Thermodynamic Parameters for Predicting Adhesion Between Functional Polyethylenes to Polystyrene Copolymers

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ABSTRACT:

Polystyrene and polystyrene copolymers have many unique properties that make them desirable for use in flexible packaging. Polystyrene monofilms however are not practical for use on high-speed packaging lines due to their poor heat sealability and flex cracking. Coextruded films of polystyrene with polyethylene combine the desirable properties of polystyrene with polyethylene. Still, PS coextrusions with PE are not commonplace due partly to the manufacturing challenges and partly due to the paucity of adhesives that can bond PE to PS in coextruded films.

This paper focuses on the adhesion challenges at the PS-PE interface. We will review fundamental principles of adhesion at the coex interface, present results from adhesion screening studies of a styrene-acrylic copolymer with various polyethylenes and investigate the use of thermodynamic parameters as an aid to predict or estimate the magnitude of chemical bonds at the interface. The specific approach is based on the early work of Fowkes who forwarded the theory that interfacial adhesion is fundamentally governed by Acid-base interactions and dispersion forces.

INTRODUCTION

Extrudable polystyrenes have many properties that make them desirable for flexible packaging applications. Some of these properties include; optical clarity, dimensional stability, stiffness, high oxygen permeability, resistance to scuffs, strength and thermo-formability. Polystyrene use in flexible packaging films however has been limited due to inherent deficiencies such as poor heat sealability, low flex crack resistance and low tear resistance. These deficiencies can often be overcome by co extruding the polystyrene with a polyethylene to capture the best mutual properties of both materials.

Polystyrene-Polyethylene film coextrusions however are rare due in part to the challenge of finding an adhesive to bond a given polystyrene and polyolefin together in a thin film. While there are a limited number of commercial adhesives designed for polystyrene-polyethylene coextrusions, they are typically expensive, only bond to a limited range of polystyrene copolymers available, and are difficult to process or give rheological mismatches in the coextrusion.

An existing flexible packaging application where the properties of polystyrene and polyethylene are synergistic is breathable films for fresh-cut produce. The optical clarity, surface gloss, high gas transmission rates and stiffness of polystyrene combined with the heat sealability, tensile properties and melt strength/processability of polyethylene create a unique film for retail fresh cut produce packages. An emerging need in the fresh cut produce industry is for converter films that can bond to thermoformed polystyrene trays. Polystyrene based lidding film containing a polyolefin based peelable sealant could again combine the unique properties of polystyrene and polyethylene to create a unique lidstock replacing more expensive rigid lids and specialty lidding films.

The types of polystyrenes and polyethylenes that can be used in these two applications are limited by the relatively limited choice of commercial adhesives. If a broader range of adhesives were identified that could bond to specific polystyrene types and polyethylenes the use of polystyrene and other non-polyolefins (polyesters, PC, ABS etc) in flexible packaging could grow significantly giving rise to new classes of value added films.

Screening potential adhesives by running trials on commercial film lines is often cost prohibitive. An alternate approach is use a combination of small scale or laboratory pre-screening in conjunction with predictive modeling to identify potential adhesives along with fundamental material properties that lead to good interfacial adhesion.

Predictive modeling approaches

Adhesive modeling is inherently difficult due to multiple independent material properties that can affect interfacial bond strength. For polymer-polymer interfaces, one can broadly classify factors into polymer chemical and mechanical properties of the substrate and adherend polymers. While mechanical properties affect the amount of energy required to separate or peel apart an interfacial bond, the type and degree of chemical attractions across the interface govern the actual adhesive bond strength holding together the two polymers. (Possible exception includes polymer chain entanglement).
One should theoretically be able to predict these chemical attractive forces by thermodynamic fundamentals.

One thermodynamic approach that has successfully predicted polymer-solvent compatibility is matching Hansen's three component solubility parameters. Hansen separated Hildebrand's solubility parameter into three distinct components associated with the bond energies of specific chemical interactions; □d (London dispersion or dispersive force component), □p (polar component) □p (hydrogen bonding component). They are based on the concept that like dissolves like. The component solubility parameter parameters can be used to the predict the heat of mixing for various blends of two materials:

$$\Delta Hm = C\{(\delta_1 d - \delta_2 d)^2 + (\delta_1{}^p - \delta_2{}^p)^2 + (\delta_1 h - \delta_1 h)^2\}^{1/2}$$

Where subscript 1 and 2 correspond to the individual materials, and C is a conversion constant. Numerous studies have shown that the similarity component solubility parameters correlate well with solubility and/or compatibility of several polymer-solvent combinations. A convenient tool for estimating compatibility is treating the three parameters as a point on a three-dimensional chart and "mapping" or calculating the geometric distance between two components.

Fowkes demonstrated that dispersive force contributions to surface tensions and solubility parameters provide an accurate estimate of London dispersion forces. However, many polar and hydrogen bonding attractive forces important in adhesion could be estimated more accurately if they are considered subsets of Lewis acid-base interactions. Fowkes proposed using Drago E and C constants to quantify the enthalpy of acid-base interactions at interfaces.

$$W_a = 2(\gamma_a{}^d \gamma_b{}^d)^{1/2} + k(C_A C_B + E_A E_B)(\text{moles of acid-base / unit area})$$

$\gamma_a d$ = Dispersive force contribution to surface tension
E_A - Drago electrostatic constant for acidic polymer
E_B - Drago electrostatic constant for basic polymer
C_A - Drago covalent bonding constant for acidic polymer
C_B - Drago covalent bonding constant for basic polymer

This approach has been shown to predict interfacial adhesion for many substrate adherend pairs more accurately than simply matching solubility parameters. It has been especially useful for Chlorinated polymers and solvents that have strong acid-base interactions but do not exhibit typical hydrogen bonding.

The primary purpose of this study was to screen and identify commercial polyolefins that could be used as adhesives for a Styrene-Methyl Acrylate copolymer and a Styrene-Maleic Anhydride Copolymer. The secondary objective was to investigate the usefulness of the Hansen and Fowkes approaches involving

solubility parameter matching and Drago E and C constants as aids to predict interfacial adhesion between the polystyrenes and polyolefins.

MATERIALS AND METHODS

Materials

Two commercial polystyrene copolymers, both produced by NOVA Chemicals Corporation, were used as test substrates in this study. Zylar® EX 720 is a Styrene/Methyl Acrylate copolymer and Dylark® FG 2500 is a Styrene/Maleic Anhydride copolymer.

Sixteen polyethylene copolymers or grafted tie resins were tested as general adhesives to the two polystyrene copolymers. The grades were selected on the basis of functional comonomer or graft type, commercial availability, ability to process on conventional film extrusion equipment, and relatively low cost. It is important to note that several of the grades used were blends of produced by the supplier or on a lab compounding line and contained mixed functional groups, maleic anhydride grafts and/or Elastomeric modifiers that are generally known to increase adhesive peel force. Details of the sixteen copolymers are provided in Charts 14 and 15. Adhesives were classed into the five groups according to their chemical functionality.

Test Sample Preparation and Adhesion Testing

The polystyrene copolymers were converted into 15-mil monolayer sheet and test adhesives were converted into 6 mil monolayer films on small cast film line with 10-inch die. One-inch test strips to be used for adhesion testing were cut from the center of the film or sheet in the machine direction.

Surfaces of the substrate and adhesive were wiped with acetone to remove possible contaminates. Three-inch long strips of the adhesives films were laminated to the polystyrene sheet by heat-sealing in a conventional heat-sealer at 155^{o} C seal temperature (upper and lower jaw), under 0.270 N/mm2 seal pressure and 1.0-second dwell time. The total seal area was approximately 1.0 square inch. A 3-mil oriented polyester film was placed between the adhesive and seal jaws to prevent sticking to the heated platen.

The force required to delaminate the adhesive from the polystyrene test substrate was measured using a standard tensile tester and load cell. The unsealed area of the polystyrene sheet was attached to the bottom jaw and the adhesive film was placed in the upper jaw to give a 180^{O} peel. Samples were separated at a rate of 12 inches/minute. Triplicate samples were tested for each adhesive-substrate combination. Additional tests were conducted for adhesive-substrate combinations where the range of peel forces for a three-sample set was more than 0.5 Newton.

Determination of Solubility Parameters

Dispersive, polar and hydrogen bonding solubility parameters were estimated using group contribution methods. The values were verified by measuring surface tensions of the test samples with various solvents with known solubility parameters. Estimated values showed relatively close matches with published values for similar polymers.

Drago E and C constants were not measured for the polymers used in this study. Accurate determination of Drago constants for polymers is an involved process that requires dissolution, coupling with a series of materials of known E and C constants and FTIR spectral shifts. The results from this study did not show increased adhesion between polymers containing acidic and basic functionalities.

RESULTS AND DISCUSSION

Average adhesive peel forces for each adhesive-polystyrene pair are presented in Charts 17 - 22. Adhesive films typically delaminated evenly from the polystyrene substrate until peel force reached or exceeded 12 Newtons (N). Above 12 N the adhesive sample elongated and peel was erratic and 12 N was therefore considered the maximum consistent peel force.

Adhesion Results

The ethylene vinyl acetate copolymers showed varying levels of adhesion to both the styrene/methyl acrylate and styrene/maleic anhydride copolymers. As expected, the level of vinyl acetate impacted adhesion levels with samples containing higher vinyl acetate (VA) generally having higher adhesion. Two exceptions to this trend were for the 28% VA copolymer and the EVA blends.

The 28% vinyl acetate showed only slightly higher bond strength to styrene/methyl acrylate compared to the 18% VA copolymer and less adhesion to the styrene/maleic anhydride copolymer. This may partially be due to a saturation effect where diminishing adhesion improvement occurs above 18% VA. Also, while the 28% VA sample appeared to peel consistently, it had higher elasticity modulus and appeared to elongate more which could result in lower apparent adhesion.

The blend of two EVA copolymers (80%/20% blend of two EVA copolymers containing 18% and 9% vinyl acetate) had higher bond strengths than the 18% or 28% VA copolymers despite having lower final vinyl acetate concentration. This is likely due to a toughening effect of the minor 9% VA copolymer. The 9% VA copolymer chains are believed to intimately blend with the major 18% VA copolymer and enhance the tensile mechanical properties of the blend without sacrificing bond strength. Further addition of maleic anhydride graft and elastomeric modifiers further improved the adhesion to styrene-methyl acrylate copolymer. (Sample EVA-EVA blend with maleic and elastomer).

The other copolymer samples showed varying adhesion results. The two ethylene-acid copolymer samples had very low adhesion to both polystyrene types. One might expect the acrylic and methacrylic acid functional groups to undergo bonding interactions with the more basic acrylate functional groups. The ethylene methyl acrylate copolymer and EVA-EMA blends however showed had the maximum adhesion of 12 N to both polystyrene types.

Linear low density based tie resins also showed varying adhesion results. All of the LL tie resins had low adhesion to the styrene-maleic anhydride copolymer despite the presence of maleic anhydride in both the tie resin and the styrene copolymer. Adhesion to the styrene-methyl acrylate copolymer varied. The elastomer-modified grades all had higher bond values and the hexene sample modified with an elastomer b was significantly better at 5.2 N.

Correlation of adhesion with Solubility Parameter Distance Mapping and Drago E & C Constants

Adhesion results and calculated distances on the three-dimensional solubility parameter map are summarized graphically in Charts 23 and 24. The results for the styrene-maleic anhydride combinations showed a characteristic cascade increase as the distance dropped below 3.4. Based on similar classes of adhesive polymers, one would expect the distance on a three dimensional solubility parameter map should be less than 3.4 in order to obtain significant adhesion to this type of styrene maleic anhydride substrate.

The results for the styrene-methyl acrylate copolymers did not show this definitive cascade point. When classes of materials are considered separately (i.e. EVA copolymers and LLDPE tie resins) there is a general trend of higher adhesion for combinations with lower solubility parameter distances. The two acid copolymers showed lower adhesion than the EVA samples despite the relatively low solubility parameter distances.

The adhesion results from this study did not infer the presence of acid-base interactions that would increase interfacial bond force. The styrene, acrylate and anhydride functionalities in the styrene copolymers tend to be basic and would likely interact with the acid functionality in the acid copolymers. If these acid-base interactions or reactions did occur, it did not result in significant bonding and increased adhesion across the polystyrene-acid copolymer interface.

CONCLUSIONS

Predicting adhesion between two polymers in a laminate or coextrusion is difficult due to the many chemical and mechanical properties of the substrate and adhesive polymer that affect the ultimate bond strength. A key chemical consideration is the type and level of functional components in the polymer adhesive and substrate and the degree of interaction between functionalities across an interface. Matching Hansen's component solubility parameters is a convenient approach for directionally predicting interaction and thus adhesion of polyolefins with similar functionalities to polystyrene copolymers.

Specific acid-base interactions across polymer interfaces can improve adhesion. While the results of this study did not show evidence of interfacial acid-base bonds being formed, acid-base interactions are important and should be considered in polymer adhesive design. Also, the use of Drago E and C constants for predicting these interactions needs to be explored with a broader range of polymers.

REFERENCES

1. Hansen, Charles (2000) *Hansen Solublity Parameters; A users's handbook*. Boca Raton, Fla: CTC Press ISBN 0849315255.
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5. van Krevelen, D.W. *Properties of Polymers*, 3rd Ed., Elsevier, New York, 1990, Ch. 7.

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Presented by:

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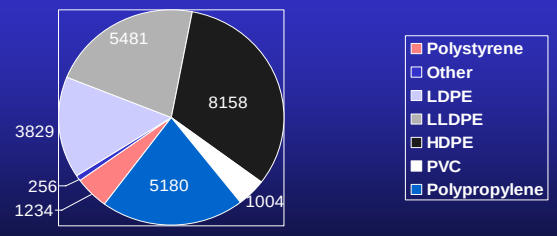
NOVA Chemicals

Thermoplastic Polymers Used in U.S. Packaging (millions of pounds)



Source: American Plastics Council; 2006 United States Resin Review

Polystyrene Properties for Flexible Packaging

Positives

- Excellent optics
- Stiffness, strength and dead-fold properties
- High gas permeation rates
- Surface functionality with certain inks
- Temperature resistance

Challenges

- Poor adhesion to polyolefins used in conventional film extrusion
- Heat sealability
- Low melt strength
- Flex crack and stress whitening

Packaging Applications Requiring Polystyrene-Polyolefin Adhesion

Film Lidstock for Polystyrene Trays

- Applications: high clarity, light-weight lidding film
- Benefits: material reduction, hermetic seals

PS/Polyolefin Coextruded Film

- Applications: high clarity, breathable films
- Benefits: retail optics, longer produce shelf-life

Identifying Adhesives for a New Substrate

DOE
Iterative Process

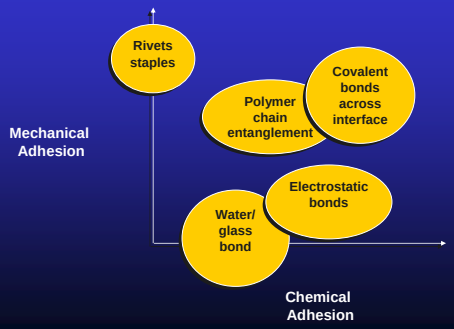
Ideal Screening

- ✓Rapid results
- ✓Low cost
- ✓Numerous inputs

Ideal Modeling

- ✓Based on proven fundamentals
- ✓Flexible

"No unifying theory exists that describes all interfacial bonds" *



*Douglas J. Gardner: University of Maine

Modeling Approach 1
Matching Hansen Solubility Parameters

Theory:

Adherends with solubility parameters similar to PS will have lower heat of mixing and a higher degree of interfacial chain entanglement.

δ^d = Dispersive component of Solubility Parameter
δ^p = Polar component of Solubility Parameter
δ^h = Hydrogen bonding component of Solubility Parameter

Heat of solution prediction

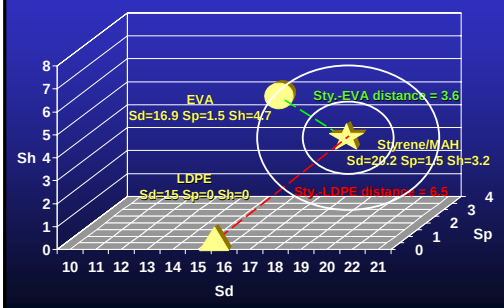
$$\Delta H_m = c\{(\delta_1^d - \delta_2^d)^2 + (\delta_1^p - \delta_2^p)^2 + (\delta_1^h - \delta_2^h)^2\}^{1/2}$$

"Distance" on Solubility Map

$$D_{(1-2)} = [a(\delta_1^d - \delta_2^d)^2 + b(\delta_1^p - \delta_2^p)^2 + c(\delta_1^h - \delta_2^h)^2]^{1/2}$$

δ_1 = component solubility parameter for test polystyrene
δ_2 = component solubility parameter for test adherend
a,b,c = empirical constants

Solubility Parameter Distance Mapping



Modeling Approach 2 - Fowkes
Maximizing Specific Acid-Base Interactions

Theory:

Adherends and substrates with complimentary E and C constants will form stronger bonds across the interface.

$$W_a = W_a^d + W_a^{ab}$$

$$W_a^d = 2(\gamma_A^d \gamma_B^d)^{1/2}$$

$$W_a^{ab} = k(C_A C_B + E_A E_B)(\text{moles of acid-base / unit area})$$

E_A - Drago electrostatic constant for acidic polymer
E_B - Drago electrostatic constant for basic polymer
C_A - Drago covalent bonding constant for acidic polymer
C_B - Drago covalent bonding constant for basic polymer

Importance of Acid-base Bond Formation Across EVOH / Tie-Resin Interfaces

Model System:

Ethylene Vinyl Alcohol (38 mol% ethylene)

Tie resin (Maleic anhydride modified LLDPE)

$W_a = W_a^d + W_a^{ab}$

$W_a^d = 2(\gamma_A^d \gamma_B^d)^{1/2} = 0.006$ J/cm

$W_a^{ab} = k(C_A C_B + E_A E_B)(0.0000001) = 0.22$ J/cm

*assumes 0.1% of bond area is occupied by acid-base pairs

Objectives

- **Evaluate commercial polyolefins, adhesives and tie resins for adhesion to PS-Methyl Acrylate copolymer and PS-Maleic Anhydride Copolymer**
- **Evaluate component solubility parameters and Drago's E and C constants as aids to predict interfacial adhesion between the polystyrenes and polyolefins used in this study**

Polystyrene Copolymer Test Substrates

Type	Grade	Supplier
Styrene Methyl Acrylate Copolymer	**Zylar® EX 720 15 mil Sheet**	**NOVA Chemicals Corporation**
Styrene Maleic Anhydride Copolymer	**Dylark® FG 2500 15 mil Sheet**	**NOVA Chemicals Corporation**

Zylar® is a registered trademark of NOVA Chemicals Corporation.
Dylark® is a registered trademark of NOVA Chemicals Corporation.

Adhesive Test Films

Group 1 – Ethyl/ Vinyl Acetate Functionality

EVA 12% - 12 weight % Vinyl Acetate Content. Tubular reactor
EVA 18% - 18% Vinyl Acetate Content. Tubular reactor
EVA 28% - 28% Vinyl Acetate Content. Autoclave reactor
EVA Blend - Blend of EVA #1 and EVA #2. 16% Vinyl Acetate Content final

Group 2 – Ethyl/ Methyl Acrylate Functionality

EMA - Ethylene Methyl Acrylate Copolymer, 22% Methyl Acrylate Content, 2 MI

Group 3 – Acid Functionality

EAA - Ethylene Acrylic Acid Copolymer - 9.7% Acrylic Acid, 5 MI
EMAA - Ethylene Methyl Acrylic Acid Copolymer – 9% Methacrylic acid, 10 MI

Adhesive Test Films

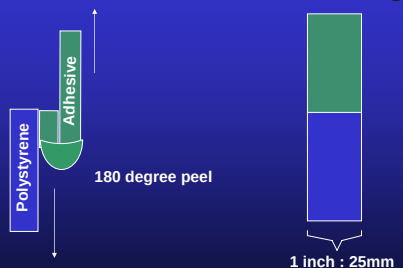
Group 4 – EVA Blends

EVA Tie Resin # 1: EVA - 9% VA Copolymer with Maleic Anhydride (MAH) modification
EVA Tie Resin # 2: EVA blend modified with MAH and elastomer
EVA Tie Resin # 3: EVA - 18% VA Content blended with Ethylene Methacrylic Acid Copolymer

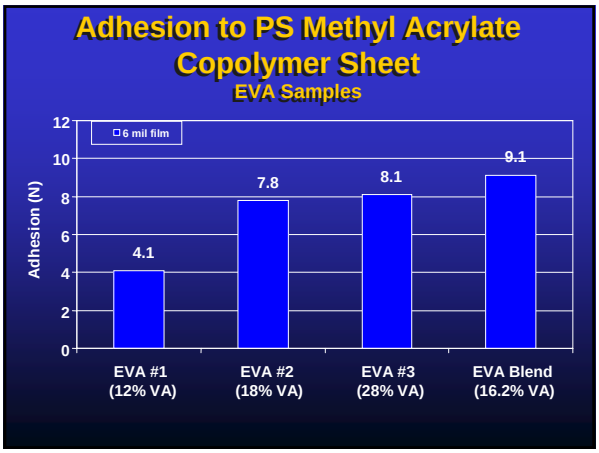
Group 5 – Linear Low Density PE with Maleic Anhydride Functionality

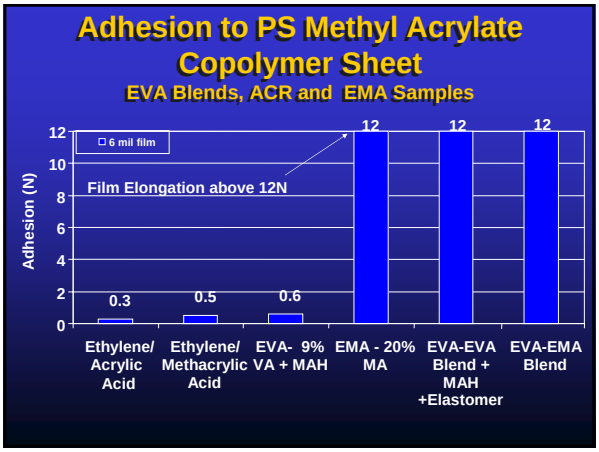
Butene LLDPE with low levels of MAH modification
Butene LLDPE with medium level of MAH modification
Butene LLDPE with high level of MAH modification
Butene LLDPE blended with elastomer A and medium level of MAH modification
Hexene LLDPE blended with elastomer A and medium level of MAH modification
Hexene LLDPE blended with elastomer B and high level of MAH modification

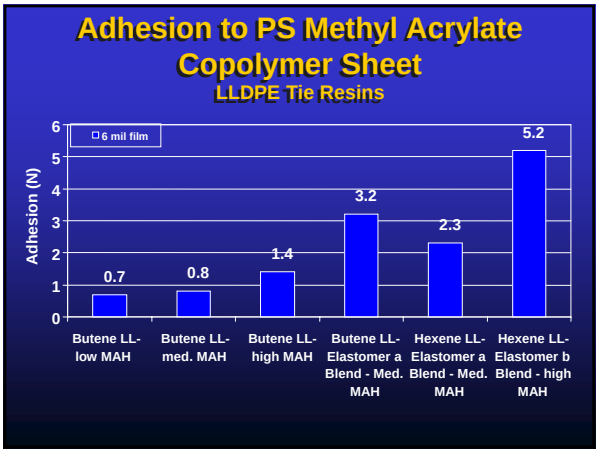
Adhesion Screening
Heat Seal, T-Peel Adhesion Testing

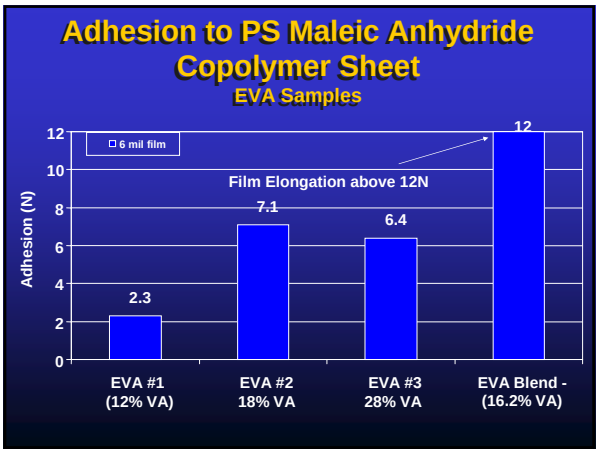


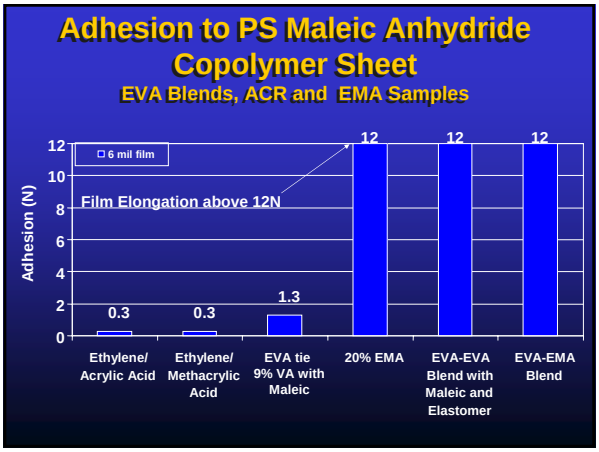
- 155º C seal temp. (upper and lower jaw)
- 0.270 N/mm^2 seal pressure
- 1.0 second dwell time
- 12 in/min separation rate

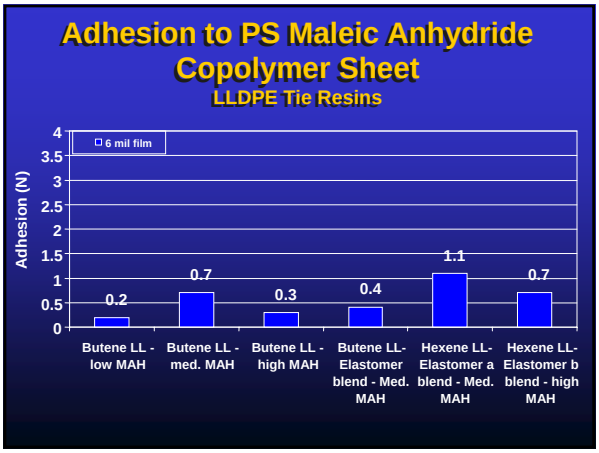

Adhesion to PS Methyl Acrylate Copolymer Sheet
EVA Samples
6 mil film
Adhesion (N)
12
10
8
6
4
2
0
4.1
7.8
8.1
9.1
EVA #1 (12% VA)
EVA #2 (18% VA)
EVA #3 (28% VA)
EVA Blend (16.2% VA)


Adhesion to PS Methyl Acrylate Copolymer Sheet
EVA Blends, ACR and EMA Samples
6 mil film
Film Elongation above 12N
Adhesion (N)
12
10
8
6
4
2
0
0.3
0.5
0.6
12
12
12
Ethylene/ Acrylic Acid
Ethylene/ Methacrylic Acid
EVA- 9% VA + MAH
EMA - 20% MA
EVA-EVA Blend + MAH +Elastomer
EVA-EMA Blend

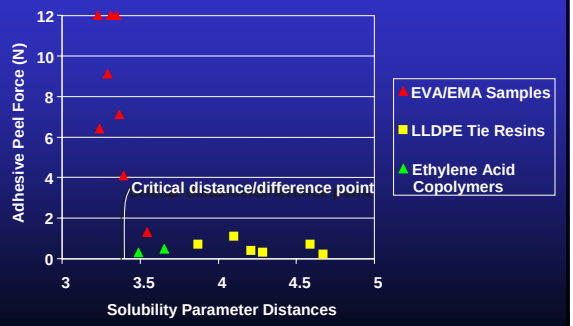

Adhesion to PS Methyl Acrylate Copolymer Sheet
LLDPE Tie Resins
6 mil film
Adhesion (N)
6
5
4
3
2
1
0
0.7
0.8
1.4
3.2
2.3
5.2
Butene LL- low MAH
Butene LL- med. MAH
Butene LL- high MAH
Butene LL- Elastomer a Blend - Med. MAH
Hexene LL- Elastomer a Blend - Med. MAH
Hexene LL- Elastomer b Blend - high MAH


Adhesion to PS Maleic Anhydride Copolymer Sheet
EVA Samples
6 mil film
Film Elongation above 12N
Adhesion (N)
12
10
8
6
4
2
0
2.3
7.1
6.4
12
EVA #1 (12% VA)
EVA #2 18% VA
EVA #3 28% VA
EVA Blend - (16.2% VA)

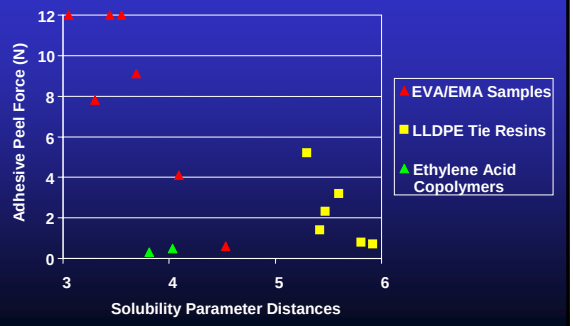

Adhesion to PS Maleic Anhydride Copolymer Sheet
EVA Blends, ACR and EMA Samples
6 mil film
Film Elongation above 12N
Adhesion (N)
12
10
8
6
4
2
0
0.3
0.3
1.3
12
12
12
Ethylene/ Acrylic Acid
Ethylene/ Methacrylic Acid
EVA tie 9% VA with Maleic
20% EMA
EVA-EVA Blend with Maleic and Elastomer
EVA-EMA Blend


Adhesion to PS Maleic Anhydride Copolymer Sheet
LLDPE Tie Resins
6 mil film
Adhesion (N)
4
3.5
3
2.5
2
1.5
1
0.5
0
0.2
0.7
0.3
0.4
1.1
0.7
Butene LL - low MAH
Butene LL - med. MAH
Butene LL - high MAH
Butene LL-Elastomer blend - Med. MAH
Hexene LL-Elastomer a blend - Med. MAH
Hexene LL-Elastomer b blend - high MAH

Adhesion vs. Hansen Parameter Distances
PS Maleic Anydride - Adhesive Combinations



Adhesion vs. Hansen Parameter Distances
PS Methyl Acrylate - Adhesive Combinations



E and C Constants for Polymer Functional Groups

Basic Functionality	Eb	Cb
Methyl Acrylate	1.63	0.95
Styrene (Aromatic)	0.7	0.45
Vinyl Acetate	1.41	0.49
Anhydride	1.86	1.29

Acid Functionality	Ea	Ca
Acrylic Acid	1.72	0.86
Methacrylic Acid	1.68	0.92

Conclusions

- Component solubility parameter matching is a convenient method for directionally predicting adhesion of polyolefins with similar functionalities to polystyrene copolymers.
- The type and level of functional components in the polymer adhesives and substrates along with mechanical properties significantly affect interfacial adhesion and should be considered in adhesive development.
- Specific acid-base interactions across polymer interfaces can improve adhesion. The use of Drago E and C constants for predicting these interactions needs to be explored with a broader range of polymers.

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Thank you

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Please remember to turn in your evaluation sheet...