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2006 PLACE Conference

September 17-21
Cincinnati, Ohio

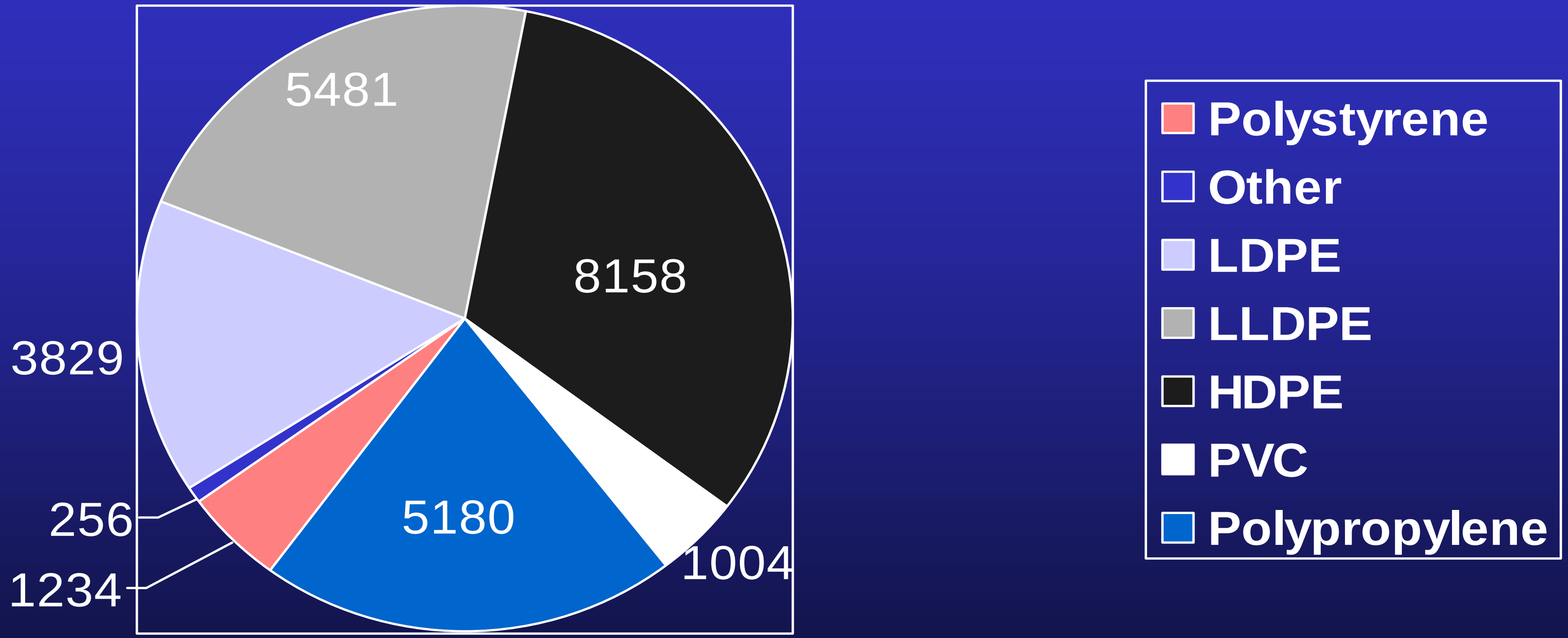
Thermodynamic Parameters for Predicting Interfacial Adhesion Between Polyethylene and Polystyrene

Presented by:

Dan Ward – Technical Service Specialist

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

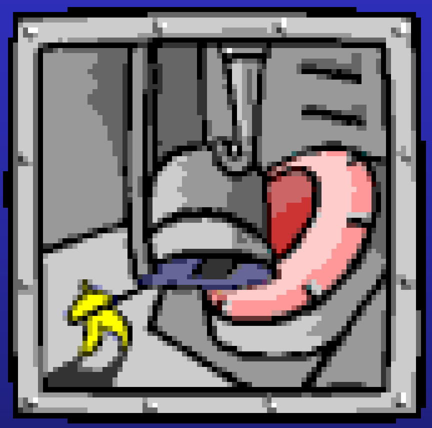
Film Lidstock for Polystyrene Trays

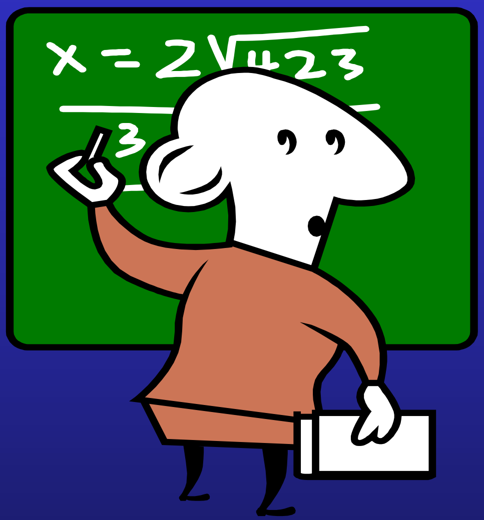
- Applications: high clarity, light-weight lidding film
- Benefits: material reduction, hermetic seals

PS/Polyolefin Coextruded Film

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

Identifying Adhesives for a New Substrate





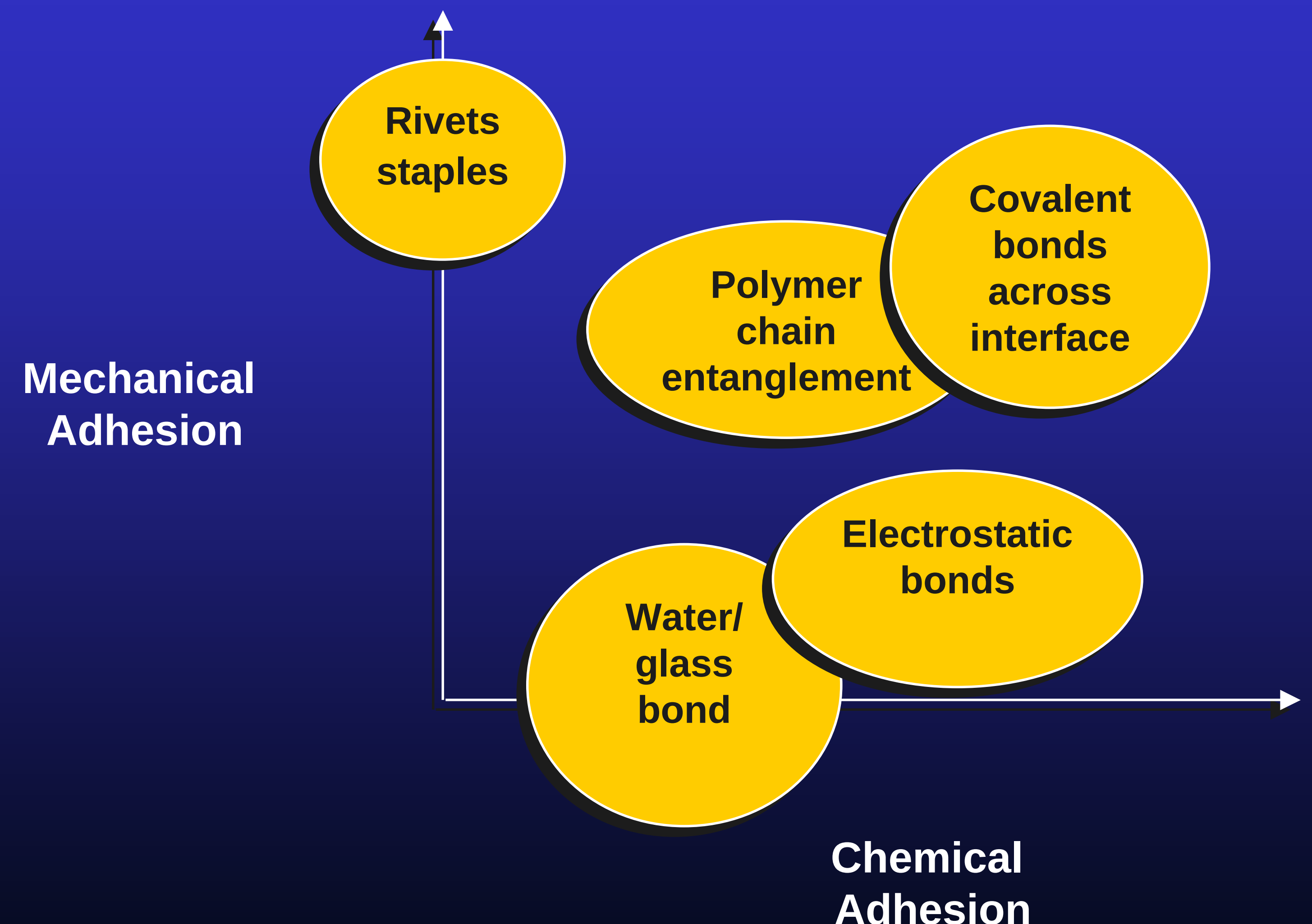
Ideal Screening

- ✓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

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

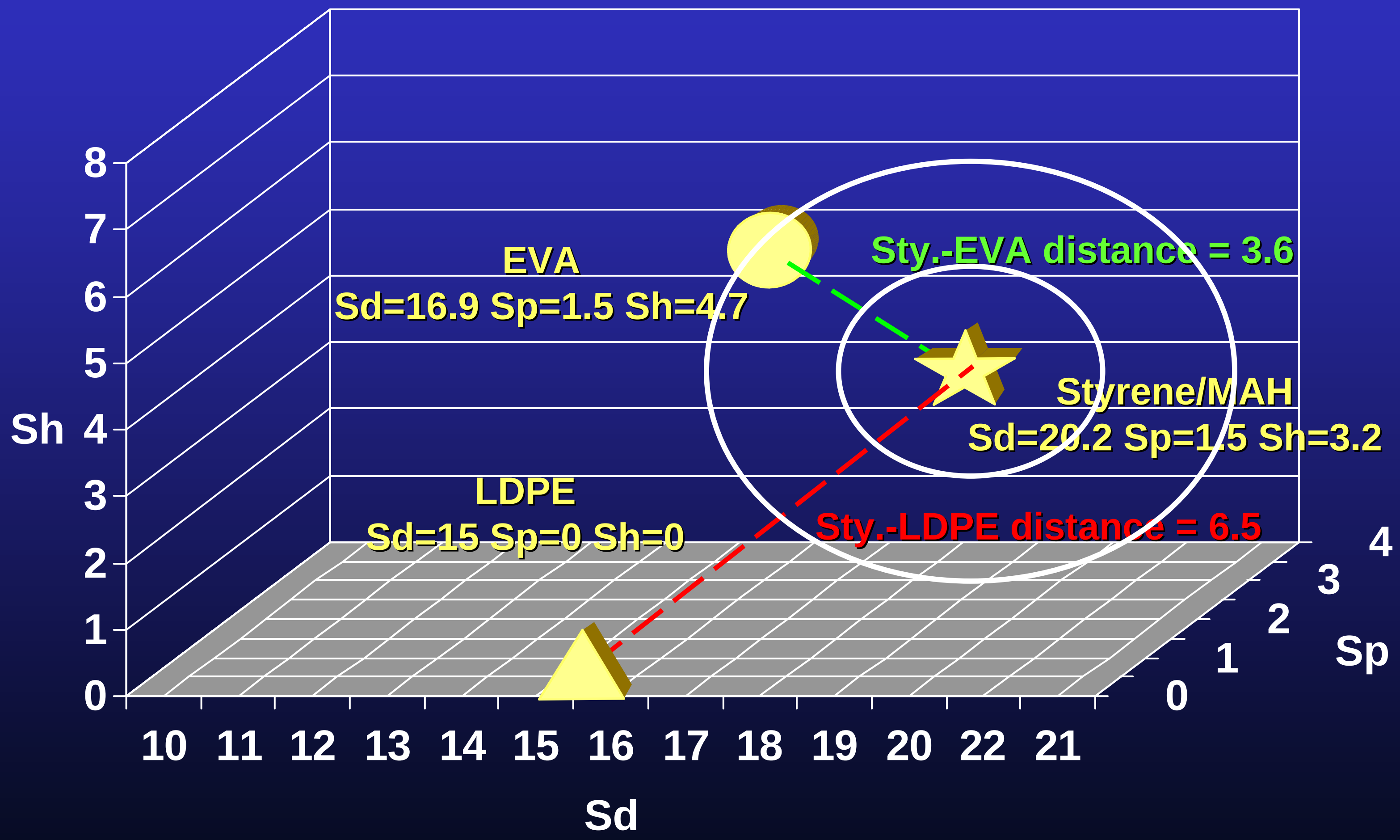
$$D_{(1\text{-}2)} = [a(\delta_1^d - \delta_2^d)^2 + b(\delta_1^p - \delta_2^p)^2 + c(\delta_1^h - \delta_2^h)^2]^{1/2}$$

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)

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

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

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

*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

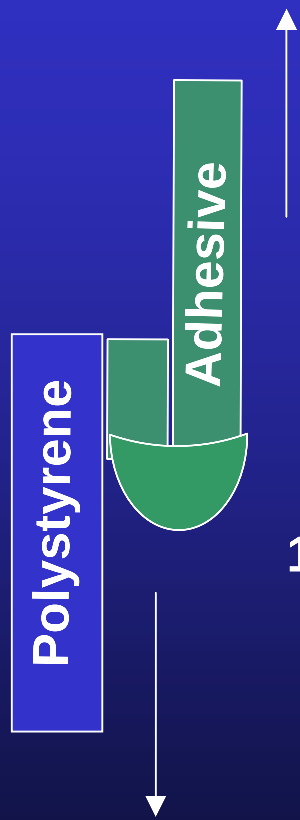
Butene LLDPE with high level of MAH modification

Butene LLDPE blended with elastomer A and medium level of MAH modification

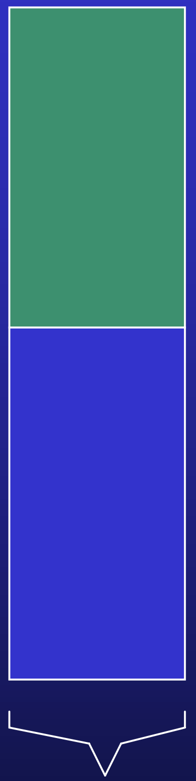
Hexene LLDPE blended with elastomer A and medium level of MAH modification

Hexene LLDPE blended with elastomer B and high level of MAH modification

Adhesion Screening
Heat Seal, T-Peel Adhesion Testing



180 degree peel

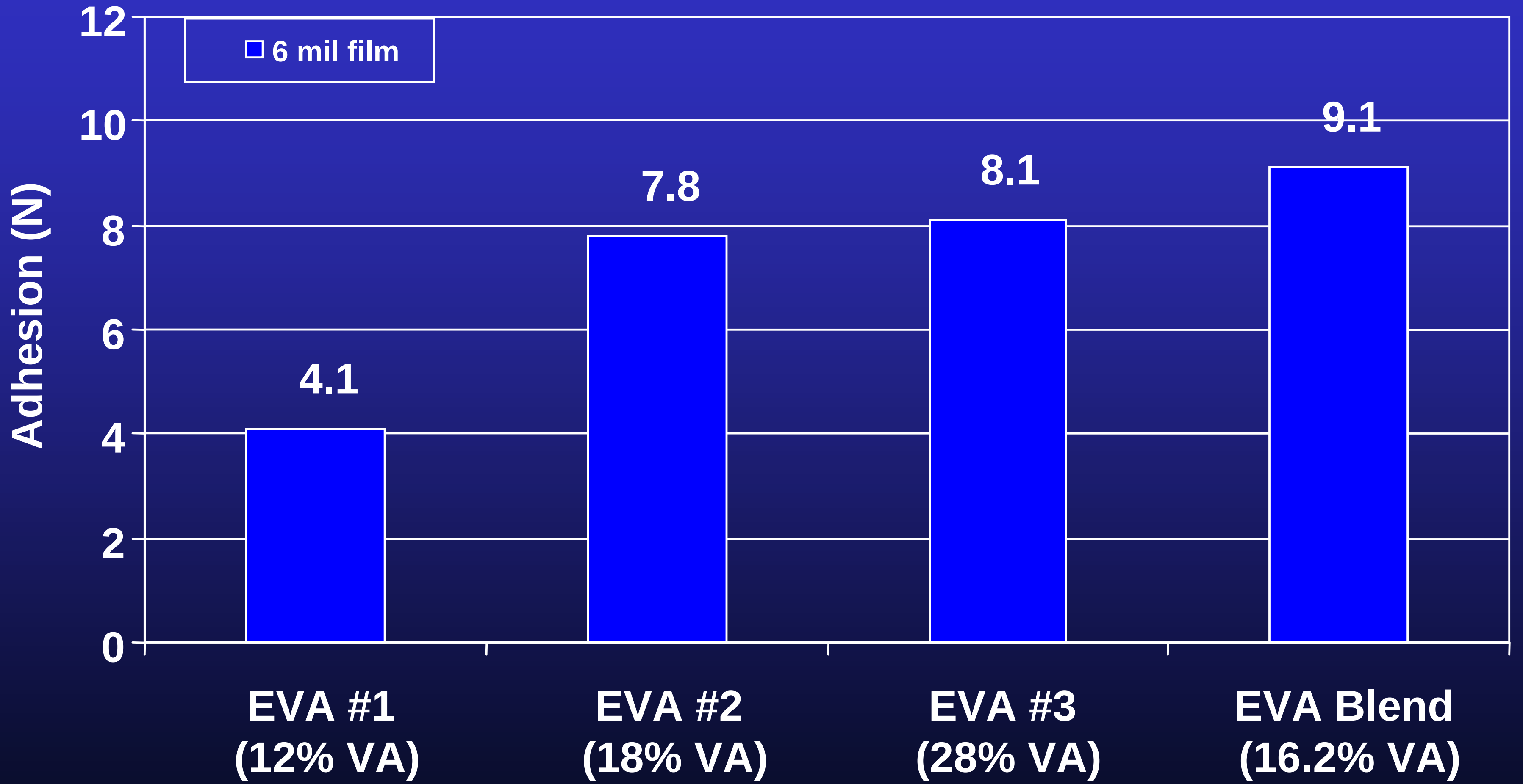


1 inch : 25mm

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

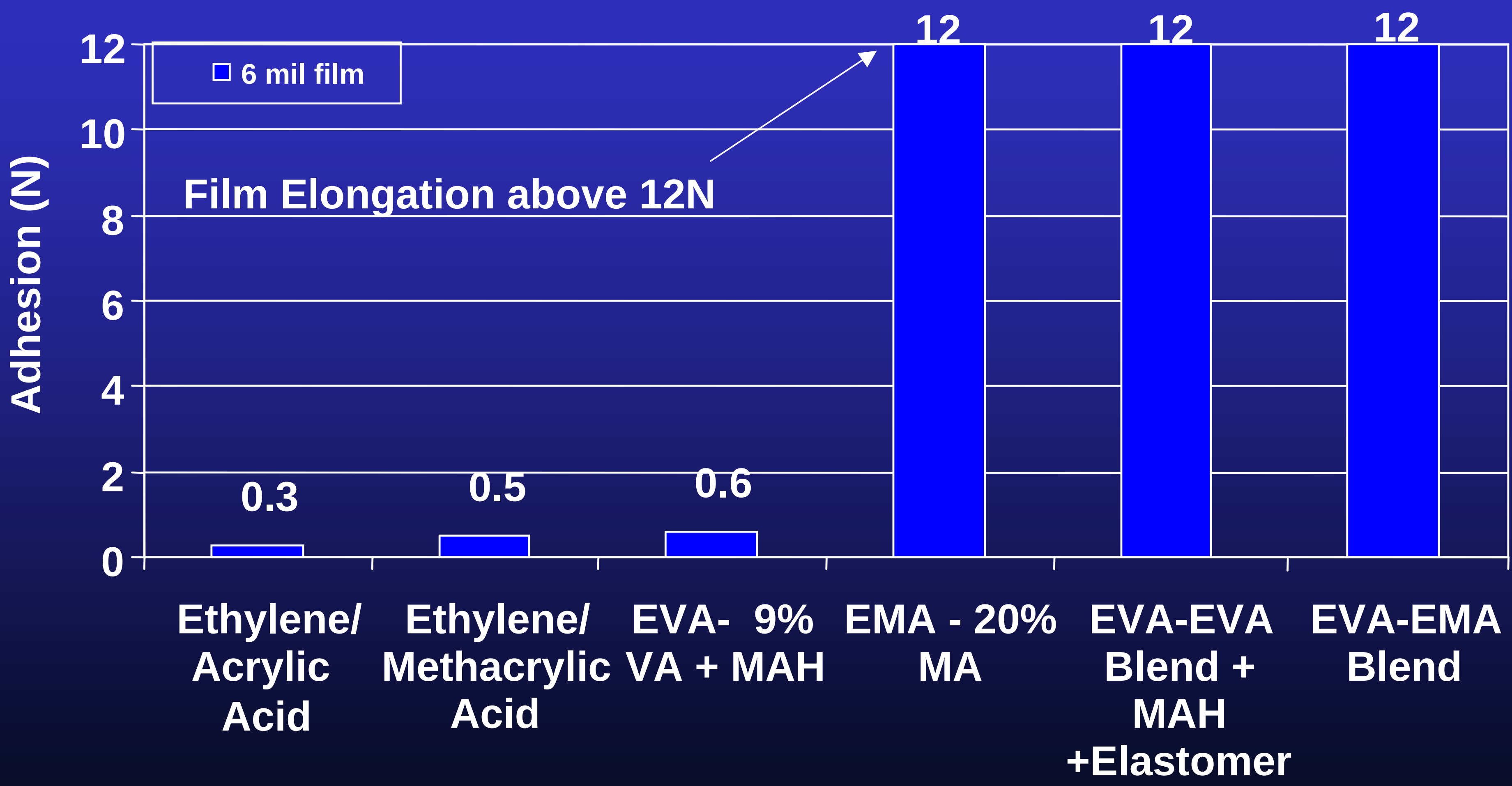
Adhesion to PS Methyl Acrylate Copolymer Sheet

EVA Samples



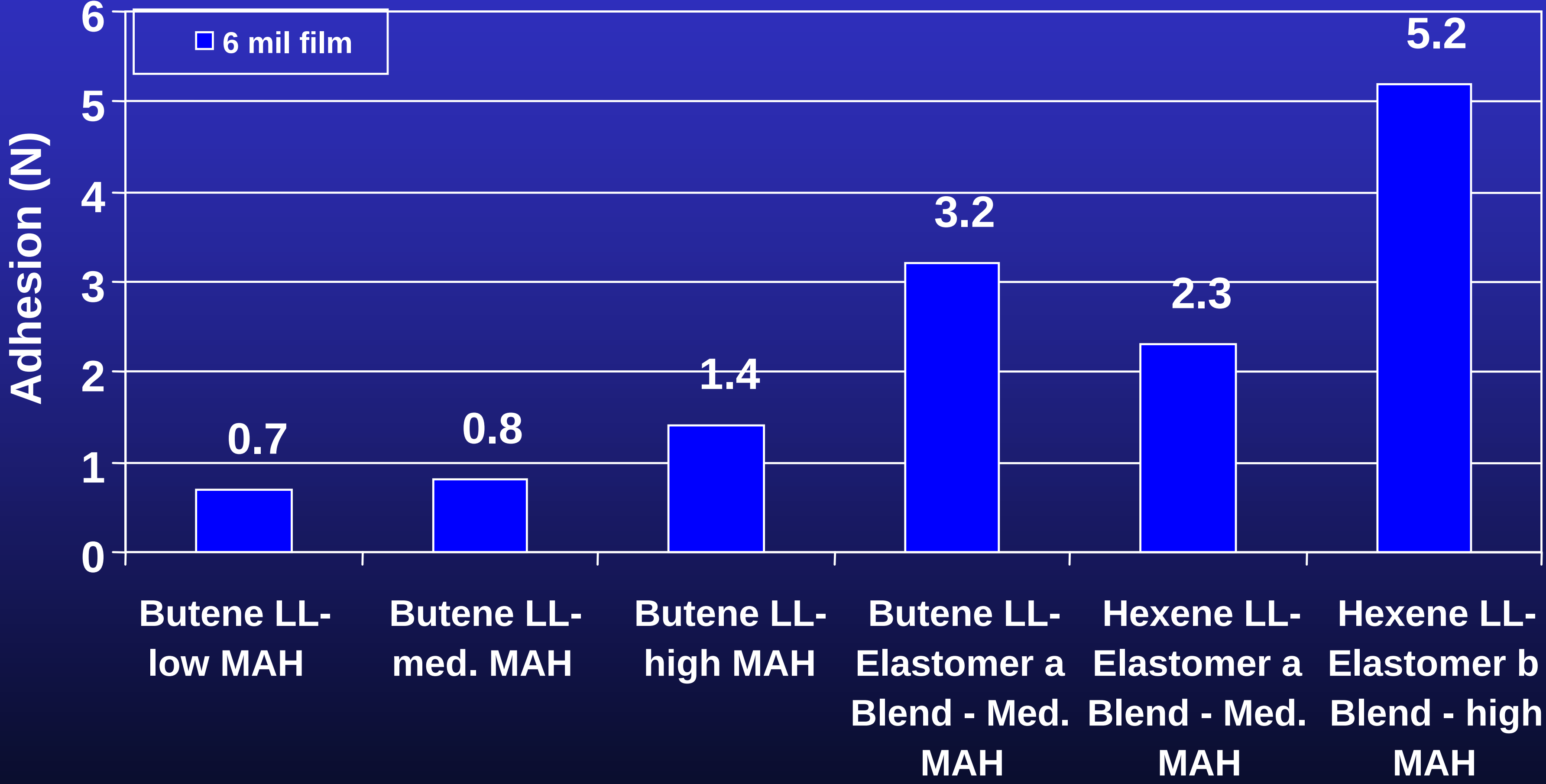
Adhesion to PS Methyl Acrylate Copolymer Sheet

EVA Blends, ACR and EMA Samples



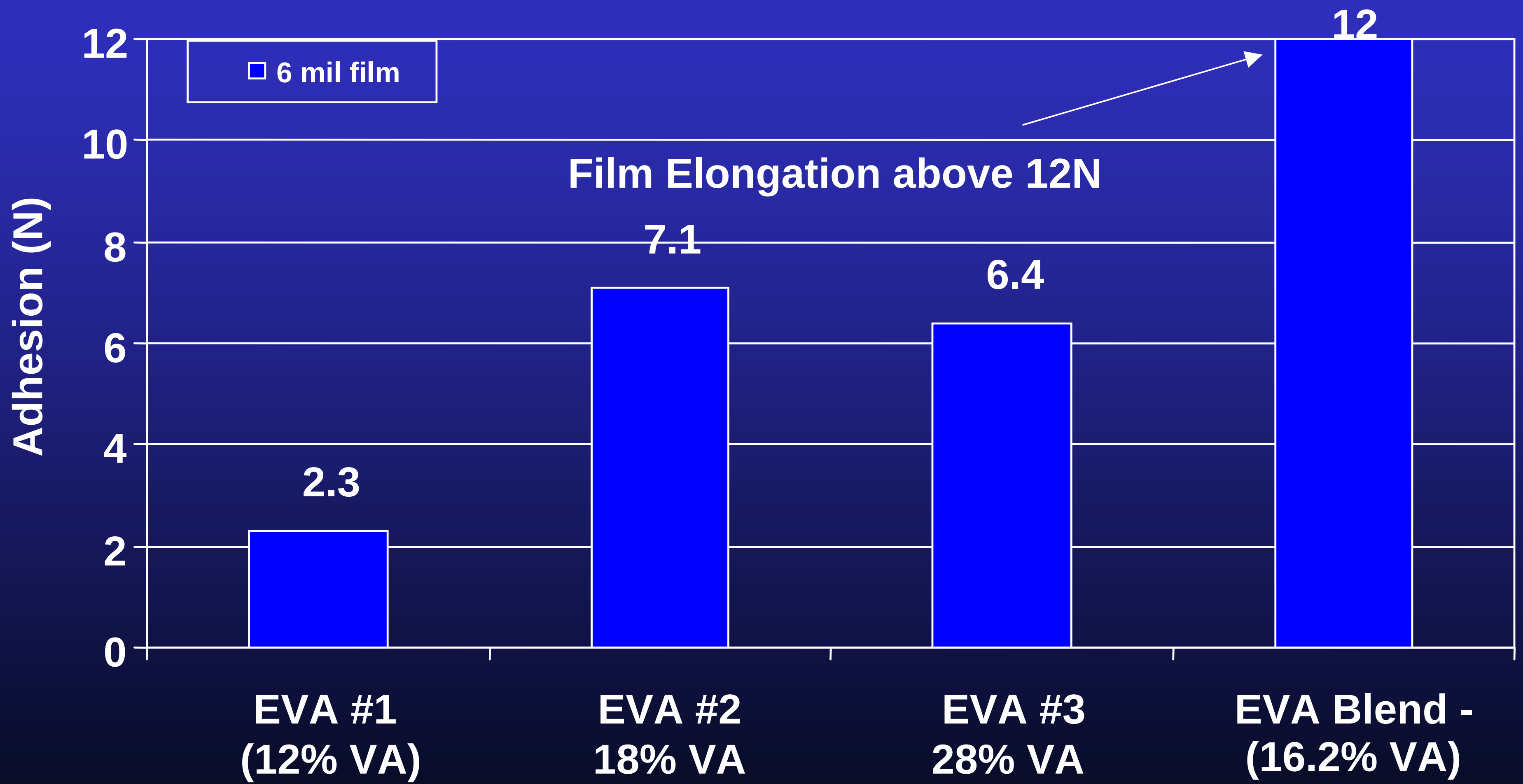
Adhesion to PS Methyl Acrylate Copolymer Sheet

LLDPE Tie Resins



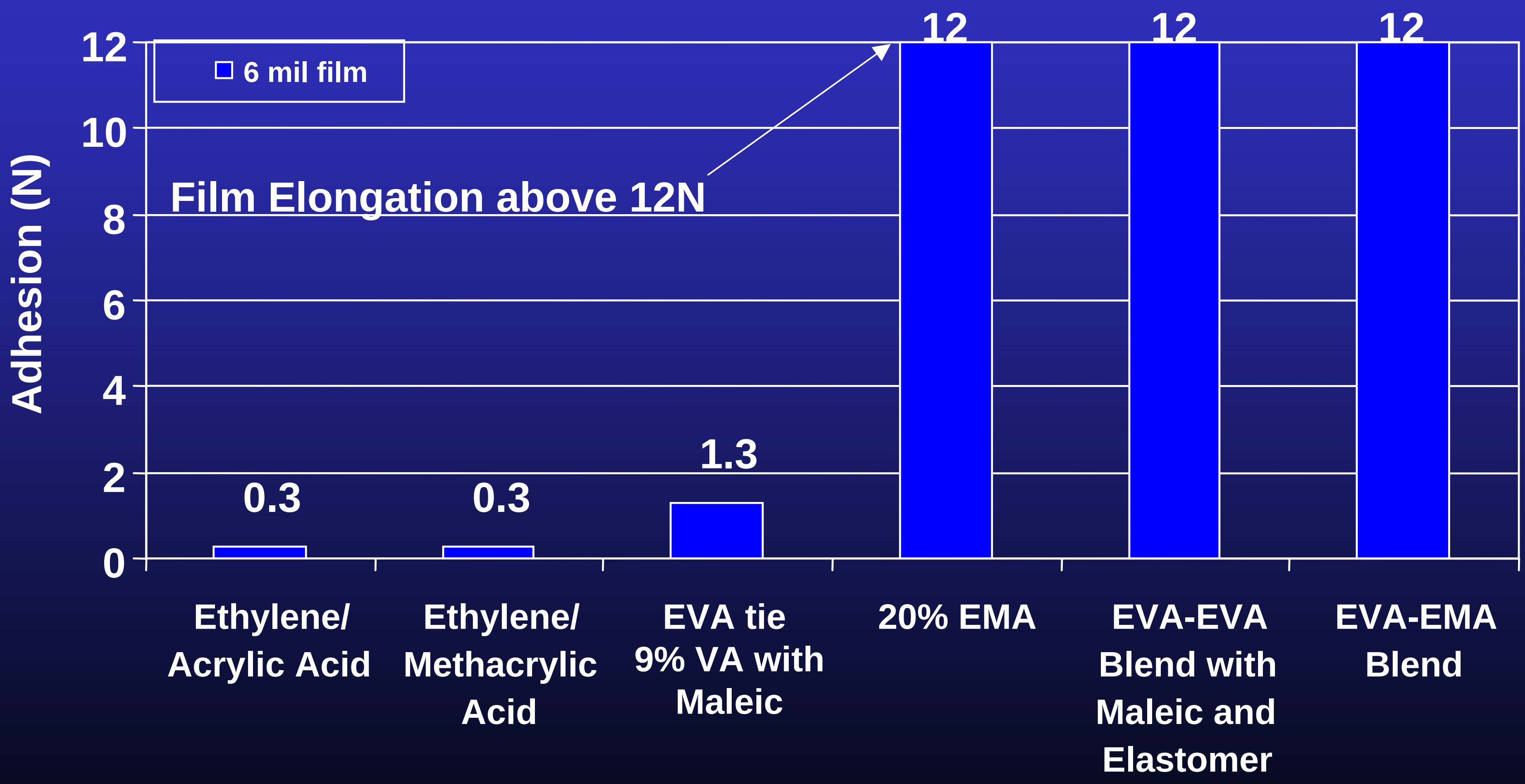
Adhesion to PS Maleic Anhydride Copolymer Sheet

EVA Samples



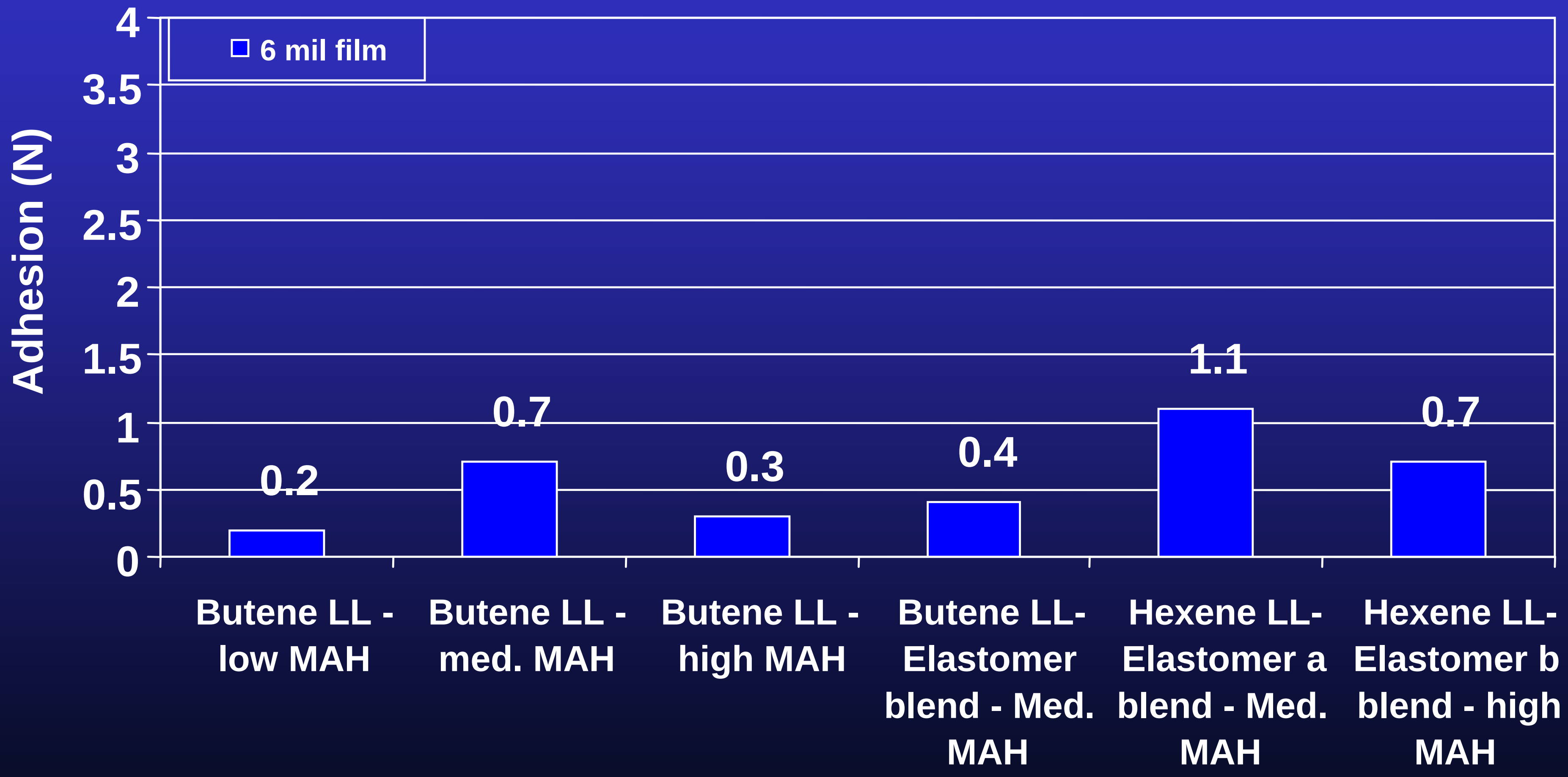
Adhesion to PS Maleic Anhydride Copolymer Sheet

EVA Blends, ACR and EMA Samples

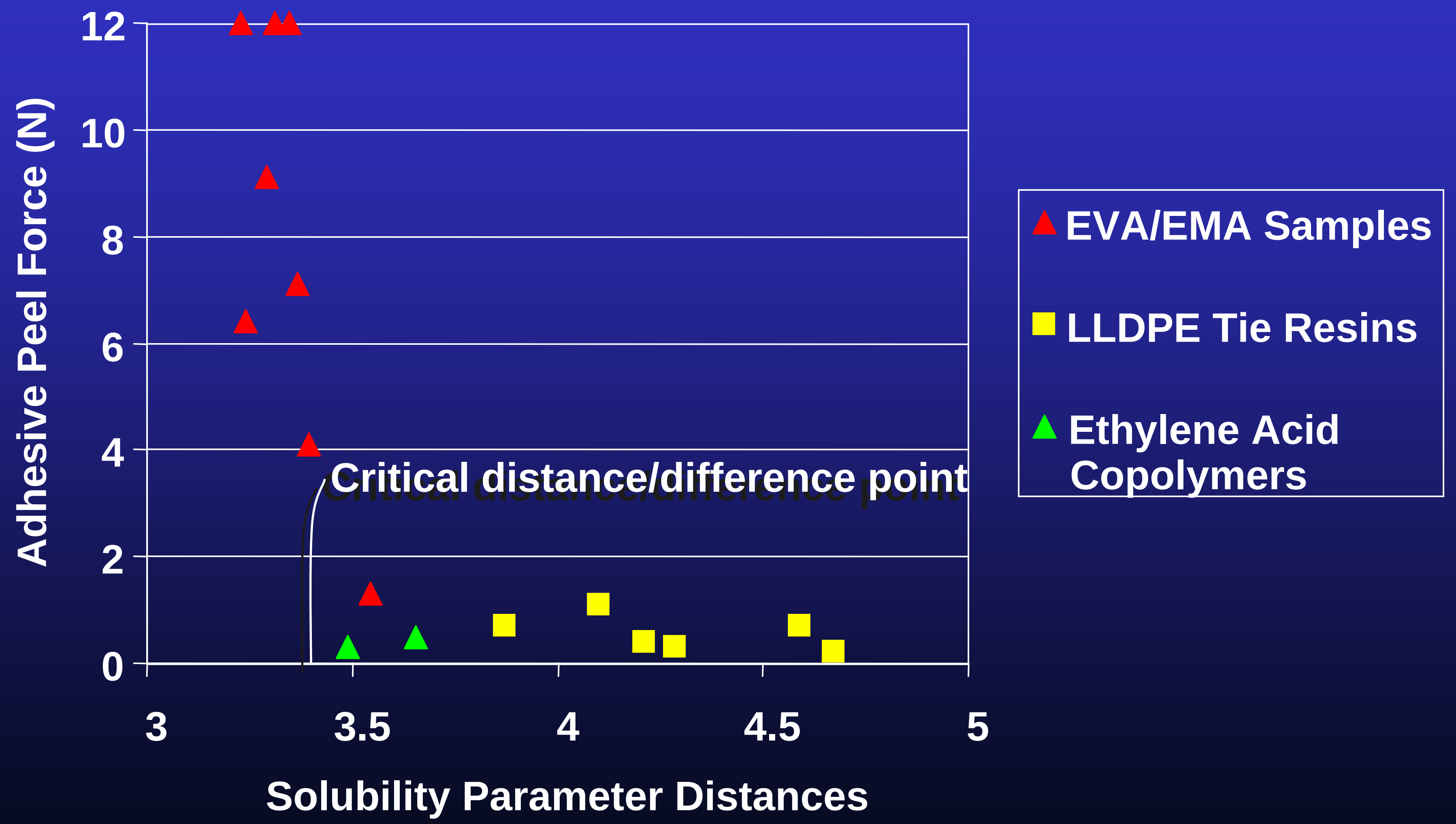


Adhesion to PS Maleic Anhydride Copolymer Sheet

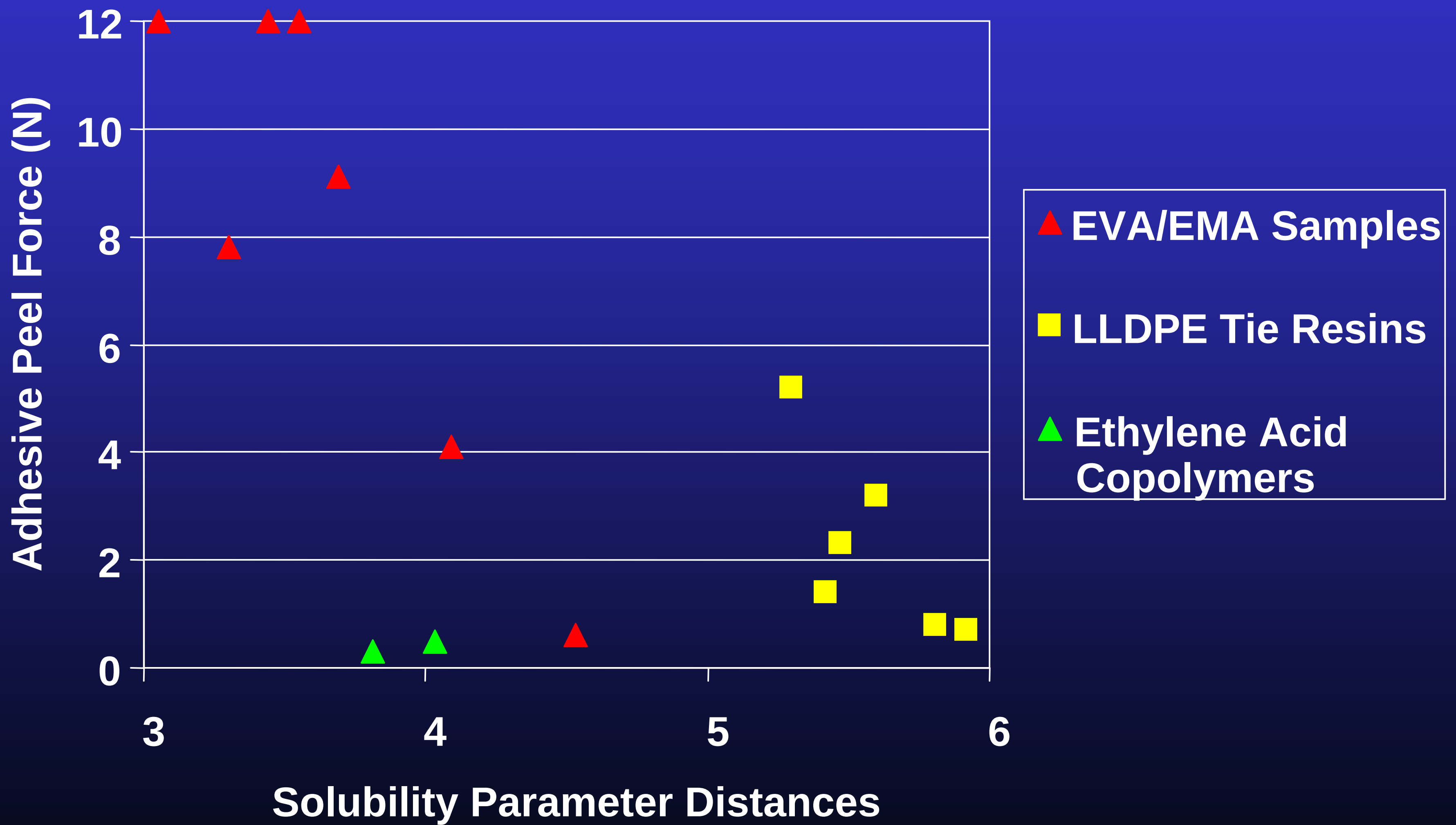
LLDPE Tie Resins



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.

Acknowledgements

- NOVA Chemicals Corporation
- NOVA Chemicals’ Analytical, Applications and Physical Test Labs
- Dr. Robert Keown – University of Delaware (Retired)

Thank you

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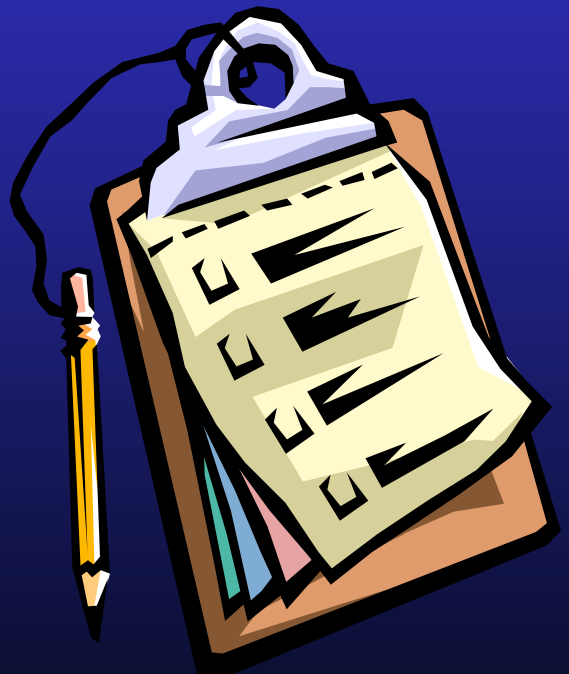

Please remember to turn in your evaluation sheet…