Improving adhesion between low-density polyethylene and aluminum foil

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Adhesion between low-density polyethylene and aluminum foil increases with increasing extrusion temperature.

Low-density polyethylene (LDPE) is widely used both as a tie layer and as a sealant layer in flexible packaging structures containing aluminum foil. Adhesion between LDPE and aluminum foil is affected by many factors, including extrusion-coating conditions, the properties of the polymer substrate, and the surface characteristics of the aluminum foil.

In a previous study (*1*), extrusion-coating parameters were varied in an effort to determine the process conditions for optimum adhesion between LDPE and foil. It was found that the resin's adhesion to aluminum increased with increasing thermal oxidation of the polymer during extrusion. The increase in oxidation of the polymer surface promotes formation of the polar groups essential for chemical adhesion between LDPE and foil. Chemical adhesion at the polymer–foil interface can be related to the acid-base interactions occurring between the two materials. Consider, for example, ethylene acrylic acid (EAA) copolymers, whose adhesive strength increases with increasing percent acrylic acid content. Adhesive strength is further enhanced when the number of basic sites on the foil surface is large (*2, 3*).

In this article, we examine the effects of acid-base interactions on polymer adhesion to aluminum foil. The acid and base functionalities of LDPE resins and aluminum foils were measured using flow microcalorimetry (FMC). Results obtained via FMC were then related to the strength of adhesion between the polymer and foil interfaces.

Materials and methods

Two aluminum foils were used, Foils A and B. The wettability of the foils was determined using standard wetting solutions, with Foil A being more wettable than Foil B.

The nominal melt index and density values of the LDPE resins included in the study are listed in **Table I**. Both are commercially available extrusion-coating resins.

I. Resin properties

	Density, g/cm³	Melt index, g/10 min
$LDPE_1$	0.917	8.0
$LDPE_2$	0.918	7.0

Aluminum adhesion was tested on extrusion-coated samples. A 1.0-mil coating thickness was applied to an aluminum foil slip sheet (50-lb kraft paper/0.5-mil LDPE/ 0.0005 in. foil) using a laboratory extrusion coater at 85 rpm and a line speed of 444 ft/min. A 6-in. air gap was maintained throughout all experiments. Aluminum adhesion was tested according to ASTM F-904-84 on an Instron tensile tester. The 1-in. (25 mm) wide strips were pulled using a 90° "T" peel with a crosshead speed of 10 in./min. Three samples for each resin were tested and averaged. All adhesion values reported here were measured six days after fabrication.

The acidic and basic sites on the foil and resins were quantified using a flow microcalorimeter (Model 3A) manufactured by Microscal. This is an extremely sensitive instrument capable of detecting energy changes of 1 μJ and temperature changes as little as 10^{-5}°C. However, the sample chamber is extremely small and can accommodate only small sample volumes. To compensate for this, it was necessary to maximize the surface area of the samples. Extrusion-coated films, delaminated from the foil surface, did not provide adequate surface area. Surface area was maximized by fabricating LDPE resins into fibers using melt temperatures identical to those used for extrusion coating. Duplicating the coating temperature for the fabrication of the fibers is believed to be representative of the oxidation the polymer undergoes during the extrusion-coating process.

Aluminum foil samples were cut into strips (1 mm) and wound onto the fiber spool. Microsyringe pumps were used

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to deliver solvent (cyclohexane) to the sample. After equilibrium had been established, the flow stream was switched from pure solvent to a 25m*M* solution containing probe molecules for detecting acidic or basic sites. A pyridine (basic) probe was used to detect acidic sites, and a phenol (acidic) probe was used for basic sites. The heat of interaction (adsorption) between the probe solution and the chemically active sites on the sample surface was monitored by sensitive thermistors in the calorimeter cell. The flow was again switched back to pure solvent after equilibrium had been re-established. The heat removed (desorption) was also monitored by the thermistors. The algebraic sum of the heats of adsorption and desorption is taken as the heat of chemisorption. The heat of chemisorption is a measure of the strength of acidic or basic surface sites.

Results

The reproducibility of the FMC technique for LDPE fibers was evaluated. Two separate runs were performed on $LDPE_2$ samples fabricated at 288°C. The results for the pyridine probe are listed in **Table II**. The chemisorption values vary by 12%.

The values reported for LDPE fibers are very low in relation to functionalized polymers such as EAA copolymers. Fibers of EAA give chemisorption values for pyridine that are approximately 20 times higher than the LDPE values listed in Table II. The results for the phenol probe (basic sites) indicated that the concentration of basic surface sites on the LDPE fibers was at the lower detection limit of the instrument. The work presented here focuses on the acid functionality of the LDPE polymers studied.

Extrusion-coating temperatures for $LDPE_1$ were varied from 288°C to 315°C. The adhesion values in **Fig. 1** show increasing adhesive strength with aluminum at higher fabrication temperatures.

The relative surface chemistry of the films was obtained using fibers fabricated at 288°C and 315°C. The FMC results are listed in **Table III**. The heat of chemisorption for the acidic sites (pyridine probe) appears to increase with the higher fabrication temperature and corresponds to the higher adhesive strengths seen in Fig. 1. The FMC results in Table III suggest that the increased adhesion is due to increased surface acidity.

The surface chemistry of two aluminum foils was characterized using FMC, and the results are shown in **Table IV**. Both foil surfaces contain acidic and basic sites, with Foil B containing more acidic sites, as indicated by the high heat of chemisorption for the pyridine probe.

The basicity of a foil is usually a good indication of the foil's affinity for a polymer containing adequate acid functionality (*2*). The heat of adsorption for the phenol probe on Foil A indicates that this foil should have the highest affinity for polymers with acid functionality. However, both foils gave positive heats of chemisorption for the phenol. Positive values could indicate that other species (surface contaminants or oils on the foil surface) were removed in addition to the probe.

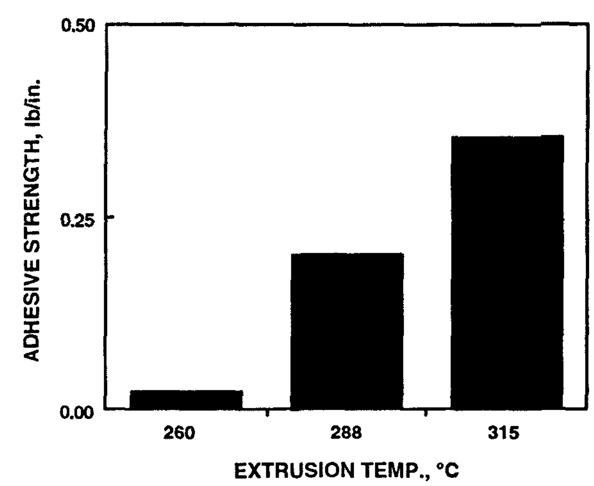
The adhesive strengths between each of these foils and $LDPE_1$ and $LDPE_2$ are presented in **Fig. 2**. For both resins, adhesive strength increased dramatically with Foil

II. Reproducibility of FMC results (pyridine probe for acidic sites) for $LDPE_2$ fibers*

	Heat transfer, mJ/g		
	Adsorption	*Desorption*	*Chemisorption (adsorption + desorption)*
Run 1	-267	82	-185
Run 2	-291	128	-163

*Fibers fabricated at 288°C.

1. Effect of extrusion temperature on LDPE adhesion to foil



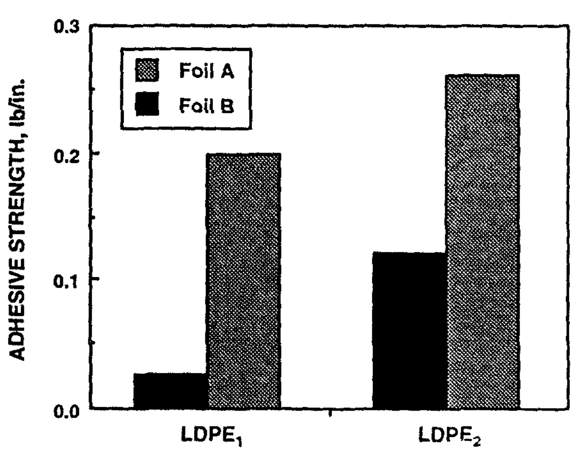
III. FMC results (pyridine probe for acidic sites) for $LDPE_1$ fibers fabricated at 288°C and 315°C

	Heat transfer, mJ/g		
	Adsorption	*Desorption*	*Chemisorption (adsorption + desorption)*
288°C	-353	209	-144
315°C	-198	33	-165

IV. FMC results for Foils A and B

	Heat transfer, mJ/g		
	Adsorption	*Desorption*	*Chemisorption (adsorption + desorption)*
	Pyridine probe for acidic sites		
Foil A	-1988	457	-1531
Foil B	-2940	309	-2631
	Phenol probe for basic sites		
Foil A	-696	2337	1641
Foil B	-281	385	104

2. Adhesion of $LDPE_1$ and $LDPE_2$ to Foils A and B



V. FMC results (pyridine probe for acidic sites) for $LDPE_1$ and $LDPE_2$ fibers*

	Heat transfer, mJ/g		
	Adsorption	*Desorption*	*Chemisorption (adsorption + desorption)*
$LDPE_1$	-353	209	-144
$LDPE_2$	-267	82	-185

*Fibers fabricated at 288°C.

A. This increase corresponds to the higher surface basicity of Foil A, as seen in Table IV.

The heats of pyridine chemisorption for $LDPE_1$ and $LDPE_2$ are presented in **Table V**. The higher heat of chemisorption for $LDPE_2$ indicates greater acid functionality. This corresponds to the results in Fig. 2, which showed that $LDPE_2$ had higher adhesion than $LDPE_1$ on both Foils A and B.

Conclusion

Adhesion between LDPE and aluminum foil increases with increasing extrusion-coating temperature. The results presented here suggest that superior adhesion is a function of the heightened formation of acidic sites on the polymer surface at elevated temperatures. With a greater number of acidic sites on the polymer surface, there is a greater opportunity for interaction with the basic surface sites on the foil.

A foil with high surface basicity should increase the adhesive strength of a given LDPE. Conversely, an LDPE resin with a greater number of acidic sites on its surface will provide a bond of greater adhesive strength with a given foil, regardless of the foil's surface basicity.□

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