FORMULATING STRATEGIES FOR ADHESION TO DIFFICULT SUBSTRATES

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RADTECH 2020

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WITH YOU IN MIND

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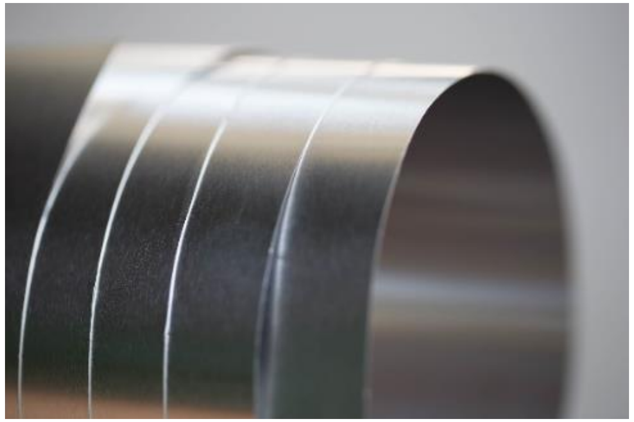
ACKNOWLEDGEMENTS

- Manjuli Gupta
- Jon Scholte
- Elaine Ruiz
- Bill Schaeffer
- Mike Bailey
- Don Herr
- Anna Johnson
- Chris Orilall

Join us at Booth# 501

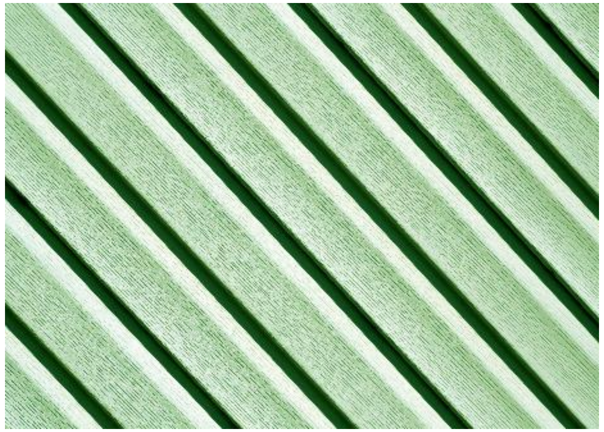
AGENDA

- Introduction
  - Adhesion to Difficult Substrates
  - Factors affecting adhesion
    - Substrate
    - Coating/adhesive
  - Mechanisms of adhesion
- Adhesion to metal
- Adhering metal to plastic
- Adhesion to plastic
  - Swellable plastic
  - Non-swellable plastic
- Summary



ADHESION TO DIFFICULT SUBSTRATES

- Adhesion is the most important property of any coatings application
- Strong adhesion to certain substrates can still be difficult
- Its important to a formulator to understand the factors that can affect adhesion
  - Coating/adhesive formulation architecture
  - Substrate architecture




FACTORS AFFECTING ADHESION

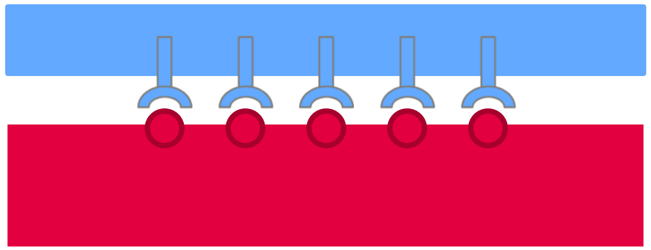
Coating/Adhesive

- Solubility parameter
- Shrinkage
- Surface Tension/Wettability
- Viscoelastic properties
- Coefficient of Thermal Expansion

Substrate

- Porosity
- Surface Energy
- Cleanliness
- Surface Treatments

Chemical Bonding

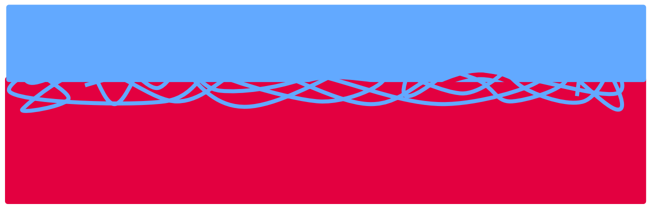


Ionic, metallic, covalent bonding can occur between coating and substrate

Physical Adsorption

Van der waals, electrostatic, hydrogen bonding interactions

Interpenetrated network (IPN) Formation



Swelling substrate with reactive monomer

FORMULATING FOR ADHESION TO METAL

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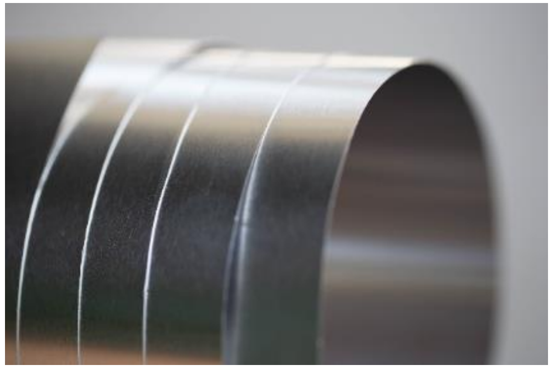
FORMULATING FOR ADHESION TO METAL

- Formulating for adhesion to metal is not as difficult as other substrates
- Maintained through a chemical and physical bonding mechanism
- Factors that influence selection of monomer/oligomers for coating
  - Abrasion resistance
  - Chemical resistance
  - Corrosion resistance
  - Weatherability



FORMULATING FOR ADHESION TO METAL

Base Formulation

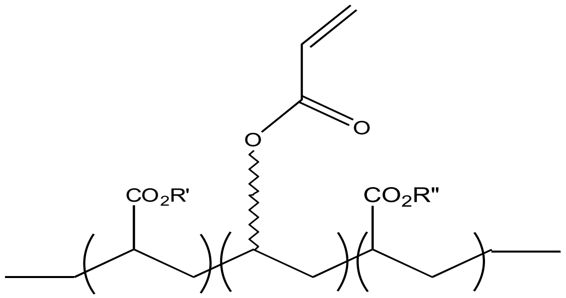
- Polyester Acrylate Oligomer 50.0%
- 3EO TMPTA 20.0%
- DPGDA 12.5%
- TPGDA 12.5%
- Photoinitiator 5.0%

Application & Cure Conditions

- 2.5 wire bar, 5 microns
- 300 W/in. “H” Lamp, 100 ft/min

Substrates Tested

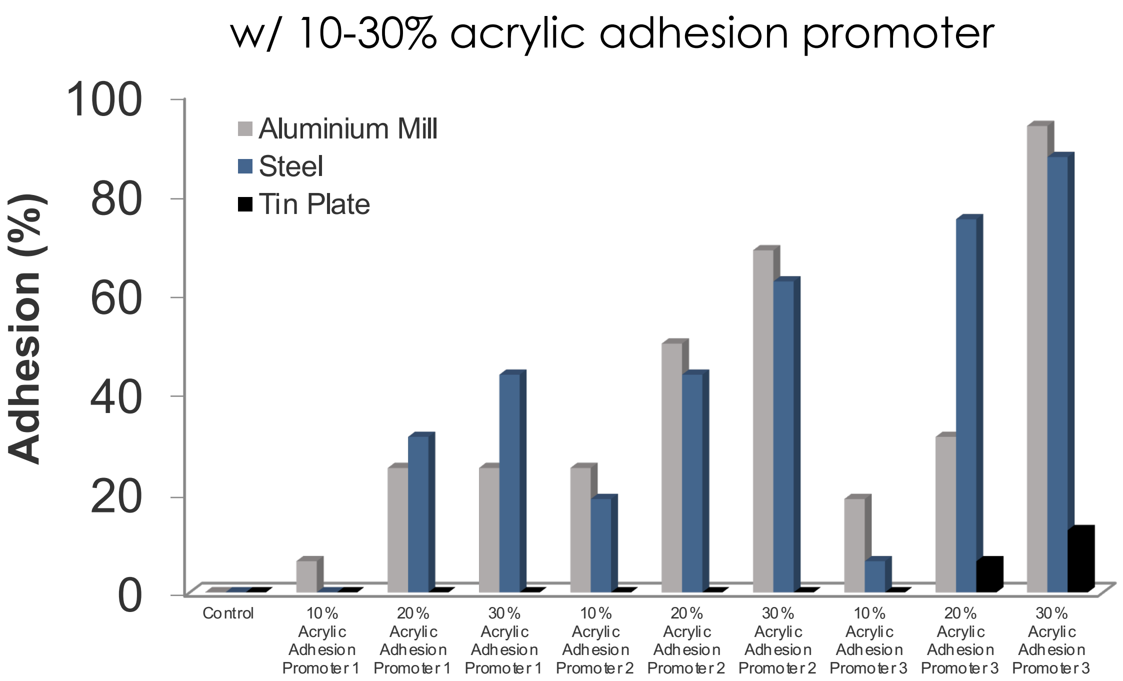
- Mill finish Aluminum
- Cold Roll Steel
- Tin-Plated Steel

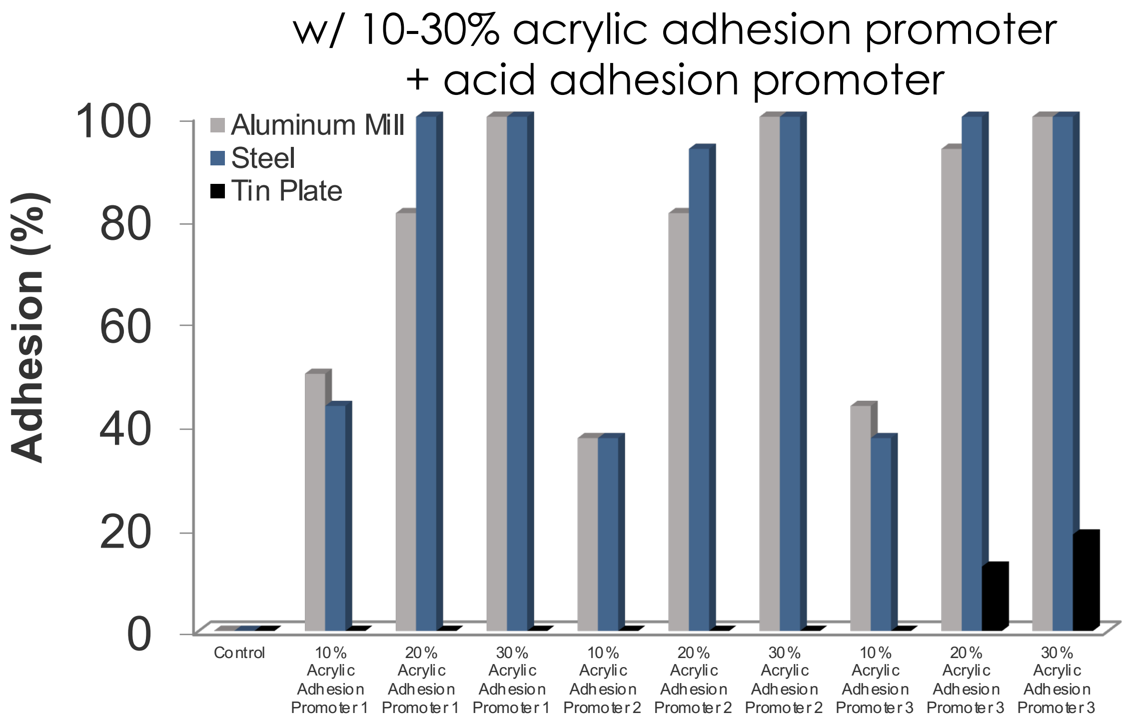


	Acrylic Adhesion Promoter 1	Acrylic Adhesion Promoter 2	Acrylic Adhesion Promoter 3
Weatherability		Yes	Yes
Chemical Resistance		Yes	Yes
Flexibility	Yes		
Adhesion	Plastic Metal	Plastic Metal	Plastic Metal Glass

10, 20, 30% of three different acrylate adhesion promoters and one acid adhesion promoter were added to the base formulation

CROSS HATCH ADHESION TESTING (610 TAPE)





- **Acrylic adhesion promoters help lower shrinkage, more flexible**
- **Additional advantage with acid adhesion promoter**
- **Coatings showed improved chemical resistance (>200 MEK rubs) and weatherability with no loss in hardness**

FORMULATING FOR ADHERING METAL TO PLASTIC

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FORMULATING FOR ADHERING METAL TO PLASTIC

- May need to formulate an adhesive that binds two different substrates together
- Bonding plastic-to-plastic or metal-to-metal can be much easier than bonding plastic-to-metal
- The type of plastic used can depend on the application

FORMULATING FOR ADHERING METAL TO PLASTIC

- LED (385 nm) curable adhesive to bond both PC to PC and PC to NPS
- Testing Reqs:

Test	Conditions	Value
Viscosity at 25°C	ASTM D1084	40-80 cP
Glass Transition Tempearture (T_g)	ASTM D1640-13	>85°C
Hardness (Shore D)	ASTM D2240	75
Lap Shear (PC to PC)	ISO 4587	15 Mpa
Lap Shear (PC to NiPS)	ISO 4587	10 MPa

- Curing Conditions: 385 nm LED, less than 4s at 3 in. away from source

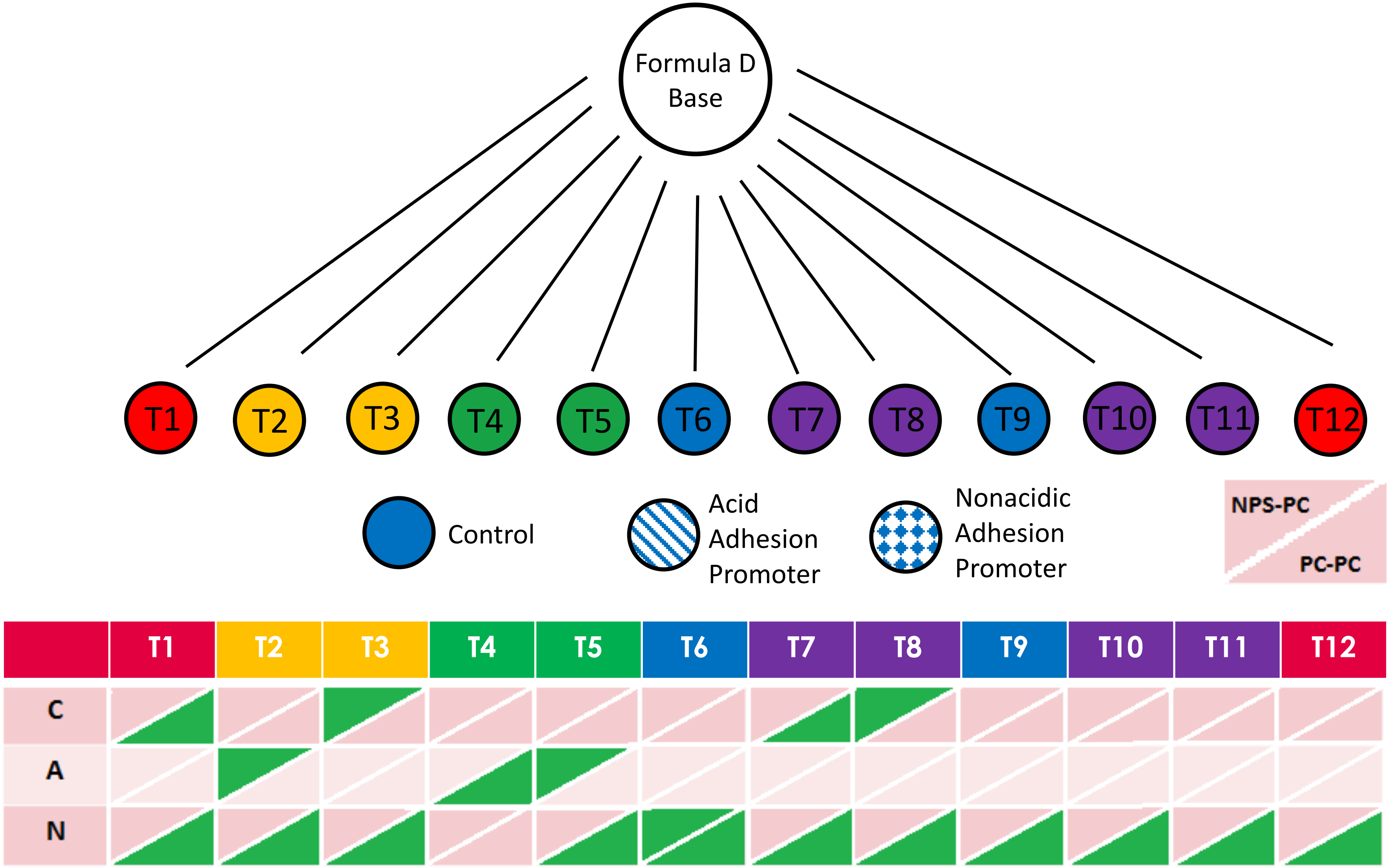
FORMULATING FOR ADHERING METAL TO PLASTIC: PRELIMINARY BLENDS A-E

- Five formulations targeting 70-80cP with high strength and adhesion

	Target	Formula A	Formula B	Formula C	Formula D	Formula E
Viscosity @ 25°C	40-80cP	78	75	71	75	70
Shore D Hardness	80 ± 10	82	83	79	80	80
Tensile Strength	15 Mpa	16.9	26.1	21.6	25.9	25.4
Elongation (%)	-	11.6	12.1	10.2	10.7	12.2
Modulus (Mpa)	-	235.1	337.9	316.5	332.3	366.1
NPS Lap Shear Stress	10+ Mpa	23.3	22.8	23.5	34.3	10.7
PC Lap Shear T0	15+ MPa	5.1	5.7		12.8	
NPS Lap Shear T=300hrs			1.9		13-15	

- Formula D demonstrated the best potential for accelerated conditioning at 65°C/85% humidity

FORMULATING FOR ADHERING METAL TO PLASTIC: DOE STUDY



SUMMARY

- Multiple blends meet both of the technical requirements
- All formulations demonstrate good lap shear adhesion
- Additional adhesion promoters (both acidic and nonacidic) have been identified with on going tests

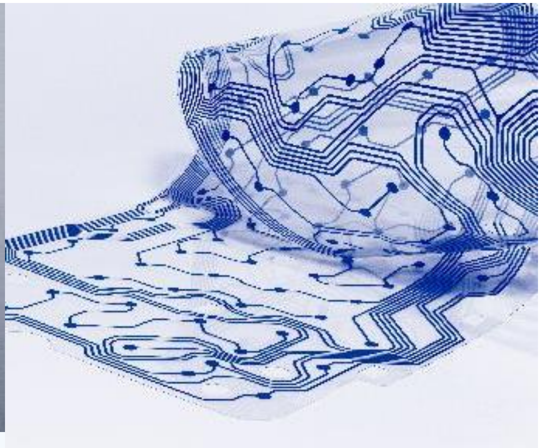
	T_g (1 Hz, 10 Hz)	Viscosity (25°C)	Lap Shear (PC:PC) t=0	Lap Shear (PC: NPS) t=0
Formula 1	171°C, 163°C	69 cP	PC broke	13.1 MPa
Formula 2	173°C, 172°C	78 cP	PC broke	20.4 MPa
Formula 3	150°C, 148°C	77 cP	27.8 MPa	17.3 MPa

FORMULATING FOR ADHESION TO PLASTICS

FORMULATING FOR ADHESION TO PLASTICS

- Plastics can be difficult substrates to adhere to due to their low surface energy

- Formulations tactics
  - 1) Reduce crosslinking density
  - 2) Similar viscoelastic properties to substrate
  - 3) Additives that lower surface tension
  - 4) Good affinity to substrate



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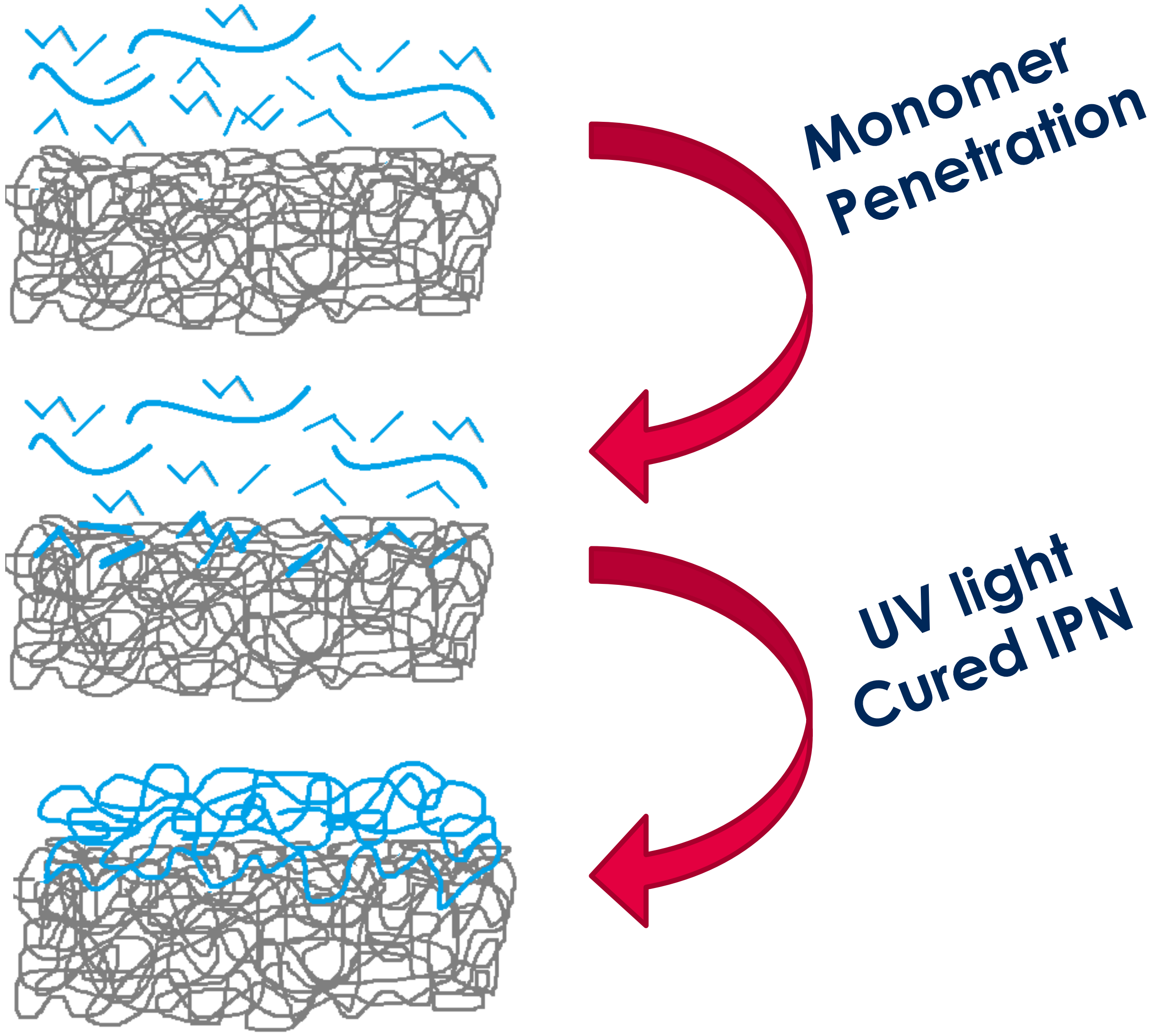
SWELLABLE PLASTICS - IPN FORMATION

- **Swellable Plastics include:**
  - PVC, Polycarbonate, Polystyrene

- **Monomers can be utilized to decrease surface tension and viscosity to improve wetting**

- **Monomers can also associate with or swell the substrate surface**



NON-SWELLABLE PLASTICS - POLYOLEFINS

- POs undergo only a physical mechanism of adhesion

- Two parameters contribute to the adherence of coatings on non-swellable plastics:
  - 1) Coating chemistry
  - 2) Thermodynamic work of adhesion

- Formulation Tactics:
  - Materials with good wetting and low shrinkage

ADHESION TO PLASTIC SUBSTRATES

- Polymer substrates were gathered for adhesion study

- Several techniques used to evaluate substrate and coating
  - FTIR, Contact Angle, DMA, Cross hatch adhesion

- Mixture of high and low SE substrates
  - PS, PMMA, PE, PP

PLASTIC SUBSTRATES

Substrate #	Composition qualifier by FTIR	Surface Energy (Dynes)	Contact Angle	Glass Transition Temperature (Tg, °C)
1	90.26% Polystyrene	43	67	123 (Tension film)
2 Side 1	93.4% Polyethylene	33	83	-114 (Tension film)
2 Side 2	95.85% Polyethylene	44	66	-114 (Tension film)
3	96.47% Polypropylene, isotactic	36	79	0
4	90.65% Polystyrene	31	87	123
5	94.96% Poly(methyl methacrylate)	41	72	132 (single cantilever)

PLASTIC ADHESION STUDY: FORMULATION STRATEGY

- Starting Point formulations were made (Table 1)
- Clear coating applied by draw down (#10 wire bar, 1 mil thickness)
- Adhesion results for the base formulation indicates PE poses issues (Table 2)

Table 1

Product	Wt %
Aliphatic UA	10
Cycloaliphatic monoacrylate	87
PI	3

Table 2

Substrate	Adhesion %
1 (PS)	100
2 (PE)	**50**
3 (PP)	100
4 (PS)	100
5 (PMMA)	100

PRODUCTS EVALUATED

Description	Properties	Loading Wt%
HMW Epoxy Acrylate	HMW, Flexible Oligomers, limited by viscosity	5%
Acrylated PEA adhesion promoter		
THFA	High solvency monomers	20%
Alkoxylated THFA		
Alkoxylated NPGDA	non-polar monomers, linear	20%
Aliphatic Diacrylate		
Cycloaliphatic Acrylate Ester	non-polar monomers, cyclic	20%
CTFA		
Cycloaliphatic Acrylate		
TMCHA		
2-PEA	Aromatic monomers	20%
Chlorinated Epoxy Acrylate	Chlorinated oligomer, limited by viscosity	5%
Urethane monomer	Low Tg monomer	20%

ADHESION TESTING RESULTS

	HMW, Flexible Oligomers		High solvency monomers		Non-polar monomers, linear		Non-polar monomers, cyclic				Aromatic monomers	Chlorinated oligomer	Low Tg monomer
Substrate # / type	**HMW EA**	**PEA**	**THFA**	**Alk THFA**	**Alk NPGDA**	**Al DA**	**Cyclo AE**	**CTFA**	**CAA**	**TMCHA**	**2-PEA**	**Cl EA**	**UA**
1 (PS)	100	100	100	100	100	100	100	100	100	100	100	100	100
2 (PE)	70	80	25	25	25	50	50	25	75	85	25	70	25
3 (PP)	90 - 95	100	95 - 100	100	25	25	85	50	100	100	100	90	75
4 (PS)	100	100	100	100	100	100	100	100	100	100	100	100	100
5 (PMMA)	100	100	100	100	100	100	100	100	100	100	100	100	100

- **Best Overall performance with >70% PE and 100% PS , PP & PMMA**
  - **HMW Epoxy Acrylate**
  - **TMCHA**
  - **Cycloaliphatic Acrylate**
- **Identified addition of high boiling solvent to TMCHA formulation improved adhesion on PE to 100%**

SUMMARY

- Formulators find that adhesion can be a challenge depending upon the substrate
- Understanding the chemical nature of the coating, the chemical nature of the substrate, and the numerous factors affecting coating-substrate affinity, can help a formulator improve adhesion dramatically
- Other factors, such as surface tension, coefficient of thermal expansion, internal stress due to crosslinking, and tensile properties of the coating all influence the coatings ability to adhere to the substrate
- It is up to the formulator to test these concepts and determine what is necessary to satisfy the technical requirements of their coating and application