Radiation Curable Coatings and Water-based Automotive Trim Adhesives from Soybean oil and its Derivative

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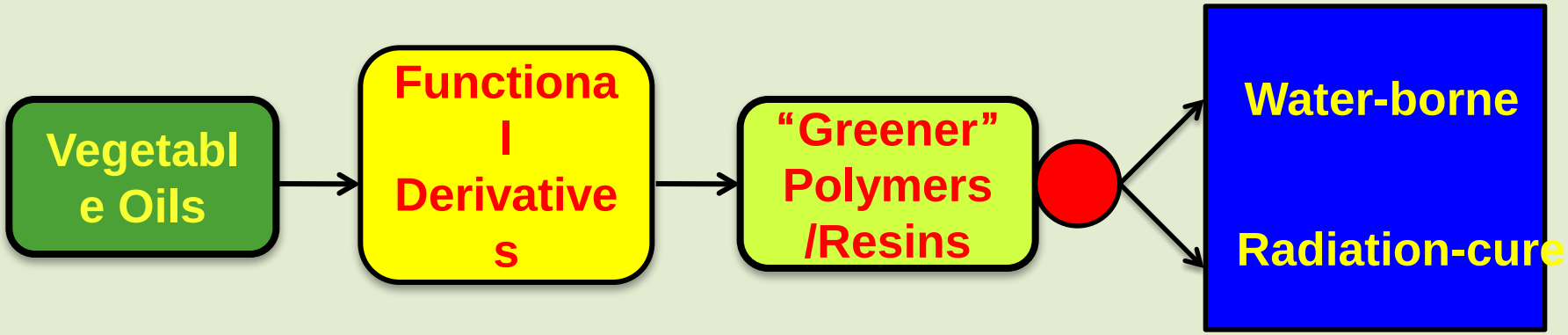
Diversified Chemical Technologies, Inc.
Detroit

Overall Goal

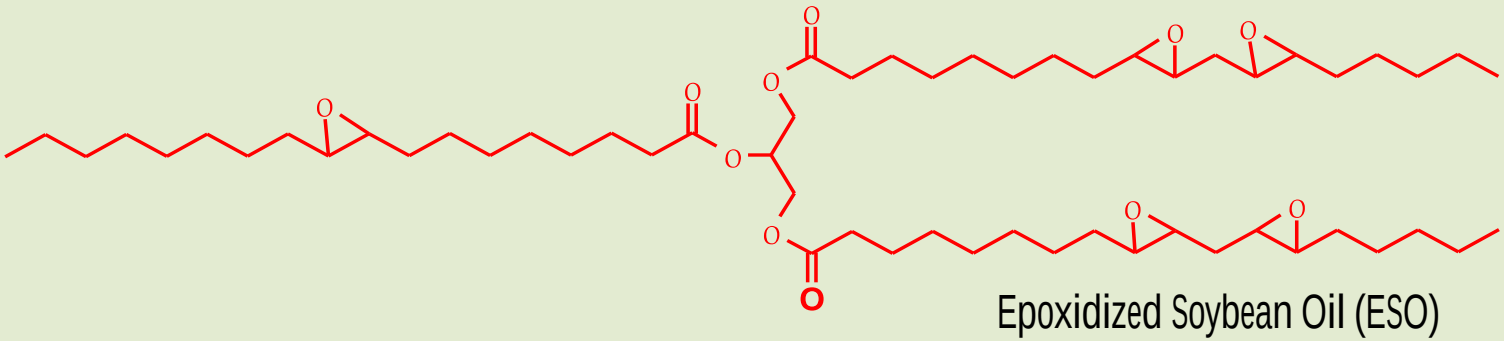
To synthesize and develop value added coating and adhesive materials from vegetable oil based polyols.



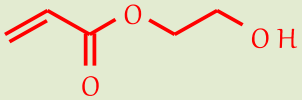
Why Used Epoxidized Vegetable Oil?

- Epoxidized vegetable oil (EVO) is commercially available low cost renewable bio-based material.
- EVO contains reactive oxirane functionality through which number of chemical modifications are possible.
- The most important reaction is ring-opening reaction of EVO with nucleophilic compounds & acid catalyst.
- Depending upon the oxirane content, extent of reaction and reaction conditions, EVO yields a range of polyols with useful end use applications.

Synthesis of Novel Acrylic Polyols (ESO)

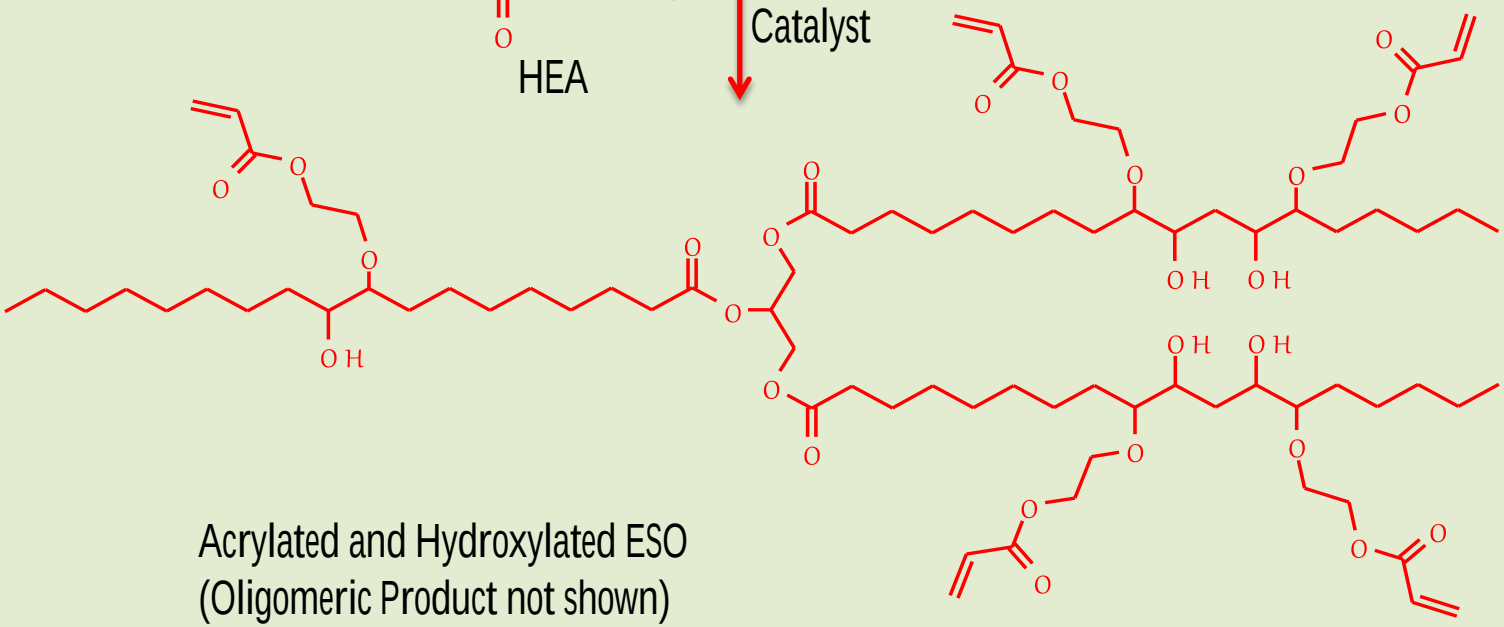


Epoxidized Soybean Oil (ESO)



HEA

Acid
Catalyst

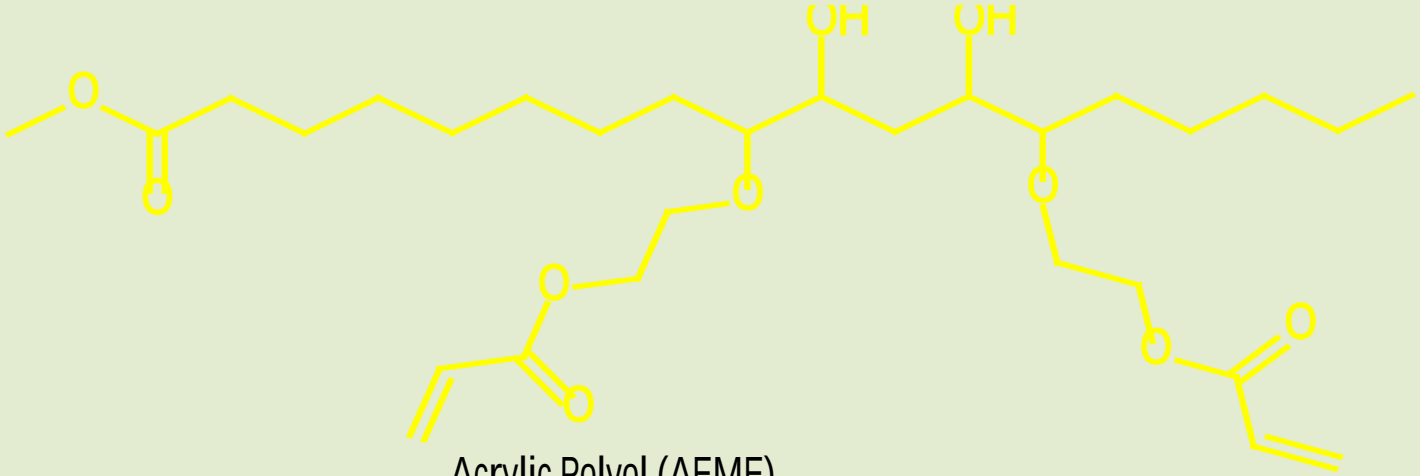


Acrylated and Hydroxylated ESO
(Oligomeric Product not shown)

Synthesis of Novel Acrylic Polyols (EME)

Epoxidized Fatty Acid Methyl Ester (EME)

Acid
Catalyst

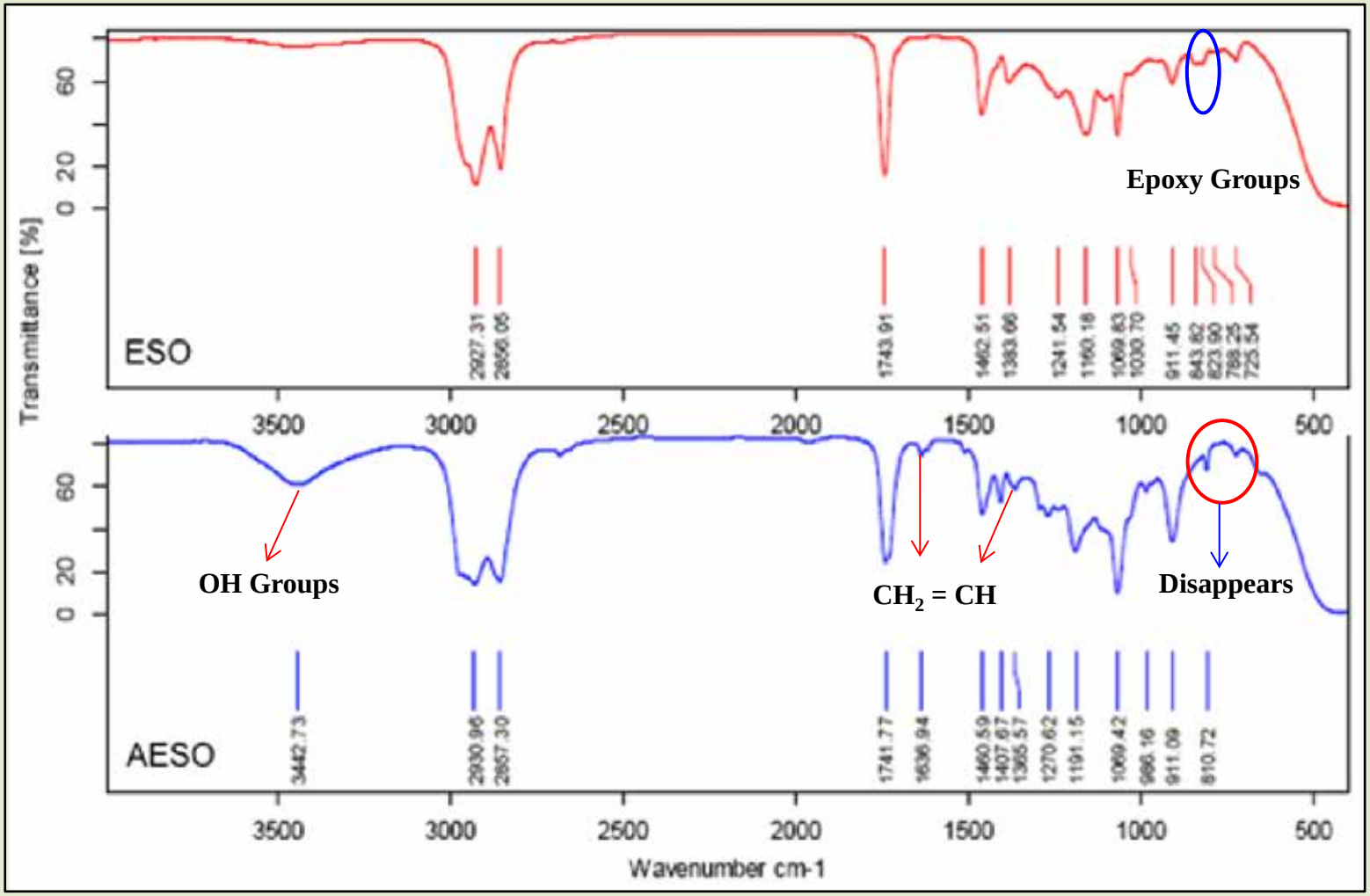


Acrylic Polyol (AEME)

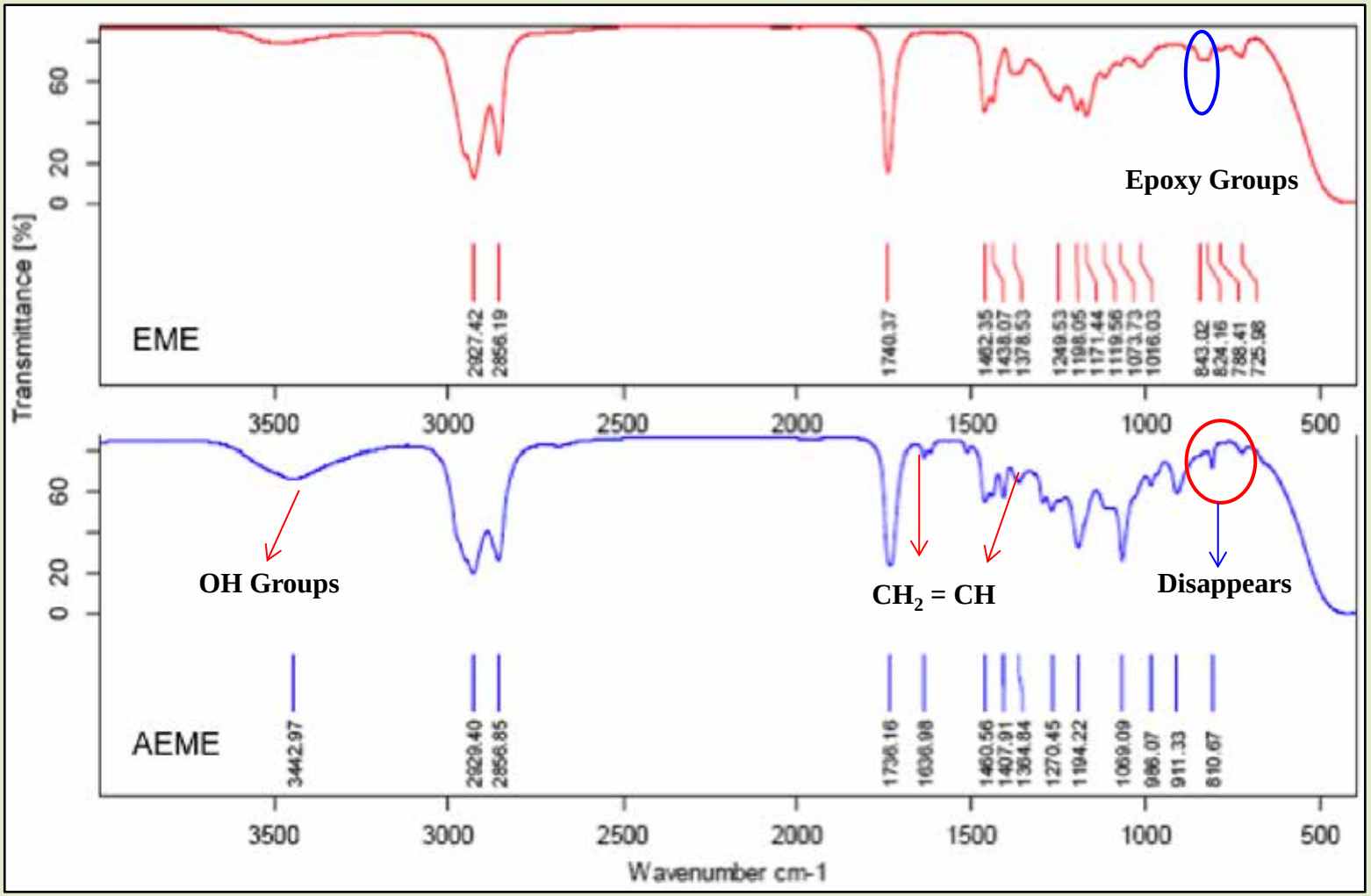
Acrylic Polyol - Characterization

Properties	ESO	AESO	EME	AEME
Oxirane Oxygen Content (%)	7.0	0.0	7.0	0.0
Iodine Number (g Iodine/100g)	2.5	52.2	3.0	72.7
Viscosity (cPs)	417	5406	76	109
Hydroxyl Number (mg KOH/g)	0.0	113.3	0.0	155.1
% Acrylation	0.0	86.0	0.0	97
Acrylated Equivalent Weight	0.0	486.6	0.0	349.6
Molecular Weight (mg KOH/g)	993.0	1840.0	231.0	583.0

FT-IR- Characterization



FT-IR- Characterization

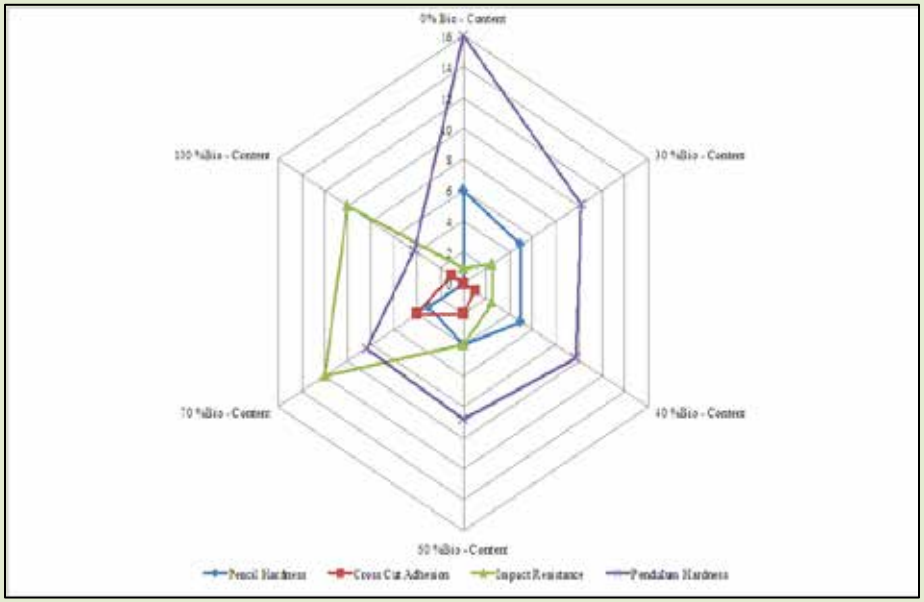


^{1}H NMR- Characterization

H NMR Spectra (Signal Peak - ppm)	AESO**	AEME*
0.8 - 0.9	CH_3 (terminal group)	CH_3 (terminal group)
1.2 - 1.4	CH_2 (aliphatic backbone)	CH_2 (aliphatic backbone)
1.5 - 1.7	β CH_2-(C=O)-O (methylene proton adjacent to carbonyl group)	β CH_2-(C=O)-O (methylene proton adjacent to carbonyl group)
*2.2 - 2.3 / **2.2 - 2.	α CH_2-(C=O)-O (methylene proton adjacent to carbonyl group)	α CH_2-(C=O)-O (methylene proton adjacent to carbonyl group)
3.4 - 3.5	OH groups	OH groups
3.6 - 3.9	CH_2-O-CH_2 (polyether backbone)	CH_2-O-CH_2 (polyether backbone)
4.1	CH_2	-
4.2 - 4.4	Protons of saturated CH_2 in HEA	Protons of saturated CH_2 in HEA
5.2	CH	-
5.8 – 6.5	CH_2 = CH (acrylic moiety)	CH_2 = CH (acrylic moiety)

Compositions and Cured Film Properties

Raw Materials		AESO	AEME	PEA	Polyester Acrylate/ AESO Ratio (by wt.)				
					100:00	70:30	60:40	40:60	30:70
Polyester (CN2282*) (g)				5	5	3.5	3	2	1.5
AESO (g)		5			-	1.5	2	3	3.5
AEME (g)			5						
TPGDA(SR306*)		-	-	-	1.5	1.5	1.5	1.5	1.5
DPGDA (SR508*) (g)		-	-	-	1.5	1.5	1.5	1.5	1.5
3EoTMPTA(SR350*) (g)		-	-	-	1.5	1.5	1.5	1.5	1.5
Photo Initiator (Daracure 1173**) (g)		0.25	0.25	0.25	0.5	0.5	0.5	0.5	0.5
Resin and Cured Film Properties									
Viscosity (cPs) @ 25°C		5406	109	70000	453	310	285	235	222
Dry Film Thickness (µm)		35	35	35	35	35	35	35	35
Pencil Hardness		F	6B	F	6H	5H	5H	4H	3H
Pendulum hardness(Koenig)		42	12	42	160	102	97	88	84
MEK Double rub		50	0	200	200	200	200	200	200
Adhesion (Cross-hatch)		B	0B	B	0B	0B	B	2B	4 B
Impact Resistance(lbs.in)	Direct	100	10	80	10	25	25	40	120
	Reverse	80	10	50	0	4	6	10	15

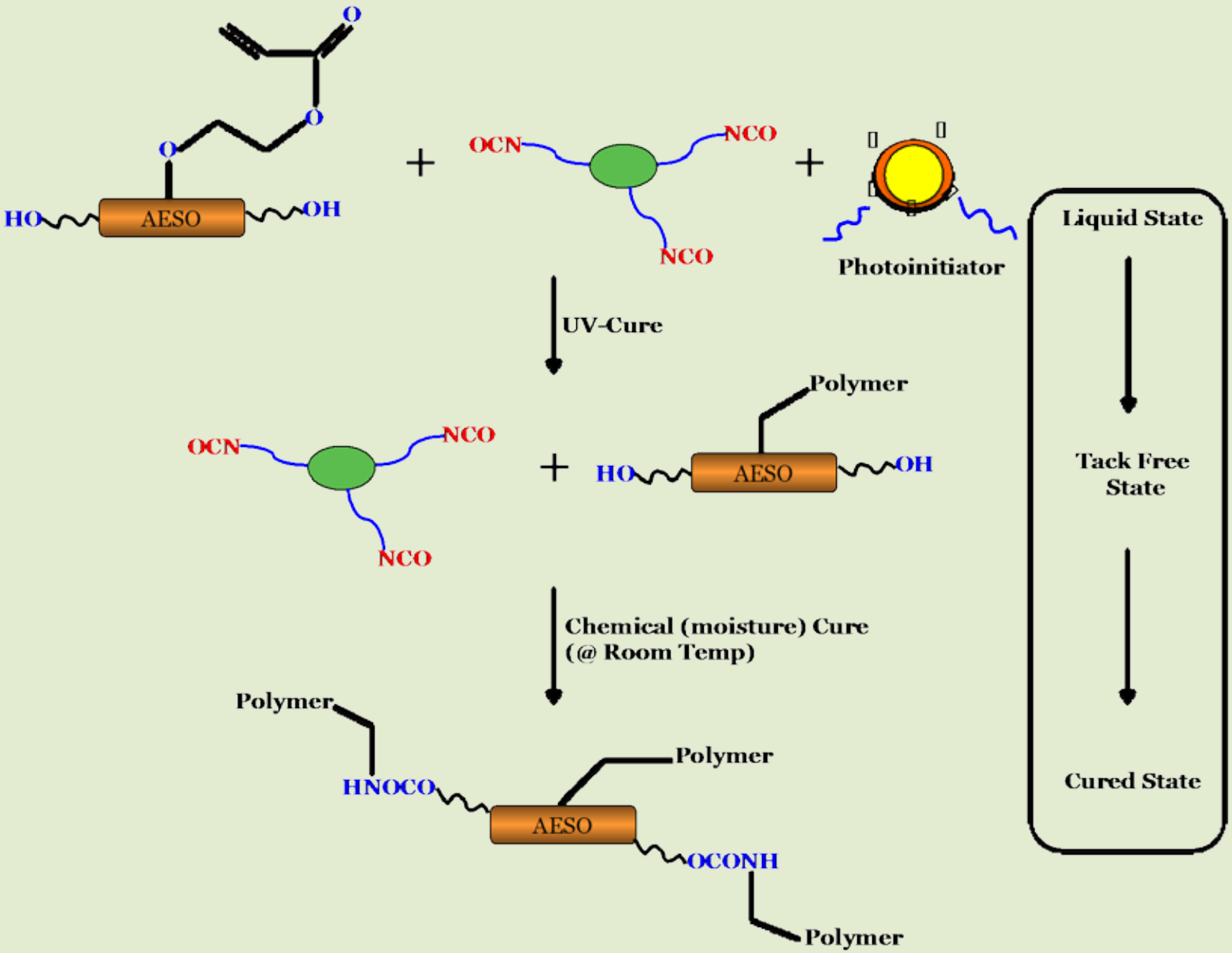


0 to 6 scale used for Pencil hardness where 0 = F hardness value and 6 = 6H hardness value.

For impact resistance (direct) & Pendulum hardness 1 unit = 10 units of respective scale of property

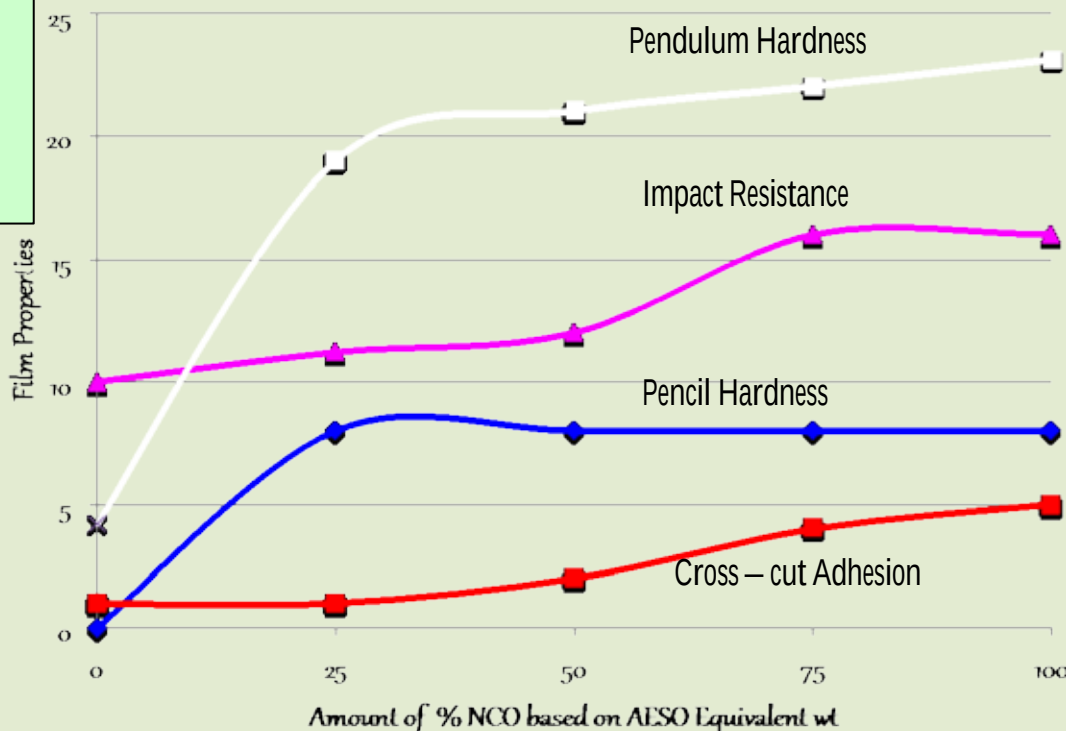
0 to 5 scale used for Cross Cut Adhesion where 0 = 0B and 5 = 5B adhesion strength

Schematic Representation of Dual Cure Coatings

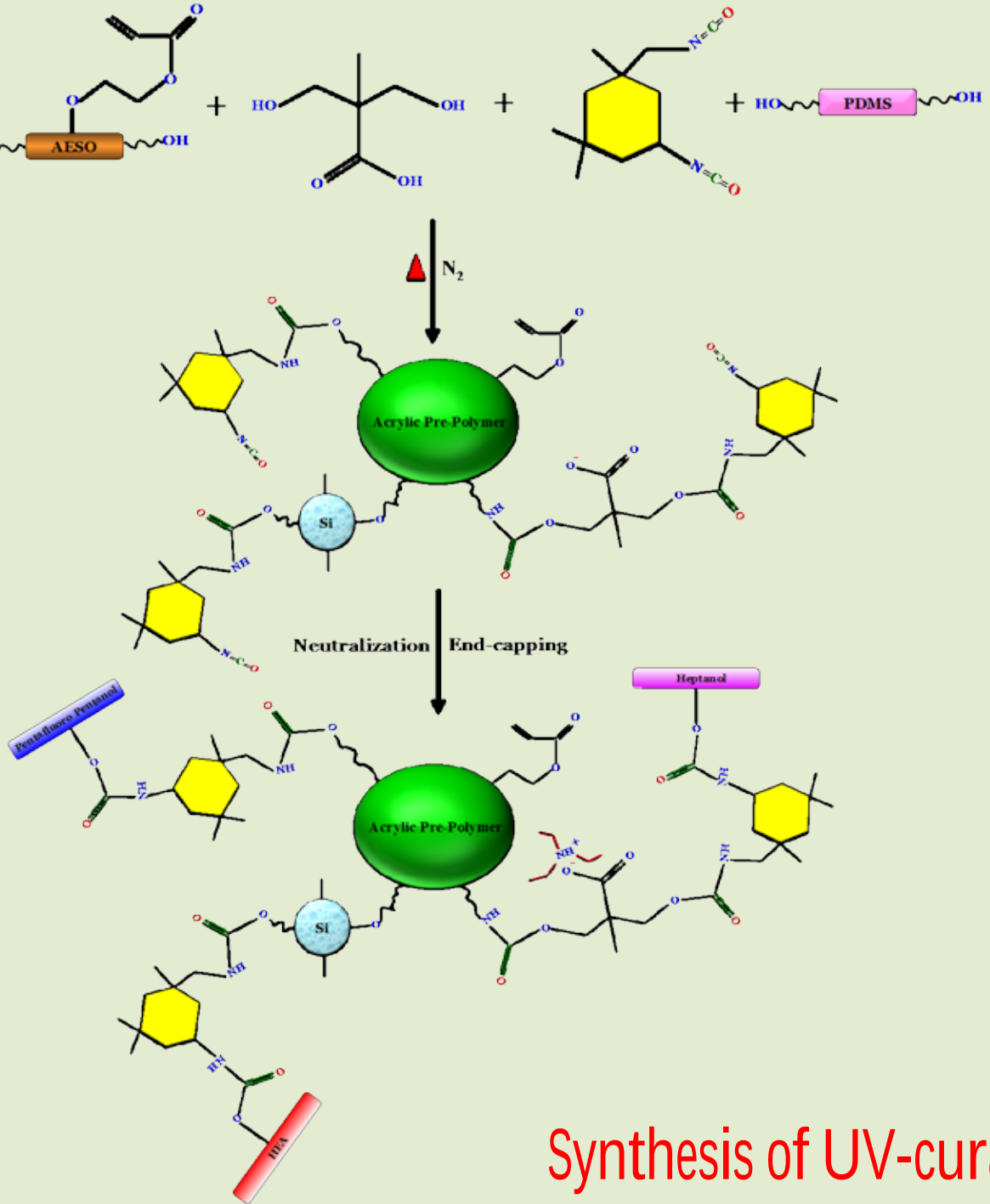


Compositions and Cured Film Properties

COATING FORMULATION		A	B	C	D
AESO		5g	5g	4g	3.5g
Photoinitiator (Darocur 1173)		0.357g	0.463g	0.456g	0.473g
HDI Trimer (Desmodur N3300)		2.13g	4.26g	5.11g	5.96g
Catalyst (DBTDL – 10% in Toluene)		0.1g	0.1g	0.1g	0.1g
Hydroxyl to NCO Equivalent weight ratio		1:0.25	1:0.50	1:0.75	1:1
Amount of HDI used (Based on OH - equivalent weight of AESO)		25%	50%	75%	100%
Resin and Cured Film Properties					
Viscosity (cPs) @ 25°C		5080	4760	4280	3898
Dry Film Thickness (μm)		35	35	35	35
Pendulum Hardness (Koenig)		190	210	220	231
Pencil Hardness		8H	8H	8H	8H
Impact Resistance (lbs x inch)	Direct	112	120	160	160
	Reverse	100	100	140	140
MEK Double Rubs		> 400	> 400	> 400	> 400
Crosshatch Adhesion		B	2B	4B	5B

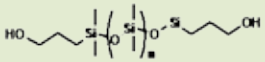
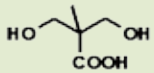
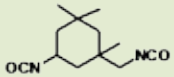
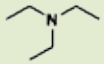
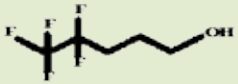
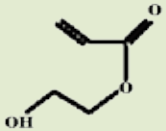


(For Impact Resistance & Pendulum Hardness 1 unit in Y axis = 10 units of respective scale of property. 0 to 6 scale used for Pencil Hardness where 0 = F and 6 = 6H hardness value). 0 to 5 scale used for Cross Cut Adhesion where 0 = 0B and 5 = 5B adhesion strength

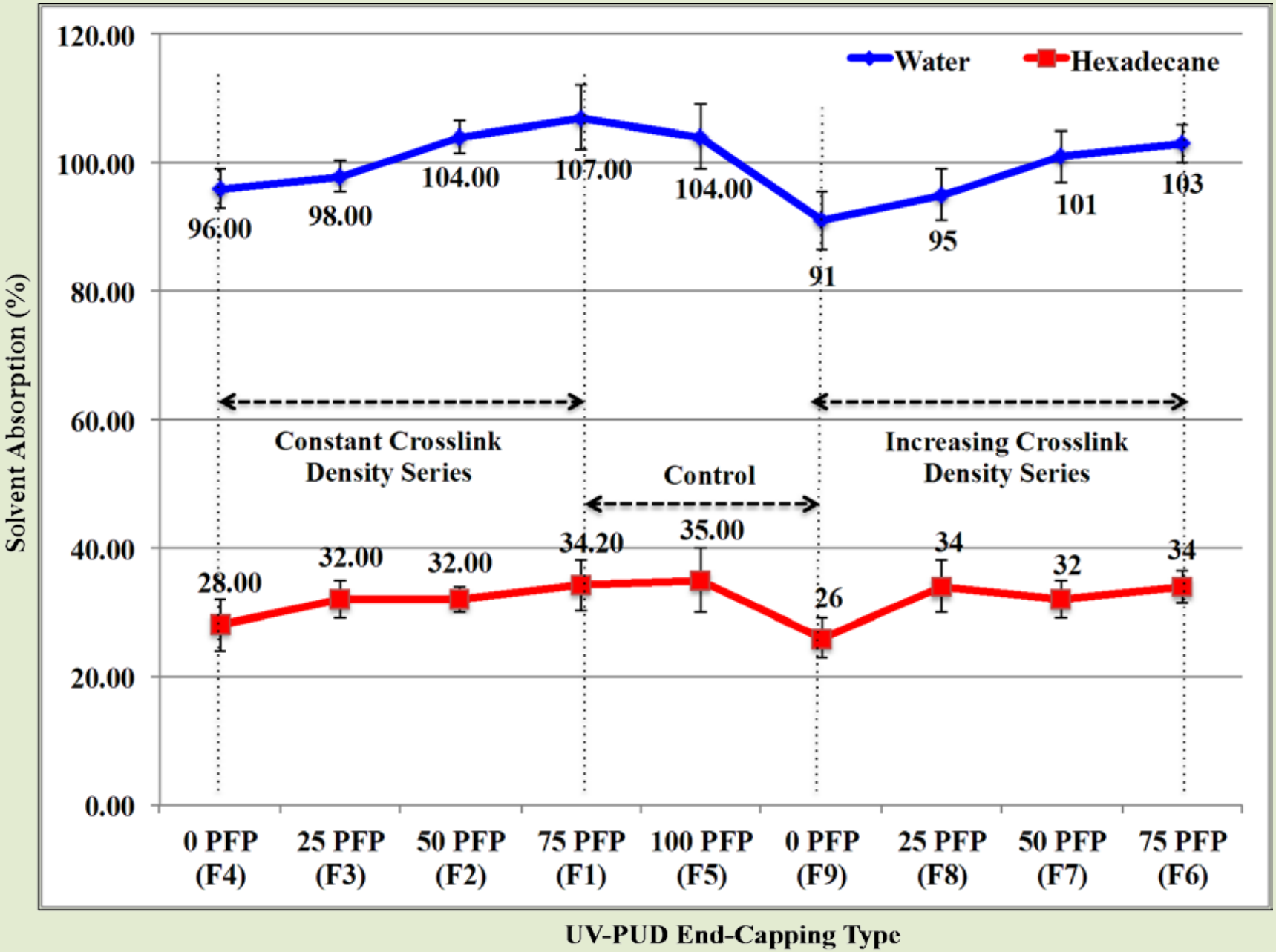


Synthesis of UV-curable PUD

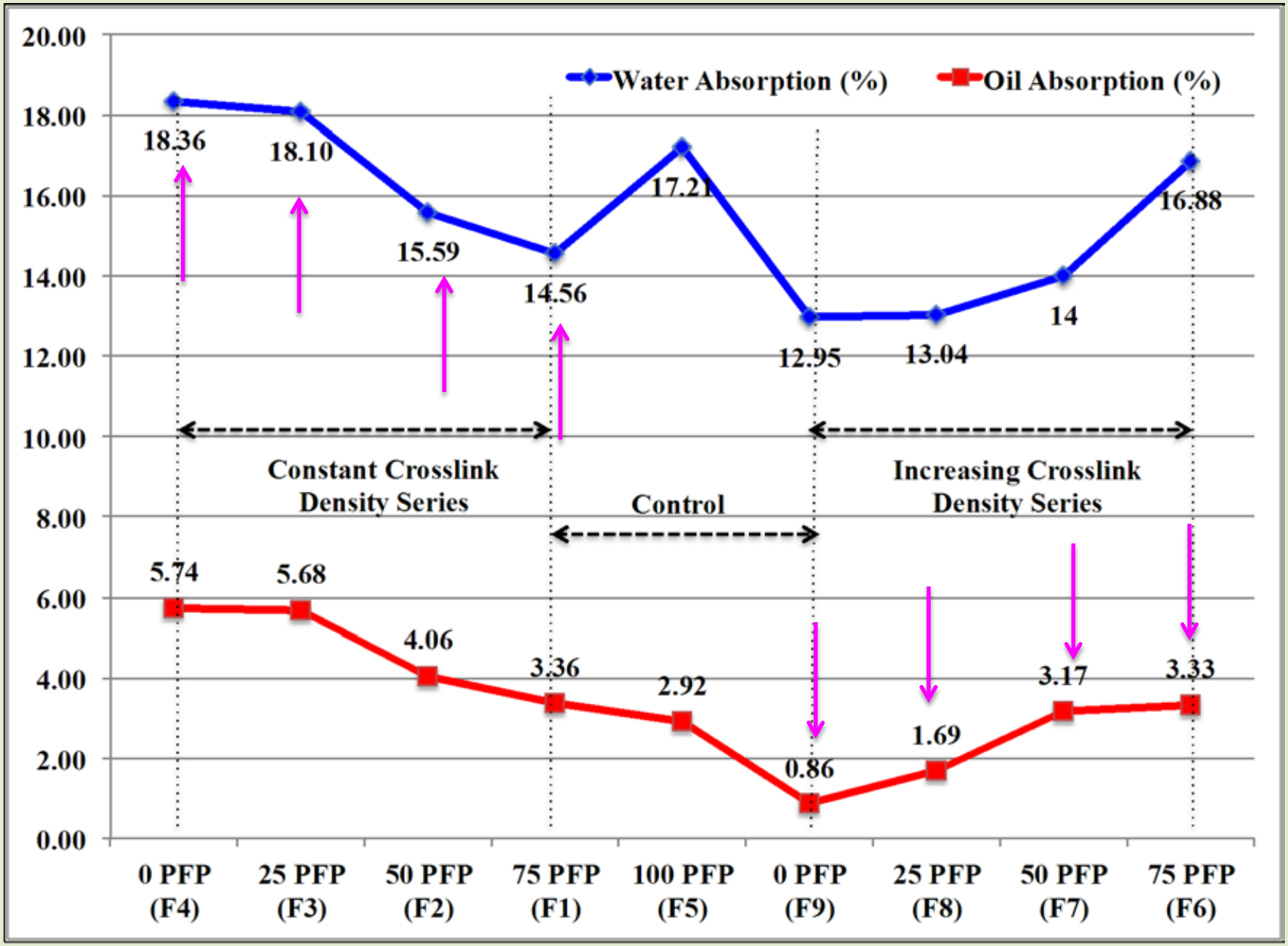
UV – PUD Composition

UVPUD - Composition	Chemical Formula	Mw (g/mol)	Constant Crosslink Density					Increasing Crosslink Density			
			F1	F2	F3	F4	F5	F6	F7	F8	F9
AESO - OH	-	1842	0.003	0.003	0.003	0.003	0.003	0.003	0.003	0.003	0.003
PDMS polyol		1000	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004
1,4 Butane diol		90	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
DMPA		134.13	0.010	0.010	0.010	0.010	0.010	0.010	0.010	0.010	0.010
IPDI		222	0.031	0.031	0.031	0.031	0.031	0.031	0.031	0.031	0.031
TEA		101	0.009	0.009	0.009	0.009	0.009	0.009	0.009	0.009	0.009
PFP		178	0.013	0.009	0.004	0.000	0.017	0.013	0.009	0.004	0.000
2HEA		116.12	-	-	-	-	-	0.004	0.009	0.013	0.017
1-Heptanol		116.2	0.004	0.009	0.013	0.017	0.000	-	-	-	-

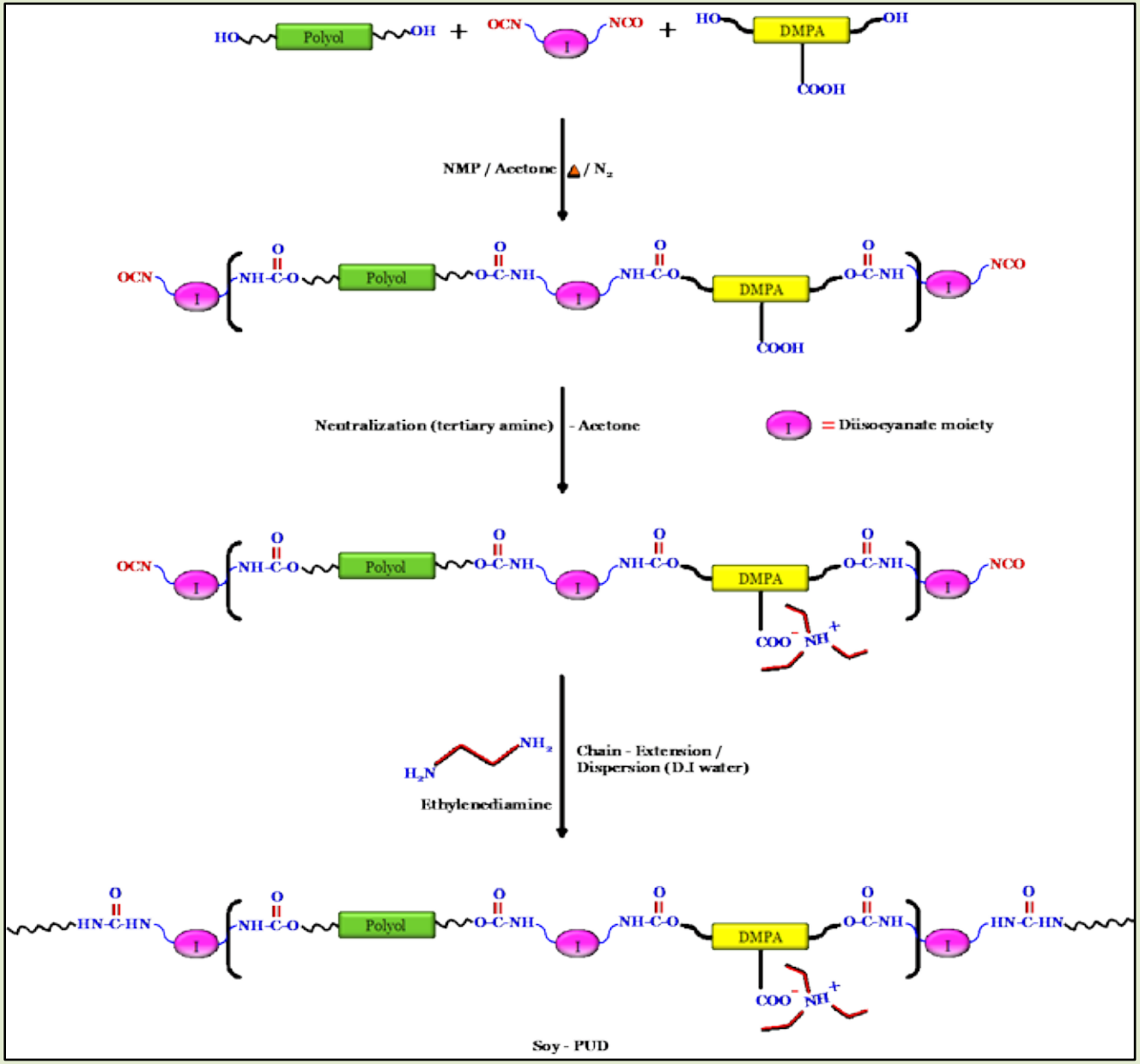
Contact Angle



Water & Oil Resistance Properties



Synthesis of Polyurethane Dispersion



Research Design

Step 1: → Pre – Polymer synthesis → Isocyanate index = 1.4
Acid value = 30 mgKOH/g

Step 2 : → Neutralization → 90%

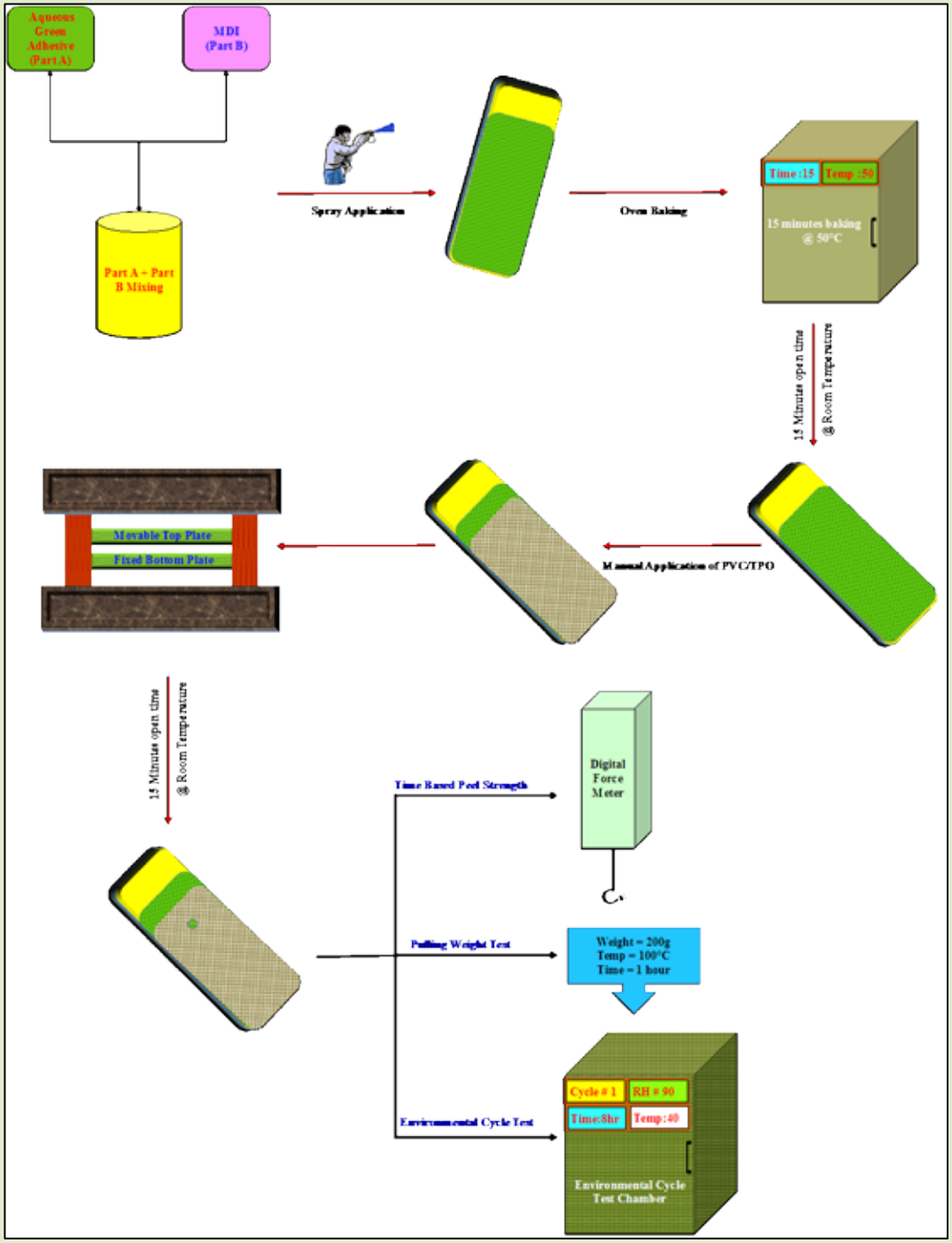
Step 3: → Chain extension / Water Dispersion → 45 % Solids, ≈ 55 % Water

Development of Aqueous Green Adhesives

Raw Materials	Formulation (gram)			
	F1	F2	F3	F4
Part A				
Green Polyurethane Dispersion (Soy – PUD)	20	30	40	50
Poly (vinyl alcohol) stabilized vinyl acetate-ethylene copolymer	60	50	40	30
Aqueous Emulsion copolymer of styrene and acrylic ester	18.5	18.5	18.5	18.5
Thickener	0.5	0.5	0.5	0.5
Biocheck 430	0.5	0.5	0.5	0.5
Defoamer	0.5	0.5	0.5	0.5
Total	100	100	100	100
Part B				
MDI	4	4	4	4

Characteristics of Water-based Trim Adhesives

Characteristics	F1	F2	F3	F4
Part A				
pH	6.5	6.53	6.6	6.8
Viscosity (cPs) @ 25 ° C	2500	2350	2300	2200
Solids (%)	48.55	47.05	45.55	44.05
Part A & Part B Mix Viscosity Profile				
0 hour	2450	2350	2200	2150
2 hours	3160	2900	3000	3025
4 hours	3650	3700	3755	3705
6 hours	4115	4205	4455	4565
8 hours	4875	4935	5000	5050
10 hours	5035	5165	5250	5325


Aqueous Green Adhesive (Part A)
MDI (Part B)
Part A + Part B Mixing
Spray Application
Oven Baking
Time :15
Temp :50
15 minutes baking @ 50°C
15 Minutes open time @ Room Temperature
Movable Top Plate
Fixed Bottom Plate
Manual Application of PVC/TPO
15 Minutes open time @ Room Temperature
Time Based Peel Strength
Digital Force Meter
Pulling Weight Test
Weight = 200g
Temp = 100°C
Time = 1 hour
Environmental Cycle Test
Cycle # 1
RH # 90
Time:8hr
Temp:40
Environmental Cycle Test Chamber

Adhesive Bond Strength

Time (hrs)	180 ° Peel Strength (lbs./ inch)							
	ABS to TPO				ABS to PVC			
	F1	F2	F3	F4	F1	F2	F3	F4
1	1.67	3.3	5.78	6.3	0	0	6	10.6
2	3.76	5.8	8.8	9.1	0	0	8.3	12.4
4	6.06	7.3	10.95	11.1	0	0	12.6	-
6	8.34	8.95	-	-	0	0	-	-
8	9.78	11.2	-	-	0	0	-	-
10	10.77	-	-	-	0	0	-	-

Bio-PUD Content:
F1 = 20 %, F2 = 30 %, F3 = 40 %, F4 = 50%

Adhesive Bond Strength (High Temperature)

Deadweight Peel Strength (200 g @ 105 ° c) Delamination Length (mm)			
ABS to TPO		ABS to PVC	
F1	5 mm	F1	4 mm
F2	3 mm	F2	2 mm
F3	0 mm	F3	0 mm
F4	0 mm	F4	0 mm

Conclusion

Thank You All!