhesion was measured by cutting 25-mm wide strips in the machine direction near the center of the web. Each strip was separated at the coating/foil interface. The force required to pull the specimen apart in a “T-peel” configuration at 300 mm/min was measured using a tensile tester. The average of five specimens was recorded as the peel strength. Green and one-week measurements were made.

MODIFIER TECHNOLOGY

Our approach for developing an adhesion modifier was to add acid functionality to the LDPE. We began by blending standard grades of ACRs with LDPE. An example is shown in Figure 1. Here ACR1 is blended with LDPE with no affect on adhesion. We hypothesize that this may be due to the incompatibility of the ACR with LDPE. Blends of incompatible polymers typically result in separate phases or domains, with the minor phase being discontinuous. The nonuniform distribution of the ACR molecules within the LDPE matrix may not favor acid groups forming at the foil boundary where they are needed for adhesion. Poor compatibility may also result in a weak cohesive strength between the ACR and LDPE phases resulting in low peel strength. To test the hypothesis, we created several special grades of ACR, blended them with LDPE (20% ACR and 80% LDPE) and tested their adhesion to Al during coating. We also prepared blown film from 50-50 blends with LDPE and measured the haze. While not an ideal test, the haze should roughly correlate with compatibility. Better compatibility results in smaller ACR domains within the LDPE matrix. Smaller domains generally refract less light. Figure 2 shows that higher adhesion to foil correlates with lower haze.

The performance of our optimized formulation, designated AE, is shown in Figure 3. It clearly gives adhesion to aluminum foil that is between LDPE and standard acid copolymers.

The performance of the blend varies significantly with processing conditions. In order to quantify the affect of these conditions, we conducted a statistically designed experiment. Preliminary tests narrowed the variables to four, which we varied over the following ranges:

- % AE modifier in blend (0 to 20%)
- Processing temperature (293 – 327°C)
- Thickness of coating (20 – 45 µm)
- Time in the air gap (60 to 100 ms)

We used a quadratic response surface model to design and analyze the experiment. The structure was 50-µm Al/Resin Blend. Time in the air gap (TIAG) was computed by dividing the air gap by the line speed (2). The air gap was kept at a constant 152-mm throughout the trial, and the line speed varied from 91 to 152 m/min to achieve the TIAG range.

The results of the analysis are shown graphically in Figures 4 to 6. In the figures, the interaction between the four variables is examined two variables at a time, keeping the values of the other variables fixed at the midpoint of the range we studied. The results are computer projections based on the statistical model of the data.
All four variables were found to be statistically significant. Peel strength increases with increasing level of AE modifier in the blend, increasing temperature, increasing thickness and increasing time in the air gap. The effect of temperature and TIAG are similar to that found with LDPE, suggesting an oxidation or stress mechanism (1). The effect of thickness is not as well understood.

**BENEFITS**

Modifying LDPE has several advantages. By adding only a minor amount of the AE modifier (20%), the processing characteristics of LDPE remain unchanged. The addition of the AE modifier improves the adhesion performance at a given set of process conditions. This improves the reliability allowing the converter to more consistently meet adhesion specifications. The higher adhesion may also allow greater productivity or lower temperatures without sacrificing adhesion performance.

An example of how the addition of AE may improve productivity is given in Figure 7. We have mapped the results of the statistically designed experiment on a contour plot. Such a plot is similar to a topographical map where each line represents a line of constant elevation. Here each line represents a constant region of peel strength. Moving along the line is like walking along a ridge on a topographical map. Moving perpendicular to the line is like walking up or down a hill. The closer the lines are together, the steeper the hill.

If we start in the lower left corner, we see that by running at 90 m/min with LDPE we will achieve 450 g/25mm of peel strength. Increasing the line speed to 150 m/min reduces the peel strength to 380 g/10min (lower right corner). By adding 20% AE, we can increase the line speed to 150 m/min and improve the adhesion to 580 g/25mm (upper right corner).

Figure 8 shows how the addition of the AE modifier may allow the processing temperature to be lowered without sacrificing adhesion. Lower temperatures should improve odor/taste issues and reduce problems associated with smoke and gel formation. Begin in the lower right corner. The peel strength for 100% LDPE at 325°C is 450 g/25mm. By moving along the 450 g/25mm contour line, we end up in the upper left corner; the model predicts that adding 20% AE modifier will allow the temperature to be reduced to 293°C while maintaining adhesion.

We used Six Sigma methodologies to demonstrate improved reliability at a converter. The converter produces a standard foil laminate for a dry food application. They were having difficulty meeting their adhesion specification of 250 g/25mm with LDPE. In Six Sigma parlance, we define a project “Y” as the peel strength to foil. This is the critical-to-quality dependent variable we wish to improve. The unit of measurement was the peel strength, using an average of 3 measurements per production lot. A defect occurs when the peel strength drops below 250 g/25mm.

Control charts for three conditions are shown in Figure 9. The top chart shows the existing situation using LDPE alone. None of the 16 production lots charted here met the 250 g/25mm specification. Indeed, the summary statistics in Table II show that the yield is only 4% or there are 960,000 defects per million opportunities (DPMO).

The middle chart shows the case of adding 20% AE to the LDPE, keeping the line speed and temperature constant. The mean peel strength increases from 166 to 308 g/25mm. Except for one data point (lot 14), all the results meet the 250 g/25mm specification. The poor adhesion with lot 14 was found to be due to special causes – poor foil quality. The summary statistics show that by adding 20% AE, the yield increases from 4% to 86% (139,000 defects per million opportunities).

The lower chart shows the case for adding 20% AE as well as increasing the temperature by 5°C. Now the mean is 384 g/25mm, yield 99.6% and defects only 4400 per million opportunities. The process reliability has been improved by four sigma.
Table II: Summary Statistics for Converter Trial

<table>
<thead>
<tr>
<th>Resin</th>
<th>Temperature deg C</th>
<th>Mean</th>
<th>Stdev</th>
<th>Yield*</th>
<th>DPMO</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDPE</td>
<td>325</td>
<td>166</td>
<td>30</td>
<td>4%</td>
<td>963,400</td>
</tr>
<tr>
<td>20% AE, 80% LDPE</td>
<td>325</td>
<td>308</td>
<td>43</td>
<td>86%</td>
<td>139,000</td>
</tr>
<tr>
<td>20% AE, 80% LDPE</td>
<td>330</td>
<td>384</td>
<td>37</td>
<td>99.6%</td>
<td>4,400</td>
</tr>
</tbody>
</table>

* Specification of 250 g/25mm or higher

CONCLUSIONS

We have found that an appropriately designed modifier can significantly improve the adhesion of LDPE to foil in extrusion coating/lamination applications. Modifier AE was developed to be compatible with LDPE while providing functional groups to bond to the foil. A blend of AE and LDPE gives adhesion values between that of LDPE alone and standard acid copolymer resins.

Statistically designed experiments are useful for mapping the effects of processing variables on adhesion performance. The performance of the AE modifier was found to increase with increasing levels of AE in the blend, temperature, thickness and time in the air gap. Benefits of the AE modifier include improved reliability and the potential to run at higher line speed or lower processing temperatures. Statistical analysis and modeling were found to be useful in demonstrating these benefits.

REFERENCES


KEY WORDS

Adhesion, peel strength, foil, extrusion lamination, extrusion coating

Figure 1: Adhesion of Blend of Standard ACR with LDPE

Figure 2: Green Peel Strength to Foil of Blends of Modifiers with LDPE (20% modifier, 80% LDPE) vs Film Haze of 50-50 Blends of Same Modifier With LDPE
Figure 3: Performance of Optimized Composition (AE) Compared to LDPE and ACR Controls

Extrusion Coating Results
50-µm Al / (8-µm blend - 38-µm LDPE)
320 C, 244 m/min line speed, 127 mm air gap

Figure 5: Model Results from Statistically Designed Experiment Showing Effect of % Modifier (AE) and Time In the Air Gap (TIAG)

Figure 4: Model Results from Statistically Designed Experiment Showing Effect of % Modifier (AE) and Processing Temperature

Figure 6: Model Results from Statistically Designed Experiment Showing effect of % modifier (AE) and thickness of coating.
Figure 7: Contour Plot Showing How Adding the AE Modifier Can Improve Productivity (Line Speed) Without Sacrificing Adhesion. Plot Generated from Model of Statistically Designed Experiment.

Figure 8: Contour Plot Showing How Adding AE Modifier Can Allow Lower Processing Temperatures While Maintaining Adhesion. Plot Generated from Model of Statistically Designed Experiment.

Figure 9: Control Charts from Converter Trial. Each Subgroup Represents One Lot of Product (Average of 3 Peel Strength Measurements).

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