Ethylene acrylic acid–polybutylene blends for packaging applications

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ABSTRACT: Blends of polybutylene (PB) with two ethylene acrylic acid (EAA) copolymers and one low-density polyethylene were extrusion-coated onto a foil-based substrate. Coated samples also were heat sealed to a variety of plastic substrates. The EAA/PB blends demonstrated a good balance of hot-tack and adhesive properties while exhibiting peelable seal characteristics. Potential applications of this technology are for snack food packaging, medical device packaging, and lidding-stock applications.

KEYWORDS: Acrylic acid copolymers, ethylene, extrusion coating, foil, low density polyethylene, mixtures, packaging, polybutylene, substrates.

The objective of this study was to develop blend technology for controlled peel strength utilizing ethylene acrylic acid (EAA) copolymers and polybutylene (PB). This technology was examined for its suitability in peelable seal applications (including both face-to-face peels and peelable adhesion to various substrates). The study focused on structures that could be produced via the extrusion coating process.

Introduction

EAA copolymers are produced by the copolymerization of ethylene and acrylic acid to form a polyolefin with carboxyl groups randomly distributed along the backbone. The carboxyl groups disrupt crystallinity and also provide a site for hydrogen bonding between molecules. The resulting intermolecular attractions produce a copolymer with toughness, tear resistance, melt strength, good hot tack, good adhesion to polar substrates such as aluminum foil, and an ability to seal at low temperatures. The unique properties of these resins allow them to be utilized as tie layers and as high-performance sealant layers in packaging applications. Because of their high heat-seal strengths, these polymers alone would not yield peelable seals (*1*).

The PB resin utilized in this study was a semi-crystalline polyolefin thermoplastic based on a poly (1-butene) homopolymer (*2*). These resins are advertised as being utilized in hot-melt adhesives, carpet backing, vessels and liners, as well as blend components for peelable seals in packaging applications.

When blended together, these two polymers form an incompatible mixture which, when used as a seal layer, will result in controlled failure of the seals. The formulation provides easily opened or "peelable" seals and allows the seal strength to be tailored for a variety of end uses. Markets in which this technology would apply are snack food packaging (cereal and cake mix box liners, snack packages, and cracker tubes) and lidding stock for yogurts and puddings, as well as for thermoform fill/seal medical device packaging.

The definition of a peelable seal varies. According to Hwo (*3, 4*), seal strengths for easy-open packaging can range from 4 N/25 mm to as high as 45 N/25 mm (1–10 lb/in.) for snack packages and from 11 N/25 mm to 22 N/25 mm (2.5–5.0 lb/in.) for lidding applications. The most common face-to-face seal-strength range for snack packaging is 9 N/25 mm to 18 N/25 mm (2–4 lb/in.).

Experimental

Variables monitored during the study were sealant thickness, sealant type, blend ratios, and seal temperature.

Preparation of blends and coatings from blends

Dry blends were composed of EAA or low-density polyethylene (LDPE) and PB ranging from 75 wt% to 100 wt% EAA or LDPE and from 0 to 25 wt% PB (**Table I**).

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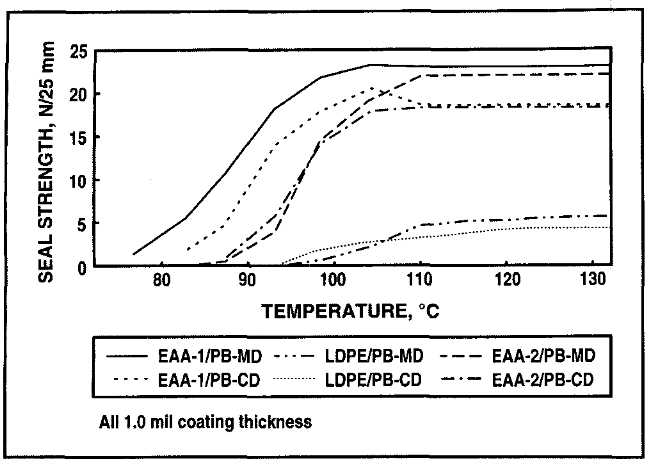
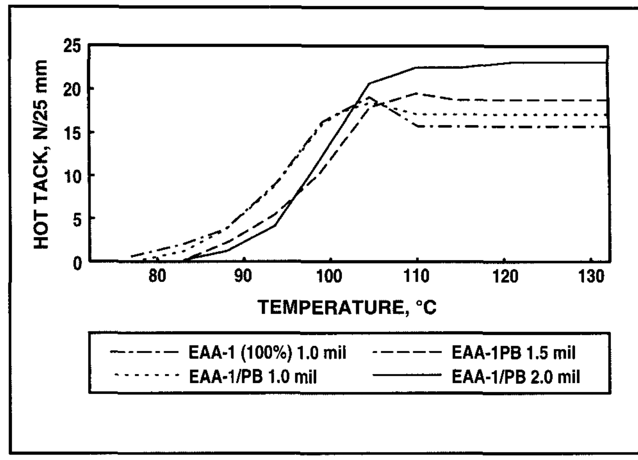
1. Average heat-seal strengths comparing machine and cross-direction seals for polybutylene blends



2. Average hot-tack values for EAA/PB blends coated onto aluminum foil at varying thicknesses. All blends are 80% EAA-1 and 20% PB.



The acrylic acid content of the polymers utilized as the major blend components were 0 wt% acrylic acid for the low-density polyethylene and 6.5 wt% and 9.5 wt% acrylic acid for the two ethylene acrylic acid copolymers. Melt index was constant at approximately 5 dg/min. All three polymers were manufactured by Dow Chemical Co. The fractional melt index polybutylene homopolymer (PB) was obtained from Shell Chemical Co.

Coatings were prepared on a Black Clawson extrusion coater (3.5-in. screw, 32:1 L/D), run at a screw rate of 85 rpm (250 lb/h output rate) and at various line speeds to yield coatings of 1.0-mil, 1.5-mil, and 2.0-mil thicknesses. Samples of a paper/poly/foil (p/p/f) structure were slip-sheeted, foil-side up, and submitted for aluminum adhesion testing and for determining hot-tack and heat-seal ranges. The p/p/f samples were also used to determine seal strengths to various "base cup" plastics.

Face-to-face seals

Aluminum adhesion values were determined by pulling the coating from the p/p/f substrate, slit in 25-mm-wide strips in the machine direction, on an Instron tensile tester at 254 mm (10 in.)/min crosshead speed in a "T-peel" configuration.

To determine heat seal, 25-mm-wide strips cut in both the machine and the cross-machine directions were mounted on a DTC hot-tack tester. A dwell time of 0.5 s at 276 kPa (40 psi) was used to seal the samples. The samples were stored at American Society for Testing and Materials conditions (22.2°C, 50% RH) for 24 h, and the heat-seal force was then determined by the use of an Instron tensile tester set at 51 mm (2 in.)/min crosshead speed.

Hot-tack values were obtained by mounting 25-mm-wide strips, slit in the machine direction, on a DTC hot-tack tester. A dwell time of 0.5 s at 276 kPa and a delay time of 0.1 s with a 150 mm/s pull rate were used.

Heat-seal strengths of coated foil to base-cup resins

The foil-coated samples were heat sealed to various plastics, in film and plaque form, at a seal temperature of 166°C, dwell time of 3.0 s, and seal-bar pressure of 276 kPa. The plastics tested are listed in **Table II**.

Discussion

Heat-seal strengths and hot-tack strengths of the coatings were obtained from the experiments. As defined in the introduction, a face-to-face heat-seal value of 9–18 N/25 mm is desirable for an easy-open peel. The standard deviation for heat-seal testing was approximately 2.2 N/25 mm (0.5 lb/in.). Good hot-tack values and adhesion to the coated substrate are

I. Blends and coatings studied

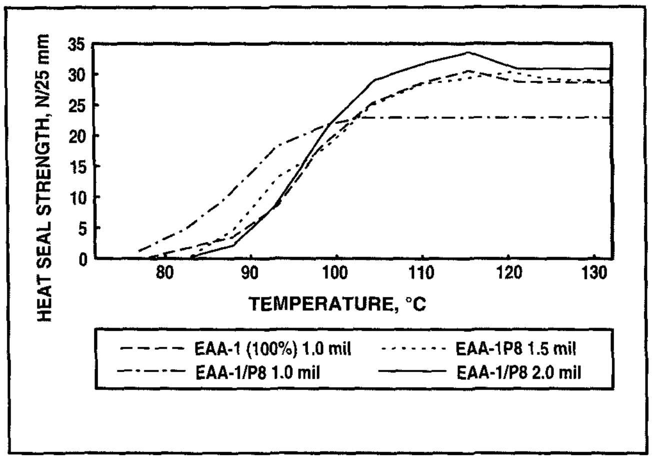
	Coatings	
Blends	*Blend, %*	*Thickness, mils*
EAA-1/PB	80/20	1.0
EAA-1/PB	80/20	1.5
EAA-1/PB	80/20	2.0
EAA-1/PB	75/25	1.0
EAA-1/PB	85/15	1.0
EAA-1	100	1.0
EAA-2/PB	80/20	1.0
LDPE/PB	80/20	1.0

EAA-1 (5.0 dg/min MI, 9.5 wt% AA), ethylene acrylic acid copolymer
EAA-2 (5.5 dg/min MI, 6.5 wt% AA), ethylene acrylic acid copolymer
LDPE (5.5 dg/min MI, 0.916 g/cc), low density polyethylene
PB (0.4 dg/min MI, 0.915 g/cc), polybutylene homopolymer

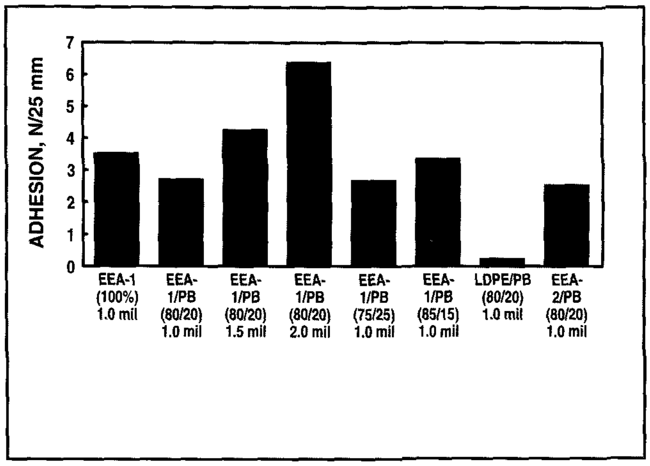
II. Plastics tested with foil-coated samples

Base cup material	*Form*
Polypropylene (PP)	Plaque
Acrylonitrile butadiene-styrene (ABS)	Plaque
Polyvinylchloride (PVC)	Plaque
High density polyethylene (HDPE)	Plaque
Polystyrene (PS)	Plaque
Polyester (PET)	Film
Polycarbonate (PC)	Film

3. Average heat-seal strength for EAA/PB blends coated onto aluminum foil at varying thicknesses. All blends are 80% EAA-1 and 20% PB pulled in the machine direction.



4. Average adhesion of polybutylene blends to aluminum foil



also desirable. Standard deviation for hot-tack testing was approximately 1.0 N/25 mm. The temperature at which a hot-tack value of 9 N/25 mm was obtained was defined as the hot-tack initiation temperature. Low initiation temperatures for the heat-seal and hot-tack ranges are indicative of a favorably broad sealing window.

In lidding applications, adhesion values to the base-cup materials of 11–22 N/25 mm (2.5–5.0 lb/in.) are desirable.

Machine-direction vs. cross-direction seal strengths

In general, the machine-direction seal strengths were higher than those taken in the cross direction (**Fig. 1**). The extrusion coating process, by nature, orients the material in the machine direction because this is the direction in which the film is drawn away from the die in the cooling process. Relatively little molecular alignment is provided in the cross direction. Therefore, the extrusion coating process favors higher seal strengths in the machine direction.

Effect of sealant thickness

Coating thickness was varied (1.0, 1.5, and 2.0 mils) for the 80/20 blend of EAA-1/PB. Increasing the thickness of the seal layer unfavorably increased the hot-tack and heat-seal initiation temperatures due to the poorer heat transfer through the thicker specimen. For example, the hot-tack initiation temperature was approximately 3°C lower for the 1.0-mil coating, i.e., 94°C vs. 97°C for the 1.5-mil and 2.0-mil coatings (**Fig. 2**). Heat-seal initiation temperature for the 1.0-mil coating was 86°C vs. approximately 91–94°C for the higher coating weights (**Fig. 3**).

As expected, ultimate hot-tack strength increased as a result of an increase in coating thickness (17 N/25 mm and 20–23 N/25 mm for the 1.0-mil coating and the higher coating weights, respectively). Similarly, heat-seal strengths also increased with coating thickness from 23 N/25 mm to 30 N/25 mm. Ultimate seal values of the EAA-1/PB blends (80/20) would be considered too high for most easy-open peel applications.

Increasing thickness resulted in an increase in foil adhesion from 2.7 N/25 mm to 6.2 N/25 mm (**Fig. 4**).

Effect of blend ratio

Minor amounts of polybutylene (0, 15, 20, and 25 wt%) were blended with EAA-1 with the intent of varying the seal strength and yet retaining the hot-tack and adhesive properties of the EAA copolymer. Hot-tack initiation temperatures of the 0 to 25 wt% PB blends were the same within experimental error (**Fig. 5**). Ultimate hot-tack values did not exhibit a definite trend with changes in percentage of PB, although the 25 wt% blend did exhibit the lowest ultimate hot-tack strength, 14 N/25 mm vs. 16–17 N/25 mm for the other blends.

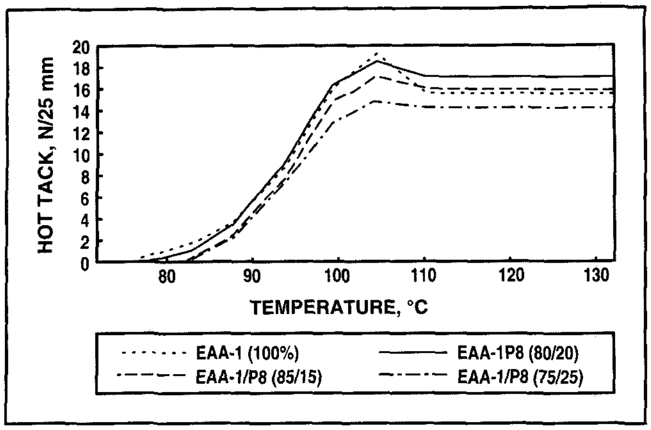
In general, heat-seal initiation temperature decreased with increasing amounts of PB from 0 to 20 wt% (**Fig. 6**). The 20-wt% PB blend exhibited the lowest initiation temperature at 86°C. At 25 wt% PB, the heat-seal initiation was 94 °C. This anomaly may be due to "phase inversion," i.e., the minor blend component, PB, has become the continuous phase of the EAA/PB blend, and therefore it predominantly affects the heat-seal initiation temperature. Ultimate seal strengths decreased from 27 N/25 mm to 15 N/25 mm with the addition of PB. This decrease in seal strength is a result of the weaker intermolecular force of the dissimilar materials. The values obtained at 25 wt% PB would be acceptable for most face-to-face easy-open peel applications.

Increasing the percent PB slightly decreased the adhesion to foil from 3.6 N/25 mm to 2.7 N/25 mm (Fig. 4).

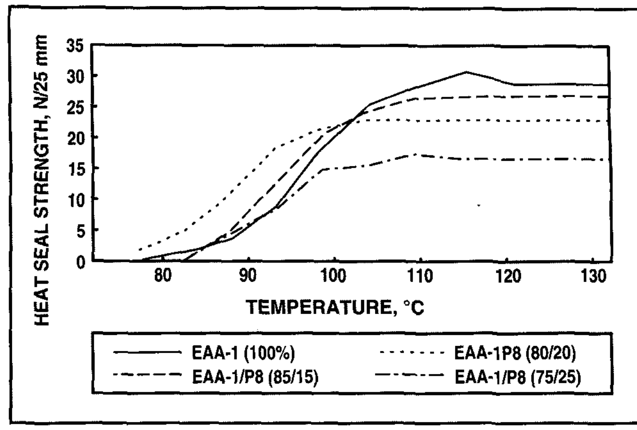
Effect of blend formulation

Three different products (0, 6.5, and 9.5 wt% acrylic acid content) were blended with the polybutylene at 20 wt% PB. Hot-tack initiation temperatures decreased with increasing percent acrylic acid (**Fig. 7**) due to the excellent low-

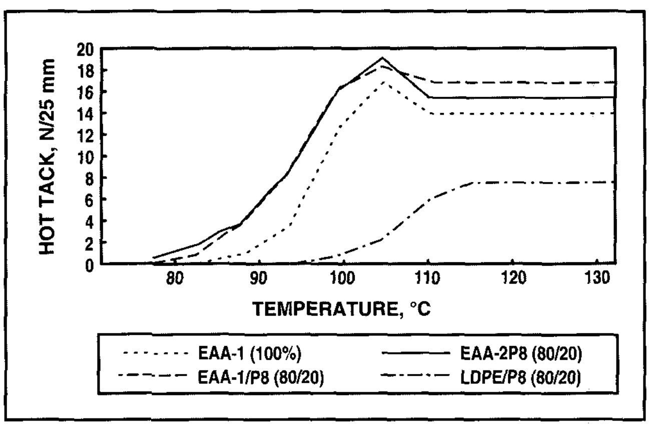
5. Average hot-tack values for EAA/PB blends at varying ratios coated onto aluminum foil. All samples have a 1-mill coating thickness.



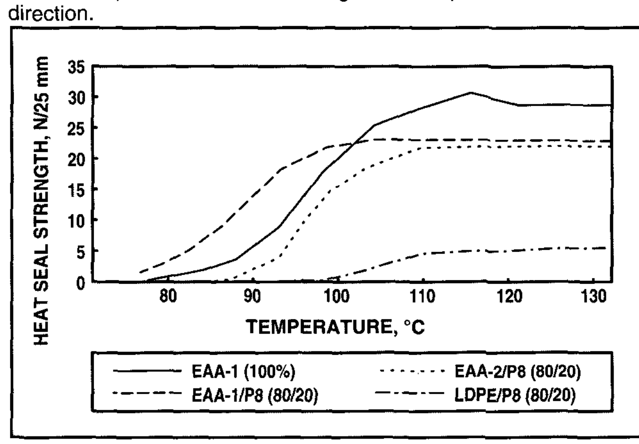
6. Average heat-seal strengths for EAA/PB blends at different ratios coated onto aluminum foil. All blends have a 1-mil coating thickness pulled in the machine direction.



7. Average hot-tack values for PB blends coated onto aluminum foil. All samples have a 1-mil coating thickness.



8. Average heat-seal strength for PB blends coated onto aluminum foil. All samples have a 1-mil coating thickness pulled in the machine direction.



temperature hot-tack properties of the EAA copolymers. The higher the acrylic acid content for an EAA copolymer, the lower the crystallinity.

Ultimate hot-tack strengths increased with increasing percent acrylic acid. EAA copolymers exhibit high ultimate hot-tack strengths due to the acrylic acid molecules which provide sites for hydrogen bonding. Ultimate hot-tack strength for the LDPE blend did not average greater than approximately 7 N/25 mm.

Heat-seal values for the LDPE blend (0 wt% AA) never reached the target heat-seal initiation value of 9 N/25 mm (**Fig.** 8). Heat-seal initiation temperatures for the EAA-2 (6.5 wt% AA) and EAA-1 (9.5 wt% AA) blends were 97°C and 94°C, respectively. Ultimate seal strengths for the EAA blends were 20–21 N/25 mm. These ultimate seal values are slightly high compared to the optimum range for face-to-face peelable seals.

Adhesion to foil averaged 0.2 N/25 mm for the LDPE blend, while the foil adhesion values for the EAA blends were much higher, 2.7 N/25 mm (Fig. 4). EAA copolymers are known for their adhesion to a variety of metallic substrates, including aluminum foil.

Heat seals to base-cup materials

Heat-seal strengths of the coated foil samples to the base-cup materials (**Table III**) were rated according to typical requirements:

- Low = 0.0–11 N/25 mm
- Optimum = 11–22 N/25 mm
- High = greater than 22 N/25 mm.

Addition of PB increased heat-seal strengths of polypropylene from "low" for EAA-1 to "optimum" for a blend of EAA-1 with 20–25 wt% PB (Table III). The EAA-2/PB and LDPE/PB blends (80/20) also exhibited "optimum" seal strengths to PP. Seal strength actually decreased as a result of increasing the coating thickness from 1.0 mil ("optimum" seal strength) to 1.5 mils and 2.0 mils ("low" seal strengths).

Seal strengths to PVC were "optimum", except for the EAA-1/PB (80/20) blend at a 2.0-mil coating thickness, which was "slightly high."

Seal strengths to PET were also improved with the addition of PB, from "low" to "optimum" for the EAA-1

III. Average heat-seal strengths of coated foil samples sealed to various substrates

	Polypropylene	*ABS*	*PVC*	*HDPE*	*Polystyrene*	*PET*	*Polycarbonate*
EAA-1 100% 1.0 mil	Low	Low	Optimum	High	Low	Low	Low
EAA-1/PB 80%/20% 1.0 mil	Optimum	Low	Optimum	High	Low	Slightly low	Low
EAA-2/PB 80%/20% 1.0 mil	Optimum	Low	Optimum	High	Low	Optimum	Low
LDPE/PB 80%/20% 1.0 mil	Optimum	Low	Optimum	Optimum	Low	Optimum	Low
EAA-1/PB 80%/20% 1.5 mils	Low	Low	Optimum	High	Low	Low	Low
EAA-1/PB 80%/20% 2.0 mils	Low	Low	Slightly high		High	Low	Low
EAA-1/PB 75%/25% 1.0 mil	Optimum	Low	Optimum	High	Low	Optimum	Low
EAA-1/PB 85%/15% 1.0 mil	Low	Low	Optimum	High	Low	Low	Low

blend with 25 wt% PB. Other samples falling in the "optimum" range were LDPE/PB and EAA-2/PB blends.

All heat-seal values to HDPE for the EAA/PB blends fell within the "high" range. The seal strength of LDPE/PB was "optimum."

No improvements in adhesion to PS, ABS, or PC were obtained. All heat-seal values to these substrates were categorized as "low."

Conclusions

The blend from this study displaying the best balance of performance properties for face-to-face peelable sealant applications was EAA-1/PB (75/25). At 25 wt% PB in EAA, a viable peelable seal can be obtained for use in easy-opening packaging. Blends were screened for good hot-tack performance and aluminum adhesion, with performance similar to that of EAA copolymers being favorable. At 25 wt% PB, aluminum adhesion for the blend was slightly lower than for the 100% EAA control. The hot-tack and heat-seal initiation temperatures of the blend were within experimental error of the 100% EAA control. Although slightly lower for the blend vs. the 100% EAA control, the ultimate hot-tack values were respectable.

Some trends noted which could be applied to designing an EAA-based easy-opening package are as follows:

1. Machine-direction heat-seal values were higher than cross-direction heat-seal values.
2. As seal layer thickness increased, heat-seal and hot-tack initiation temperatures increased. Ultimate heat-seal and hot-tack values and foil adhesion increased as a result of increased coating thickness.
3. Blend performance increased with increasing functionality. Blends with EAA-1 (9.5 wt% AA) had the highest ultimate hot-tack strengths and lowest hot-tack and heat-seal initiation temperatures. Ultimate seal strengths for EAA-1 and EAA-2 (6.5 wt% AA) blends were comparable. Blends of LDPE with PB exhibited low ultimate seal strengths and poor aluminum adhesion. Therefore, EAA-1 was determined to be the preferred component for blending with PB.
4. Increasing amounts of polybutylene in the blends did improve heat-seal strengths to PP, PVC, and PET, as would be needed for lidding-stock applications. Heat-seal strengths to HDPE were high for the 100% EAA sealant and EAA/PB blends. Only "low" adhesion values to PS, ABS, or PC were obtained.

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