**ABSTRACT**

We have blended adhesive tie-layer resins with commodity resins and made structures with excellent adhesion and water resistance. Primers were critical to success and good results were obtained even at very low extrusion temperatures. Potential benefits include improved adhesion, water resistance, processability and productivity.

We also tested unblended adhesive tie-layer resins, such as those used in the co-extrusion process. Adhesion and water resistance were greatly improved by using primers.

**INTRODUCTION**

There have been reviews of the adhesive properties of tie-layers used in coextrusions. There have also been reports of co-extrusions using tie-layers coupled with primers to make structures with superior performance. For example, Trouilhet and Foster reported a multilayer structure prepared by co-extruding polypropylene/tie-layer onto a primed polyamide film can be used to make clear, sterilizable, heat sealable packages. In this structure, the primer was essential because it covalently linked the substrate to the adhesive tie-layer.

In our paper, we have two objectives:

1. Demonstrate that in many cases, the performance of tie-layer co-extrusions may be significantly enhanced if a primer is used.

2. Demonstrate that dry blending low levels of tie-layer resins into conventional extrusion resins may dramatically improve the performance of structures made with primers. In some cases, single layers of resin blends may mimic the performance of structures produced by the higher investment co-extrusion process.

**WHAT IS AN ADHESIVE TIE-LAYER?**

As shown in Figure 1, a tie-layer is a resin typically co-extruded between a conventional extrusion resin and a substrate. The tie-layer has functional groups that bond to the substrate and the polymer backbone is designed to bond with the conventional resin melt. It functions therefore as an extrudable adhesive.

Examples of tie-layer compositions are shown in Figure 2.

Tie-layers generally bond well to metal substrates but have selective bonding to plastics. When extruded on many substrates typically used in flexible packages, such as BOPP and PET, they may form weak bonds. The application of tie-layer resins also requires capital intensive co-extrusion equipment.
WHAT IS A PRIMER?
A primer is a surface modifying coating for the substrate that assists with adhesion to the melt. The functional groups of the primer react with functional groups of the substrate and the functional groups of the extrudate to form a strong bond. Some extrudates - such as the ubiquitous polyethylene - do not have functional groups with which to bond. Polyethylene must be extruded at high temperatures to form bondable functional groups on the surface by air oxidation. This concept is shown in Figure 3. Note that the bonds are excellent only when the primer is used in combination with polyethylene extruded at a high (>300°C) melt temperature.

WHY PRIMERS CAN ENHANCE THE PERFORMANCE OF TIE-LAYERS

Figure 4 represents a tie-layer molecule. Note that there are “built in” functional groups – in this case carboxylic acid. These tie-layer resins therefore do not need to be extruded at high temperatures to generate bondable sites - the functionality already exists on the polymer backbone. In blends, the functional groups may still be present in high enough concentrations to achieve good bonds with reactive primers, even at low extrusion melt temperatures.

The primer can be tailored to bond well to both the functional groups on the substrate and the tie-layer, giving robust bonds.

EXPERIMENTAL

For testing, the substrate was corona treated and primed using a wire wound rod. The primed sheets were then taped to a paper web and extruded upon with the resin using a 2.5 cm Randcastle extrusion coating line and a 25 cm wide die. Adhesion testing was done on a Friction / Peel Tester, Thwing-Albert Instrument Company, model 225-1.

Numerous tie-layers from various suppliers were evaluated. The tie-layers presented in this study are listed below. Products by other suppliers may function similarly.

<table>
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* Melt flow is measured at 160°C, 0.325 kg; value reported is calculated for 190°C, 2.16 kg.

The following commodity resins were used as a base for blending in the tie-layer resins.
- Polypropylene (PP): Basell ProFax, SD812 a copolymer with a MFR of 16 g/10 min.
- Ethylene vinyl acetate (EVA), AT Plastics Ateva 1651, 16% VA and MI of 28 g/10 min.
- Low density polyethylene (LDPE), Voridian 808P, MI of 7 g/10 min.
RESULTS AND DISCUSSION

Extrusion on Aluminum Foil.

As a model for co-extrusion, we extruded TL-L2 on 25µ aluminum that was both primed and not primed. We assume that the primer would have no effect on the bond strength of a conventional resin to the tie-layer and that the weak bond in any structure is the bond of the tie-layer to the substrate. Figure 5 shows the bond strength of the TL-L2 to aluminum without primer is about 3 N/15mm. With primer the bond is stronger than the extrudate because the extrudate film tore at about 6 N/15mm. In fact, with primer, a 30% blend of the tie-layer with low density polyethylene (LDPE) also had a destructive bond. This was much higher bond strength than the pure tie-layer with no primer.

Figure 6 shows that the water resistance of the pure TL-L1 is good with or without primer but that in blends, the primer significantly aids the adhesion and water resistance.

These data suggest that a cost savings may be possible if the tie-layer of a co-extrusion were to be replaced by a blend with a commodity resin and a primer. Conversely, a monolayer structure using a primer could be improved at minor extra material cost by co-extruding with a tie-layer blend.

Extrusion on Films – Pure tie-layer and its LDPE blends

Figure 7 shows that the improvement in bonding of tie-layers and their blends is even more significant on films than aluminum. This is because the functional groups in primers bond to film much more strongly than the functional groups in common tie-layers. With primers, neat or in blends with polyethylene, film tear was achieved.

Note that in the blends of LDPE with tie-layer, excellent bonds were achieved when extruding at a very low temperature, 260°C. One possible use for this technology may be to lower the taste and odor of a package typically made from LDPE extruded at high temperatures.

Figure 8 shows that excellent water resistance can be achieved in tie-layer blends with polyethylene on PET substrate when primers are used.

Extrusion of EVA / Tie-layer Blends on Plastic and Aluminum Substrates.

Perhaps the most significant improvement in performance with this technology occurs when blending low amounts of tie-layer into EVA and extruding on a primed substrate.

For the highest performance applications such as lamination stock, EVA typically is ozonated and a primer is used. Because it decomposes at elevated temperatures, EVA cannot be extruded hot enough to oxidize the surface and produce binding sites. As a solution, the EVA is extruded at around 230°C in the presence of ozone.

We have found that dry-blending a low amount of the TL-L1 into EVA is sufficient to give exceptional bonding and moisture resistance. Figure 9 shows the off-line bonds of EVA containing 8% tie-layer TL-L1 extruded onto primed and non-primed PET. With no ozone, the
bonds of the primed samples exceeded the strength of the EVA at all of extrusion thicknesses
tested.

If these structures are subjected to additional heat by heat-sealing face to face, a typical test for
lamination stock, the bonds are tremendous. Figure 10 shows that the face to face heatseal bond
strength is 10 times higher than the off-line bond strength and the bonds exceed that of the
conventional ozone/primer technology.

Even more important for many applications, the water resistance is excellent as shown in Figure
11. We are currently evaluating the moisture resistance of these structures by other test methods
such as humidity testing and tropical aging. So far one severe test shows the improvement of
these systems over conventional ozone/primer structures as in Figure 12.

On aluminum the results are equally impressive providing the primer was designed for use on
aluminum. The initial bond strength (t=0) and water resistance of an 8% blend of TL-L1 with
EVA can be seen in Figure 13.

Rarely are these superior results achieved with ozone/primer systems.

Possible applications for this technology include lidding, structures for difficult-to-contain
materials, and high performance laminations stock.

Polypropylene Tie Layers and Their Blends

Figure 14 shows that a 15% blend of maleic anhydride grafted polypropylene, TL-B1, with
polypropylene can give excellent adhesion to PET or printed paper when a primer is used. We
have found that with these polypropylene blends, the primer must be applied at higher than the
normal application amounts to obtain good adhesion. We suspect that residual non-grafted
maleic anhydride may poison the primer making it ineffective at low application weights.

The MAH grafted polypropylene used in Figure 14 is highly grafted and consequently has a high
melt flow rate since grafting can cleave the polymer chain. Figure 15 show that the bonding of a
lower MFR, lower maleic anhydride grafted polypropylene is also enhanced by primers. This
grafted PP was designed for good extrusion characteristics and is recommended by the
manufacturer for coextrusion with ungrafted PP. Note that on aluminum, the primer type is
critical; primer M had very low adhesion whereas primer G had nearly 4.5 N/15mm bond
strength. Again this demonstrates that primers may enhance the performance of coextrusions
using tie-layers

CONCLUSIONS

• Co-extrusion coupled with primers can dramatically enhance the performance of
  multilayer structures.
• Monolayer extrusions using primers:
  o Low levels of specific tie-layers blended into EVA produces structures with
    superior adhesion and moisture resistance - without using ozone.
  o Specific tie-layers blended into LDPE produce structures at low extrusion
    temperatures with excellent adhesion and water resistance.
o Polypropylene, which is extremely hard to bond, can be bonded to various primed substrates by blending in low levels of MAH grafted PP.

o Blends of tie-layers and commodity extrusion resins with a primer may allow performance equal to co-extrusion using pure tie-layer and no primer.

REFERENCES


ACKNOWLEDGEMENTS

The author thanks Jessica Bodine and Jeremy Bober for their excellent laboratory work and Bruce Foster for his helpful discussions.
Figure 1: What is an Adhesive Tie-Layer?

- Functionalized polymer designed to adhere to two different surfaces
- Usually co-extruded with another resin.

![Diagram of LDPE, Co-extruded ethylene acrylic acid copolymer (Tie Layer), and Aluminum]

Figure 2: Tie-Layer Compositions

- Backbone is usually a typical extrusion resin:
  - Polyethylene
  - Ethylene copolymers
  - Polypropylene
- Functional groups are often:
  - acrylic acid
  - methacrylic acid
  - maleic anhydride
  - glycidyl ether (epoxy)
Figure 3: With PE, Oxidized (Functionalized) Surface Required for Good Bond Strength

- Polyethylene extruded at 260°C. No oxidation, poor adhesion.
- Polyethylene extruded at 315°C. Surface oxidation, good adhesion.

Covalently bonds with primer

Figure 4: Tie-Layer Structure with Built-in Functional Groups.
Figure 5: Effect of Primer on Adhesion to Aluminum of TL-L2 and its LDPE Blend (Extruded at 260°C)

Figure 6: Effect of Primer on Water Resistance (Extruded at 260°C)
Figure 7: Effect of Primer on Adhesion to PET of TL-L1 and its LDPE Blend (Extruded at 260°C)

Figure 8: Effect of Primer on Water Resistance. Blend of 30% TL-L1 in LDPE to PET (Extruded at 260°C)
Figure 9: Effect of Coating Thickness on Adhesion. Blend of 8% TL-L1 in EVA to PET (Extruded at 230°C)

Figure 10: Typical Bond Strength of Various EVA/primer/PET Structures.
Figure 11: Water Resistance of a blend of 8% TL-L1 in EVA (45m) to PET (Extruded at 230°C)

Figure 12 Bond Strength of EVA/primer/PET Structure after Exposure to 5 days at 70°C and 95%RH.
Figure 13: Water Resistance of a Blend of 8% TL-L1 in EVA (45m) to Aluminum (Extruded at 230°C)

Figure 14: Effect of Primer on Adhesion of 15% TL-B1 in Polypropylene (PP-1) to Various Substrates.
Figure 15: Effect of Primer on Adhesion of TL-B2 to Various Substrates
Using Primers in Combination With Adhesive Tie-Layer Resins, or Their Blends, to Make Structures with Unique Performance

Presented by:
Richard Allen
Mica Corporation
Shelton, CT USA

Objectives

- In co-extruded structures: primers can significantly enhance performance.
- In mono-layer extrusions with primers: low levels of tie-layers blended into conventional extrusion resins can produce structures with outstanding properties.

Previous Work

- Tie Layer:

- Coextruded Tie Layer + Primer:
What is an Adhesive Tie-Layer?

- Functionalized polymer designed to adhere to two different surfaces
- Usually co-extruded with a commodity resin.

**LDPE**
Co-extruded ethylene acrylic acid copolymer (Tie Layer)
Aluminum

Tie-Layer Compositions

- **Backbone** is usually a typical extrusion resin:
  - Polyethylene
  - Ethylene copolymers
  - Polypropylene
- **Functional groups** are often:
  - acrylic acid
  - methacrylic acid
  - glycidyl ether (epoxy)
  - maleic anhydride

What is a Primer?

- Surface modifying coating applied to substrate.
- Bonds well to both substrate and extrudate.
With PE, Oxidized Surface Required for Good Bond Strength

Polyethylene extruded at 260°C.
No oxidation, poor adhesion.

Polyethylene extruded at 315°C.
Surface oxidation, good adhesion.

Effect of Primer and Extrusion Temperature on Bond Strength of LDPE/PET Structure.

Tie-Layers Have Built-in Functional Groups.

…So no oxidation is needed with tie-layers to form strong bonds with primers.
### Tie-Layers Used in This Study

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* Calculated

**Tie-Layer L1 and L2 in Polyethylene**

- Requires extrusion at high temperature (>315°C) for oxidation.
- May extrude better at lower temperatures.
- May affect taste and odor.
Effect of Primer on Adhesion to Aluminum of TL-L2 and its LDPE Blend.

Extruded at low temperature, 260°C

Water Resistance

100% TL-L1/primer/aluminum

Blend of 30% TL-L1 in LDPE/primer/aluminum
Effect of Primer on Adhesion to PET of TL-L1 (Extruded at 260°C)

- Compare bond strength with and without primer for TL-L1.

Effect of %TL-L2 in LDPE on Adhesion to PET (Extruded at 260°C)

- Only about 10% TL-L2 needed for film tear at low extrusion temperature.

Water Resistance:
Blend of 30% TL-L1 in LDPE to PET

- Evaluate water resistance over time.
Possible Utility

- Low temperature extrusion of PE
  - Lower taste and odor?
  - Melt viscosity matching in coextrusion
- Enhanced Performance.
- Cost savings?

Tie-Layer L1 in Ethylene Vinyl Acetate

Extruded EVA

- Can generate acetic acid.
- For good bonds with primers, must extruded in presence of ozone.
Coating Thickness vs. Adhesion. Blend of 8% TL-L1 in EVA to PET

Extruded at 230°C with no ozone.

Typical Bond Strength of Various EVA / primer / PET Structures.

Water Resistance of a blend of 8% TL-L1 in EVA (45m) to PET
**Bond Strength of EVA/primer/PET Structure After Exposure to 5 days at 70°C and 95%RH.**

**Water Resistance of a Blend of 8% TL-L1 in EVA (45m) to Aluminum**

**Possible Utility**
- More robust lamination stock.
- EVA extrusions without ozone.
- Enhanced bonding to substrate in lidding.
Tie-Layer B1 and B2 in Polypropylene

Extruded Polypropylene

- Does not oxidize at high temperatures.
- VERY difficult to bond, particularly to plastic film or aluminum foil.
- Limited use in extrusion coating despite excellent properties:
  - Low cost
  - High use temperature
  - High gloss, clarity
  - Grease and chemical resistance

Effect of Primer on Adhesion of 100% TL-B2 to Various Substrates
Effect of Primer on Adhesion of 15% TL-B1 in Polypropylene to Various Substrates.

Possible Utility

- Clear, glossy, abrasion resistant, grease resistant coating.
  - Ream wrap
  - Pet food bags
- Possible clear steam sterilizable structures made by monolayer extrusion.

Conclusions

- Unique, superior or lower cost structures can be made by using primers and:
  - Tie-layers in coextrusion.
  - Tie-layers / commodity resin blends in monolayer extrusion.
Thank You

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Please remember to turn in your evaluation sheet...