New Extrusion Coating Primers for Achieving EVA Adhesion to Film and Aluminum Foil Substrates

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ABSTRACT

Conventional film/primer/EVA extrusion technology calls for modified PEI primers plus ozone assistance to achieve high bond strength. New primers based on emulsified ethylene terpolymers show promising performance without the need for ozone assistance. Additionally, the primers can pass severe service conditioning when used with ozone. Such structures may find utility as transparent encapsulation stock.

Preliminary data also suggests the new primers are suitable for aluminum foil substrates for end uses such as lidding stock. This paper compares the properties and performance of three aqueous formulations.

INTRODUCTION

Aqueous primers based on modified polyethylenimine, PEI, are well known to converters for bonding polymers that may be extruded at relatively high temperatures, such as low density polyethylene, LDPE. A very thin coat of primer (0.04 dry g/m^2) is sufficient to produce inseparable adhesion between the film and extrudate. Without primer, the peel strength is poor, typically less than 0.2 N/15mm. The mechanism that produces this adhesion relies on oxidation of the melt during the extrusion process. High melt temperature (circa 325^{o}C), ambient oxygen and sufficient time in the air gap all work together to oxidize LDPE. The PEI primer covalently bonds to these reactive sites and the adhesion is impressive (1).

It is no secret that ethylene vinyl acetate, EVA, differs in many respects from LDPE. EVA resin cannot tolerate the high extrusion temperatures described for LDPE, as its performance will suffer from unwanted crosslinking and decomposition. The extrusion temperature is related to the vinyl acetate content, and a 16 – 18% VA resin might run at a temperature of about 230^{o}C. This relatively low temperature will not generate the oxidized sites on the resin necessary for bonding to PEI primer. To overcome this, ozone gas may be directed toward the melt at the time of extrusion. Ozone is a powerful oxidizer and will add oxygenated groups to EVA that will bond to PEI (2).

There are many industrial products that employ ozone to help EVA bond to PEI-primed film substrates. One application was selected as the basis of our work – transparent film/primer/EVA structures intended for lamination (or encapsulation) stock. This type of structure represents many of the challenges we face as we attempt to achieve strong adhesion at the primed interface. In lamination stock made with PEI primer, off-machine bonds are peelable, about 1N/15mm. The film composite is used to encapsulate a document, photograph or card by an end user. The card is sandwiched between two sheets of film/EVA and hot nip laminated under varying conditions. After the lamination process, the adhesion at the primed interface becomes very strong, greater than 10N/15mm. We consider the adhesion to be inseparable, as the mode of peel test failure is not at the primed interface; rather it is typically to break the EVA.

While manufacturing film/PEI primer/EVA structures using ozone has been a tried and true process for converters for decades, a few limitations exist.

OBJECTIVES

This paper addresses two areas.

<u>Goal 1.</u> *Identify a primer that is suitable to bond to EVA extrudate without requiring ozone assistance.* Some converters do not have ozone generating equipment. We present new aqueous primers that can mimic the performance of conventional PEI primers, without the need to use ozone with EVA melt. These primers bond well to both film and aluminum foil substrates.

<u>Goal 2.</u> *Identify the materials and process that will result in maximum water resistance.* Though the bond strength after lamination is quite strong, the film/primer/EVA stock used to encapsulate the stock does not pass severe moisture resistance testing. As expected, this can result in field failures and limit the utility of the priming technology. We have demonstrated in our laboratory a way to make structures that can survive rigorous humidity testing.

The control primer in our study is a conventional PEI type primer that is the industry standard for manufacturing transparent laminating stock. It is an aqueous dispersion of PEI polymer, which has been crosslinked and otherwise formulated to improve bond strength, flow resistance and water insolubility. We will compare three developmental water based primer variants to the control. The backbone of the new primers is a terpolymer of ethylene, alkyl acrylate and maleic anhydride. The terpolymer has been emulsified and formulated to produce clear, continuous coatings that are tack-free. Like PEI, the new primers are acceptable for use in food packaging applications.

EQUIPMENT and MATERIALS

The equipment and materials used in this study are detailed in Appendix 1 and 2, respectively.

EXPERIMENTAL

For many tests, we extrusion coated EVA onto primed film and reported the results. Since we do not have an ozone generator on our lab extruder, some data were generated by drawing down primer with a wire wound rod onto sheets of film in the laboratory. Instead of extrusion coating the resin, EVA film was heat sealed to the primed substrate. To simulate the affects of ozonation, we corona treated the EVA film prior to heat sealing to the primer, with the belief that the results can reasonably approximate those attainable on a commercial extrusion coating line. In cases where we wanted to compare adhesion without ozone, we made heat seals with untreated EVA film. We selected heavy gauge BOPET (50µ) film for our work because it offered the strength necessary to withstand peel testing at high bond strength. Thinner gauge film was prone to breaking. The experimental details for the lab extrusion coating process, draw down testing technique, lamination conditions and severe moisture resistance testing are collected in Appendix 3.

RESULTS AND DISCUSSION

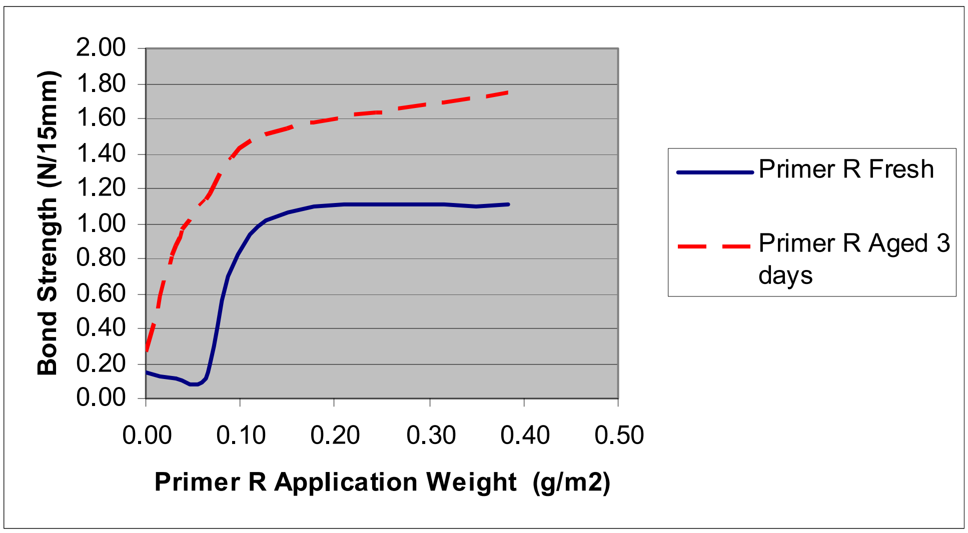
FILM PRIMER FOR EVA (NO OZONE)

To tackle goal 1, we evaluated terpolymer Primer R as an alternative to PEI primer for processes where ozone is either unavailable or undesirable to employ.

The first step was to measure the influence of Primer R application weight on adhesion performance. We used the lab extruder to coat 23µ of 16% VA EVA resin onto BOPET primed with varying amounts of Primer R. Bond strengths were measured fresh (within one hour of manufacture) and again after three days to determine any changes with age. The results are shown in figure 1.

Figure 1. Primer application weight study

50µ BOPET/primer/23µ EVA (no ozone)



The data shows us that the optimal application weight of Primer R is about 0.08 dry g/m^2 and the bond strength ages up about 40 to 80% after three days at ambient temperature.

Next, we wanted to directly compare the performance of Primer R with the conventional PEI primer. Using our results from the primer application weight experiment above, we held Primer R coat weight at 0.08 dry g/m^2 for the balance of our work. For PEI primer, its optimal application weight was used, 0.04 dry g/m^2. Figure 2 shows a comparison between Primer R, PEI primer and no primer. The samples were made by extrusion coating 16% VA EVA resin at 25µ onto primed, treated BOPET film. The structures were allowed to age three days prior to peeling. We observed that unprimed samples have high variability in bond strength.

In the next test, we examined the influence of melt thickness on adhesion with Primer R. See figure 3. To compare, we know that in the presence of ozone PEI primer adhesion is linked to melt thickness; the heavier the melt, the better the PEI performance.

Figure 2. Comparison of Primer R with PEI and no primer

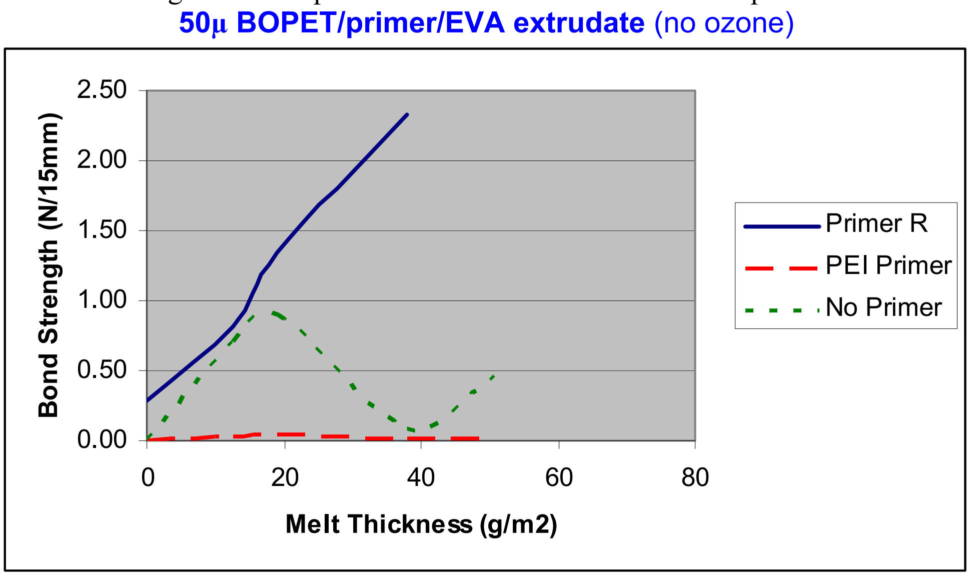
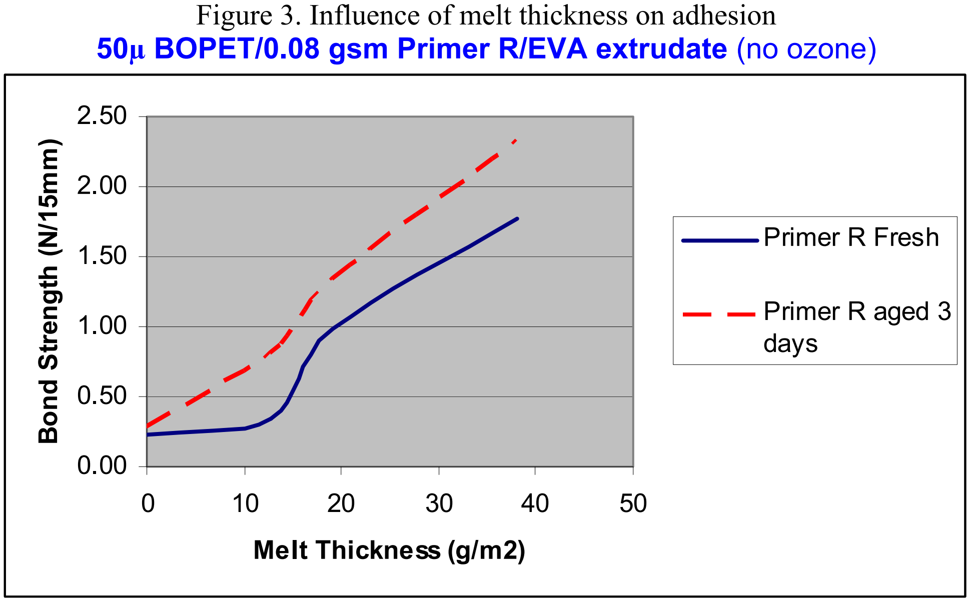


Figure 3. Influence of melt thickness on adhesion



In the last set of extruder trials, we attempted to learn more about the affects of vinyl acetate content and resin additives on adhesion with Primer R. We were interested knowing how vinyl acetate percentage would influence adhesion. We thought that slip and antiblock agents might have the potential to diminish adhesion. The data, presented in figures 4 and 5, do not show dramatic changes in adhesion corresponding to these variables.

Figure 4. Influence of vinyl acetate content on adhesion with Primer R

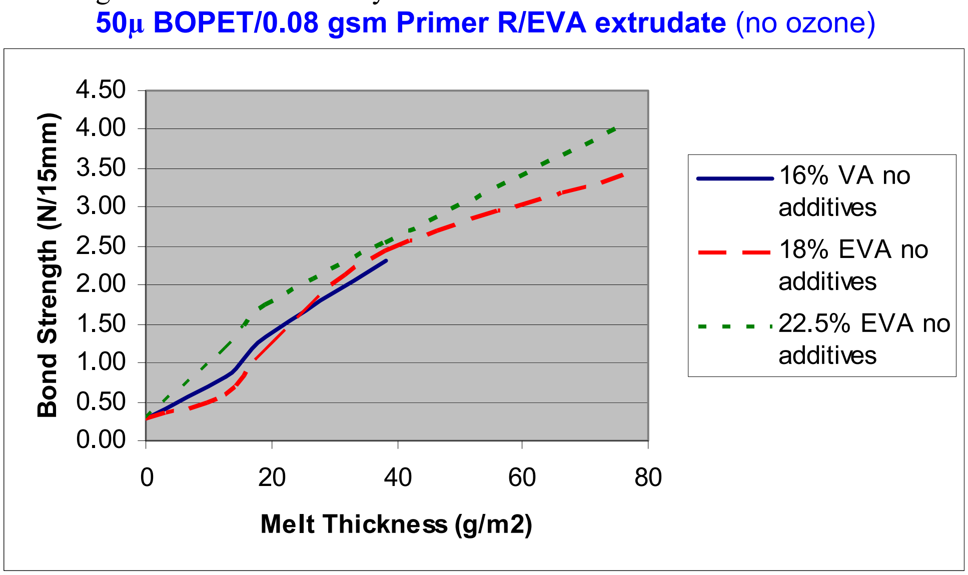
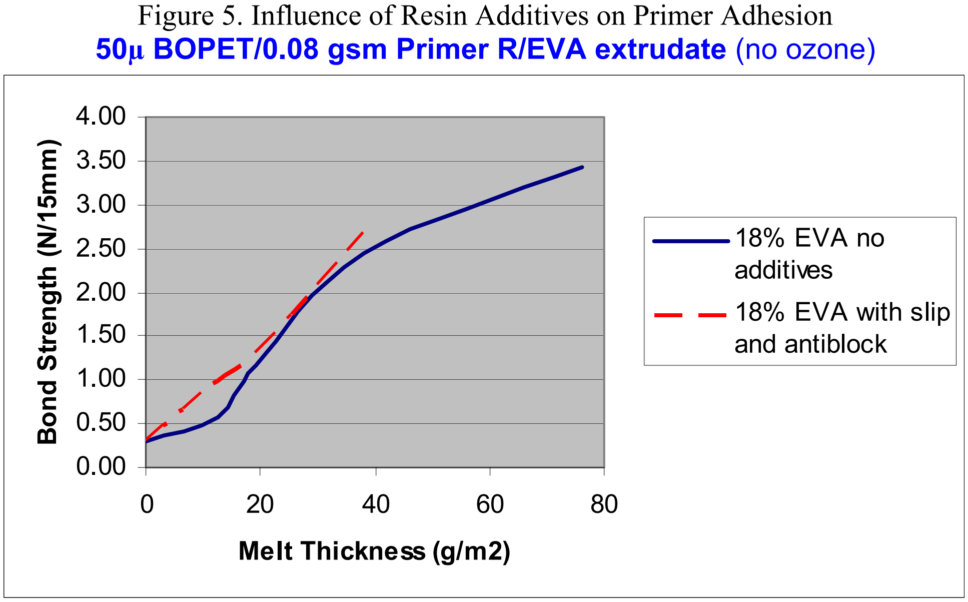


Figure 5. Influence of Resin Additives on Primer Adhesion



PERFORMANCE AFTER LAMINATION

The above data studies the off-machine performance of Primer R. Commercial laminating processes call for encapsulating a document and squeezing the sandwiched structure together under conditions of heat and pressure. The heat from the lamination process should elevate adhesion levels to the point where the bond at the primed interface is inseparable and peel test failure occurs within the polymer layer. To test, we prepared heat seal samples with Primer R and PEI according to the lamination method described in Appendix 3. The following table shows the data we collected for adhesion at the primed interface. Recall that treating the EVA film is intended to simulate the use of ozone in extrusion coating.

TABLE 1. Adhesion at the primed interface after heat sealing at 135°C, 3 sec.
Wet peel strength dry and after 45 minutes water immersion (N/15mm)

50µ BOPET/primer/76µ EVA film

Primer and Application Weight	EVA Treatment	Dry Adhesion (N/15mm)	Wet Adhesion (N/15mm)
No Primer	No	0.2	0
No Primer	Yes	Inseparable	0.6
0.04 g/m^2 PEI Primer	No	9.1	0.3
0.04 g/m^2 PEI Primer	Yes	Inseparable	5.5
0.08 g/m^2 Primer R	No	Inseparable	1.8
0.08 g/m^2 Primer R	Yes	Inseparable	4.3

This data demonstrates that commercial structures made with PEI primer plus ozone exhibit some moisture resistance, but water immersion weakens the bond. Primer R shows improvement over PEI in cases where ozone was not used. With ozone, Primer R is no better than PEI.

IMPROVING MOISTURE RESISTANCE

At this point, we have found that Primer R can mimic the performance of the standard PEI primer for hot nip lamination applications. Despite the strong adhesion after lamination, the bonds become peelable after extended exposure to moisture, with or without ozone assistance. This can be troublesome for some high end stock intended for high moisture environments, identification badges (worn outside, they can get wet in the rain), laminated outdoor signs, and so on. In goal 2, we described our desire to find a primer with improved moisture resistance. With this in mind, a variation of Primer R was created, namely Primer M.

To test Primer M, we prepared laboratory samples with the draw down method (Appendix 3). They were aged three days and subsequently heat sealed face-to-face (EVA-to-EVA) at 135°C for 3 seconds dwell time to simulate lamination. Again, we used corona treated EVA film to simulate the effects of EVA ozonation. The samples were subjected to the severe moisture resistance test (described in Appendix 3) and the results are described in Table 2.

TABLE 2. Severe moisture resistance testing

50µ BOPET/Primer/76µ EVA film (with and without "ozone")

Primer and Application Weight	EVA Treatment	Adhesion after lamination	Adhesion after test (N/15mm)
0.04 g/m^2 PEI	No	Inseparable	1.7
0.04 g/m^2 PEI	Yes	Inseparable	2.3
0.08 g/m^2 Primer M	No	Inseparable	4.1
0.08 g/m^2 Primer M	Yes	Inseparable	Inseparable

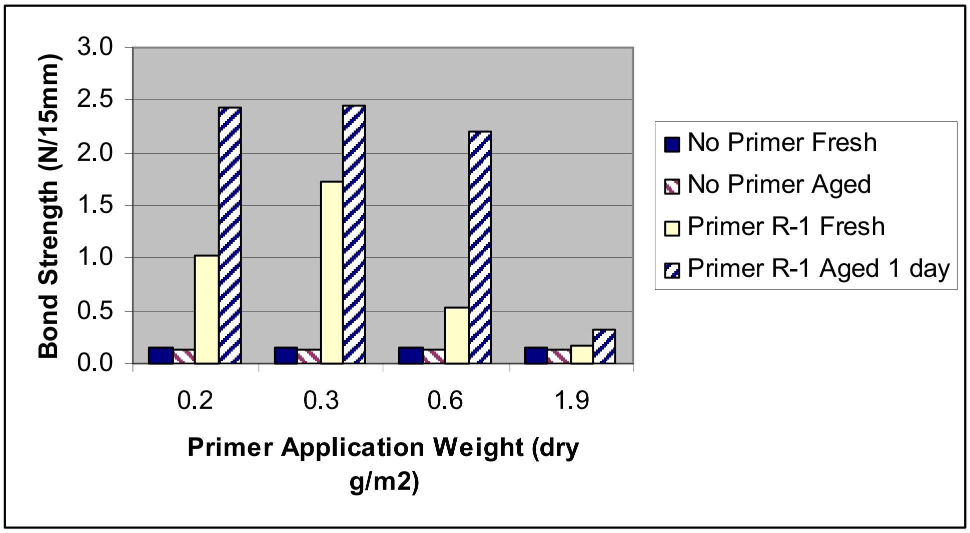
This test leads us to believe that structures made by using Primer M and EVA with ozone assistance can produce structures that are impervious to water. Scale up tests to further prove this concept were under way at the time of this writing.

ALUMINUM FOIL SUBSTRATES

In a separate set of experiments, we sought to determine whether the terpolymer emulsions had value as primers for aluminum foil substrates. Potential applications for a foil/primer/EVA structure may include lidding stock, among other things. We observed that the new primers behaved on foil in quite a similar manner to the way they performed on BOPET. We formulated a variant, R-1, to increase bond strength between extruded EVA resin and aluminum foil to slittable levels off machine. We used the lab extruder to collect some initial data about coating 16% VA EVA onto aluminum foil primed with Primer R-1. The application weight study and comparison to unprimed aluminum foil is presented in figure 6.

Figure 6. Primer R-1 adhesion on aluminum foil substrate

Aluminum Foil/app wt Primer R-1/25µ EVA extrudate (no ozone)



The data implies that 1) Primer R-1 contributes green adhesion, 2) the bond strength improves after aging one day at room temperature, and 3) too much primer will result in poor bond strength. In further tests, we found that after the EVA surface is heat sealed to itself, the bond strength increases to an inseparable level and the mode of failure during peel tests is in breaking the EVA or tearing the foil. Without primer, the bond strength after heat sealing was less than 2 N/15mm. We continue to study this technology and potential applications for foil/EVA structures.

CONCLUSIONS

We evaluated emulsified terpolymers as primers for bonding BOPET film to extrusion coated EVA. In the first comparison, we found that one variant can produce equivalent performance to the industrial standard PEI primer. The significant difference was that the terpolymer primer did not require ozone assistance to produce adhesion to EVA extrudate. This is a key point, as we have learned that without ozone, PEI primer will not bond well to extruded EVA. In lab extrusion trials, off-machine EVA adhesion to primed BOPET was fair, yet certainly slittable. Once laminated, the bond strength increased to an inseparable level (>10 N/15mm). This is equivalent to the results typically seen with PEI primer plus ozone assistance.

We further investigated the new terpolymer primers on film and found that the optimal application weight is about 0.08 dry g/m^2 and the adhesion performance increases as melt thickness increases. We also saw very slight adhesion improvement with an increase in EVA vinyl acetate content. We compared an EVA resin without additives to one with slip and antiblock and found that the adhesion of the new primer was not detrimentally affected by the presence of the additives.

Also, we identified a terpolymer primer formulation that, when used along with ozone assistance with EVA extrudate, can produce highly water resistant film composite structures. Finally, we found signs that the emulsions may fund utility as primers for aluminum foil substrates, too. Further testing is underway with this technology.

REFERENCES and FOOTNOTES

1. Cushing, G., "Chemical Primers for Extrusion Coating," TAPPI PLACE 2005 Extrusion Coating Short Course proceedings.
2. Sherman, P. (1999) "Ozonation of Polymer Melt for Improved Adhesion," *Extrusion Coating Manual* (4^{th} ed.) Atlanta, Georgia: TAPPI Press, pp 75-87.

ACKNOWLEDGEMENTS

The authors thank Jessica Bodine and Jeremy Bober for their excellent laboratory work.

APPENDICES

APPENDIX 1- EQUIPMENT Used in the Study

- Hand-held corona treater for treating sheets prior to draw downs: Electro-Technic Products, Inc. model: BD-20
- To make draw downs on film sheets: #3 wire wound rod, clip board, hot air gun
- Randcastle 2.4 cm single screw laboratory extruder
- Heatsealer: ALINE model HD-CH-12
- Friction / Peel Tester: Thwing-Albert Instrument Company, model : 225-1

APPENDIX 2 - MATERIALS Used in Study

- PEI = A-131-X, aqueous, crosslinked PEI primer
- Primer R = R-1595, aqueous terpolymer emulsion, variant 1
- Primer M = M-2420, aqueous terpolymer emulsion, variant 2
- Primer R-1 = R-1926, aqueous terpolymer emulsion, variant 3
- BOPET = 50µ treated polyester film
- EVA film = 76µ cast AT Plastics ATEVA 1641 (16% VA)
- EVA resins:
  - AT Plastics ATEVA 1651 (16% VA)
  - AT Plastics ATEVA 1841 (18% VA)
  - DuPont Elvax 3200-22 (22.5% VA)
  - Equistar Ultrathene UE 662-157 (18% VA, plus slip and anti-block)

APPENDIX 3 - EXPERIMENTAL Process Details, Settings and Techniques

EXTRUSION COATING

Some of the data were collected from experiments on our laboratory extruder. The extrusion parameters were as follows:

- Screw speed 40 rpm
- Line speed variable up to 15 m/m
- Air gap approximately 2 cm

- Melt temperature 232^{o}C
- Nip pressure 80 psi (about 550 kPa)

DRAW DOWN TECHNIQUE

1. Treated film substrate with hand held corona treater.
2. Drew down primers with #3 wire wound rod onto treated BOPET film. Note: dry primer application weights were 0.04 g/m^2 for PEI primer and 0..08 g/m^2 for Primer R and Primer M.
3. Dried thoroughly with hot air gun.
4. Heat sealed to EVA film at 120^{o}C for 5 seconds dwell time, 40 psi jaw pressure.
5. Measured green bond strength and aged bond strength on peel tester.

LAMINATION

To simulate commercial lamination conditions, film/primer/EVA samples were heat sealed EVA-to-EVA at 135^{o}C for 3 seconds dwell time, 40 psi jaw pressure.

SEVERE MOISTURE RESISTANCE TEST

Conditioned samples at 70^{o}C, 95% relative humidity for 5 days. Conducted peel test at primed interface while samples were still wet.

EMULSIFIED ETHYLENE TERPOLYMERS AS PRIMERS FOR EXTRUSION COATING

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Agenda

- Background
- New primers for film/EVA
- Experimental:
  - Compare performance of new primers to standard PEI primer
- The next step
- Summary

Background

- Protective film for lamination
- BOPET/primer/EVA extrusion
- BOPP/primer/EVA extrusion
  - High % VA, about 15 – 28%
  - Low extrusion coating temperature ~ 230°C

Lamination or (Encapsulation) Stock

Background

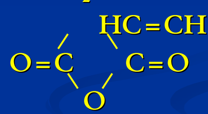
- Conventional PEI primer works well with high temperature extrudates (LDPE, ~320^{o}C)
- PEI primer limitations:
  - Low extrusion temperature resins, such as EVA, do not oxidize adequately during extrusion coating, yield poor adhesion to PEI
  - Ozone is necessary with EVA to improve adhesion to PEI primer
  - Even with ozone, some applications demand improved water resistance

New Aqueous Primers

- Coextrusion "tie-layer" terpolymers, *emulisified*
- Formulated for enhanced adhesion and moisture resistance

Terpolymer Emulsions

1. Ethylene — $CH_2=CH_2$
2. Alkyl Acrylate — $CH_2=CH\text{-}COOR$
3. Maleic Anhydride



Mysterious Ingredients

PRIMER

About the primers (continued)

- Aqueous, low viscosity liquid
- 4 to 5% solids
- Apply about 0.08 dry g/m2 via gravure
- Dry thoroughly with hot air
- Acceptable for use in food packaging

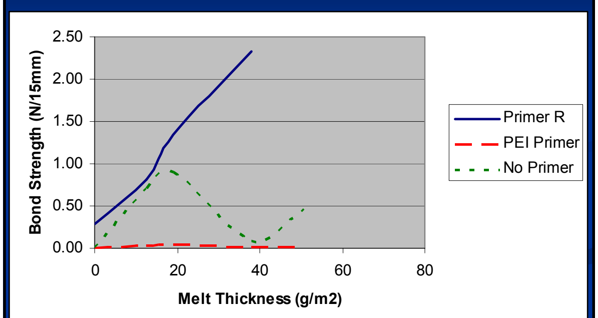
Objectives of Study

1. Identify a film/EVA primer that does not need ozone for adhesion
   - Some converters do not have ozone, or choose not to use it.

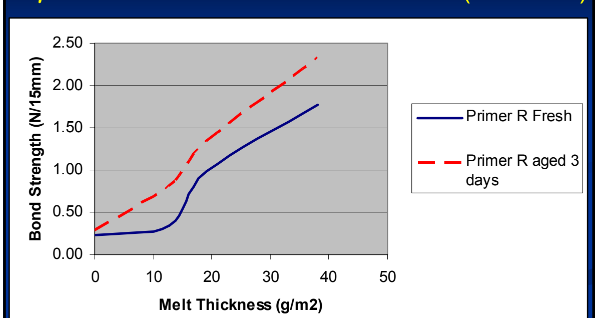
Lab Extrusion Tests

- 25mm wide Randcastle Extruder
- Screw 2.5 cm
- Line speed about 15 m/m
- Melt temperature 230°C
- EVA resins varied 16 – 22% VA

Comparison of Primer R with PEI and no primer
50μ BOPET/primer/EVA extrudate (no ozone)

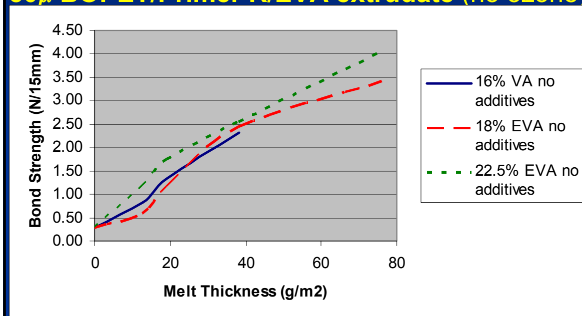


Influence of melt thickness on adhesion
50μ BOPET/Primer R/EVA extrudate (no ozone)



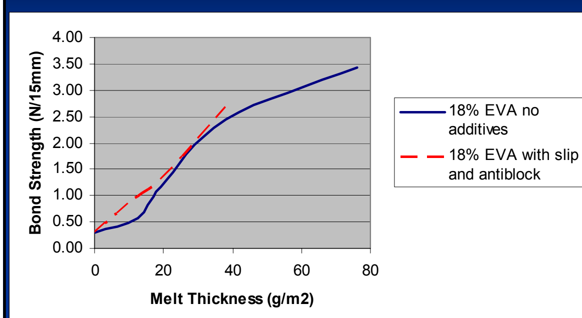
Influence of vinyl acetate content on adhesion with Primer R

50μ BOPET/Primer R/EVA extrudate (no ozone)



Influence of Resin Additives on Primer Adhesion

50μ BOPET/Primer R/EVA extrudate (no ozone)



Off-Machine and Lamination Performance: Primer R

- Off-machine bond strength slittable
  - bond strength improves with melt thickness
- Bond strength after lamination is *inseparable*
- Compared to conventional PEI type primer on film/primer/EVA
  - Equivalent bond strength WITHOUT ozone

Objective 1 Summary: Primer R

- WITHOUT ozone, bond strength of Primer R is much better than PEI primer
- Higher melt thickness produces higher off-machine bonds
- Higher VA content produces higher off-machine bonds
- Slip and antiblock additives did not harm adhesion
- Lamination performance of Primer R WITHOUT ozone is equivalent to PEI WITH ozone
  - Inseparable adhesion

Objectives of Study

1. Identify a film/EVA primer that does not need ozone for adhesion
   - Some converters do not have ozone, or choose not to use it.
2. Identify a film/EVA primer and process that will yield improved water resistance
   - Though ozone can enhance adhesion, water resistance with PEI is not perfect.

Primer M

- Similar to primer R, but requires ozone assistance
- Compared to conventional PEI type primer
  - Much better water resistance
  - Passes severe service test

Severe Service Test

1. Condition samples
   - 70 C
   - 95% RH
   - 5 days

   } This is the hard part!
2. Shake with sand ← This is the easy part.

For our work, we tested step 1

Experimental – Laboratory Tests

- Drew down primers with #3 wire wound rod onto OPET and BOPP
  - Compared standard PEI primer and experimental Primer M
- Dried thoroughly
- Heat sealed to EVA film
  - EVA was corona treated to simulate ozonation
- Measured green bond strength - inseparable
- Conducted severe service test

Results on Treated BOPET Film Severe Service Test

Primer	EVA Film	Green Bond after heat sealing*	Adhesion after Severe Service Test (N/15mm)
PEI	Untreated	Inseparable	1.7
Primer PEI	Treated	Inseparable	2.3
Primer M	Untreated	Inseparable	4.1
M	Treated	Inseparable	Inseparable

*Heat sealed face-to-face (EVA to EVA) at 120C for 5 seconds

Results on Treated BOPET Film Water Soak

Primer	EVA Film	Green Bond after heat sealing*	Adhesion after 24 Hour Water Soak (N/15mm)
PEI	Treated	Inseparable	1.2
Primer M	Untreated	Inseparable	0.9
Primer M	Treated	Inseparable	4.1

*Heat sealed face-to-face (EVA to EVA) at 120C for 5 seconds

Objective 2 Summary: Primer M

- Primer M out-performed PEI primer with and without ozone
- Primer M survived severe service humidity conditioning with ozone assistance

The Next Step

- Primer R-1 variant for aluminum foil substrates
- Lab tests show foil/Primer/EVA adhesion promising
- Potential application: peelable cup and lidding stock?
- Scale up tests in progress

Summary

- Primer R for film/primer/EVA
  - Comparable performance to PEI primer, but does not need ozone assist
- Primer M for film/primer/ozone/EVA
  - Better water resistance than PEI primer
  - Out performs PEI primer in severe service tests
- Primer R-1 for aluminum foil substrates
- Note: we expect equivalent performance to PEI on high temp melts such as LDPE

12uOPET/primer/25u EVA (18%)

Property	PEI Primer (Standard)	Primer R	Primer M
Composition	PEI	Terpolymer Emulsion	Terpolymer Emulsion
Ozone to EVA	Yes	No	Yes
Off-Machine Bond Strength	Fair	Fair	Fair
Bond Strength after thermal lamination	Excellent	Excellent	Excellent
Water Resistance	Fair	Fair	Excellent

Thank you.