

SEPTEMBER 8-9, 2022

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Introduction

Powder Coatings

- Alluring Technology:
 - **Reduced VOC Emissions** ullet
 - Ability to Recycle Overspray •
 - **Exceptional Film Mechanical Properties** ullet





Introduction

Powder Coatings

- **Alluring Technology:**
 - **Reduced VOC Emissions** ullet
 - Ability to Recycle Overspray •
 - **Exceptional Film Mechanical Properties** ullet





Introduction

Powder Coatings

- Alluring Technology:
 - Reduced VOC Emissions Ability to Recycle Overspray Exceptional Film Mechanical Properties







- Need For Continued Innovation:
 - Relatively New Technology
 - Review of History & Today's Market → Need for LTC Capabilities





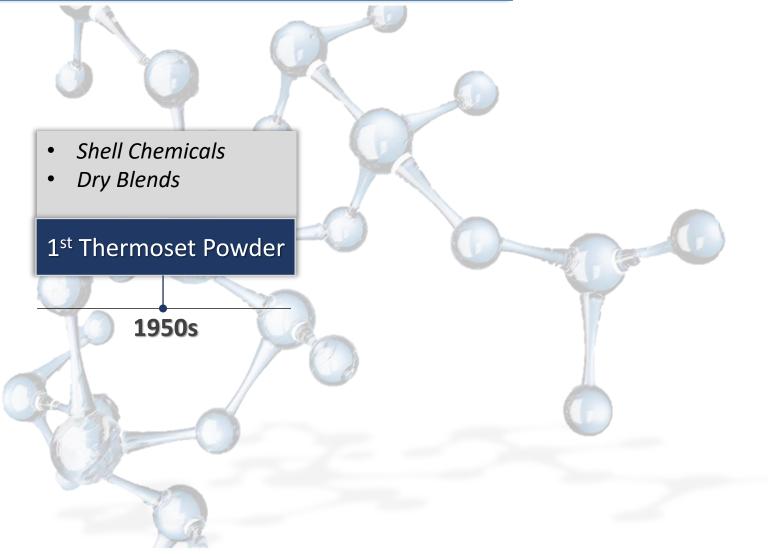
Reduce Oven Temps

Powder History *Time Line*



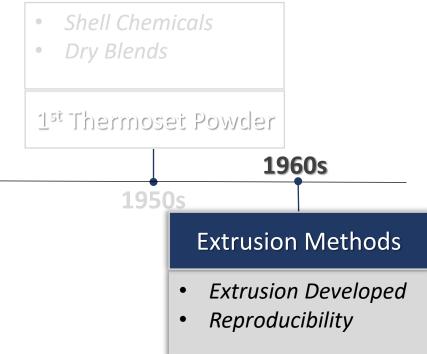


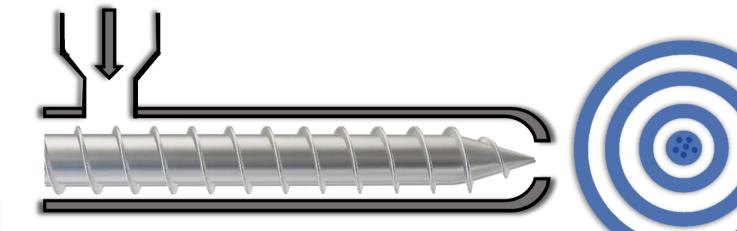










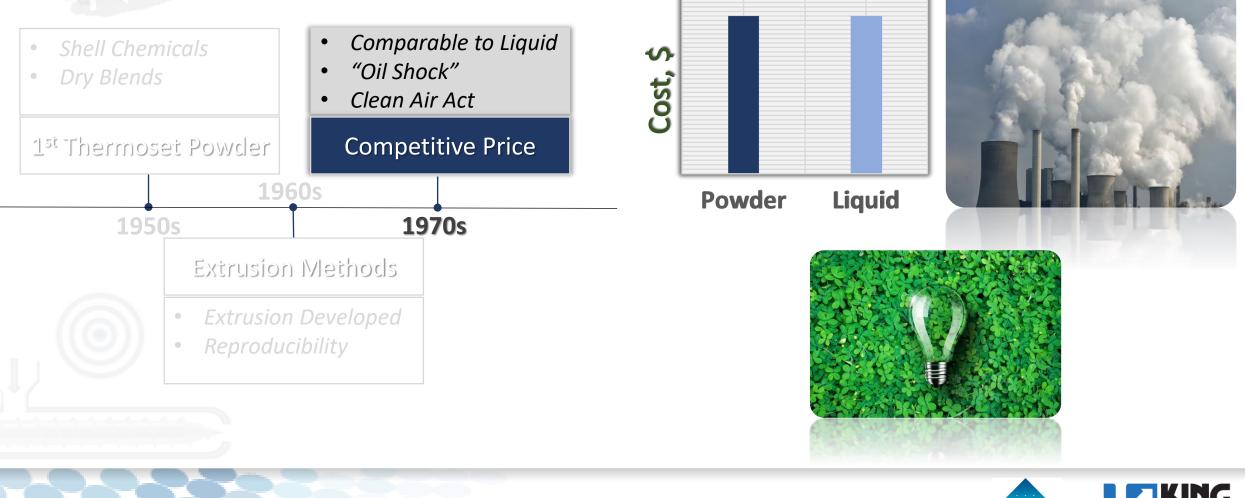


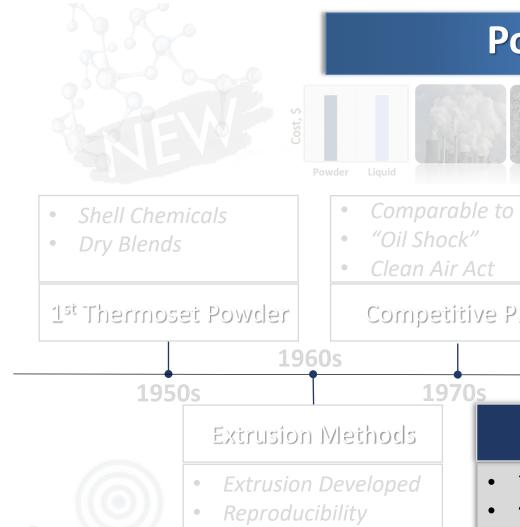
Reproducibility

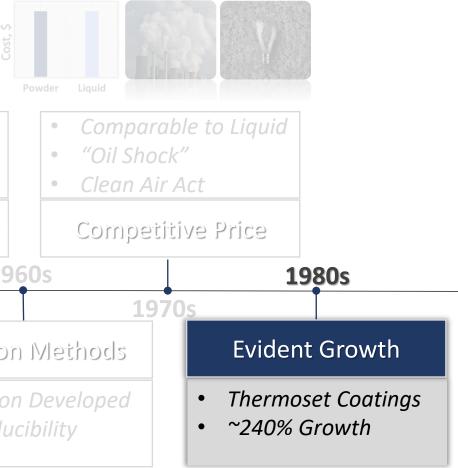


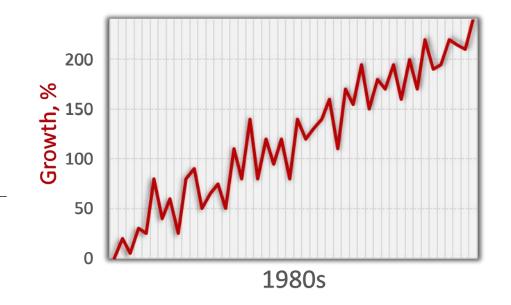
















1st Thermoset Powder

1950s

Powder History

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1980s

Evident Growth

Major Appliances

Auto. Components

Several Markets Emerge

1990s

Industrial Machinery



- Comparable to Liquid"Oil Shock"
 - Clean Air Act

Competitive Price

1970s



1960s

- Extrusion Developed
- *Reproducibility*
- Thermoset Coatings
 ~240% Growth

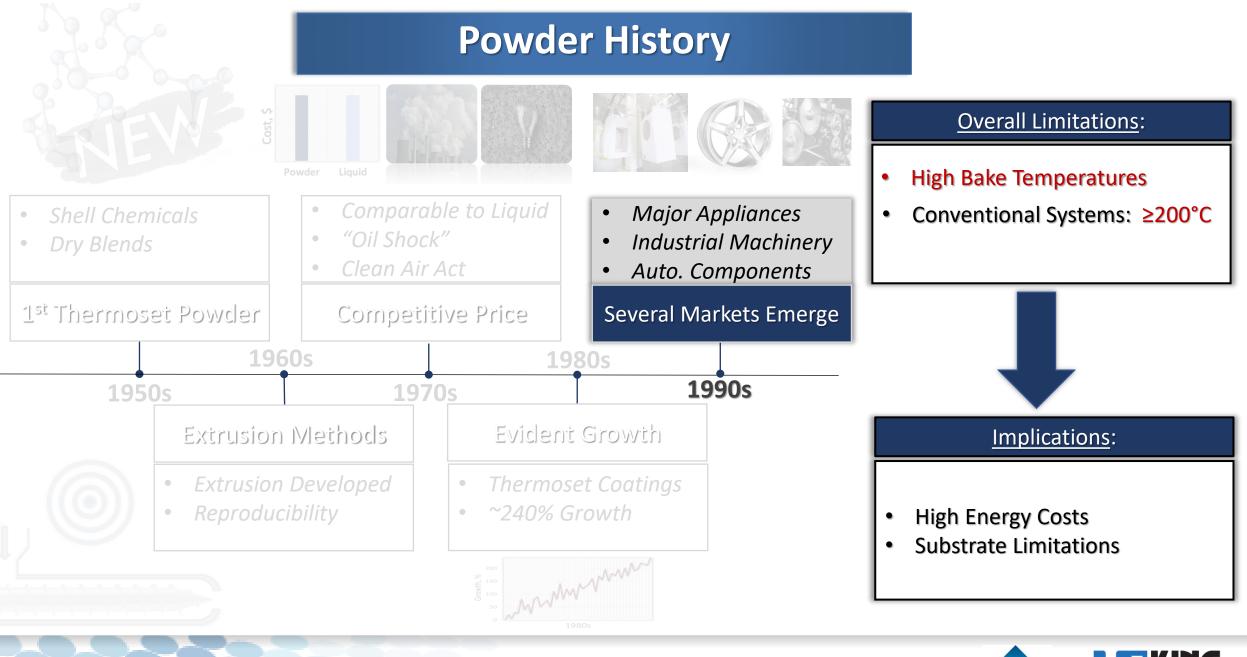




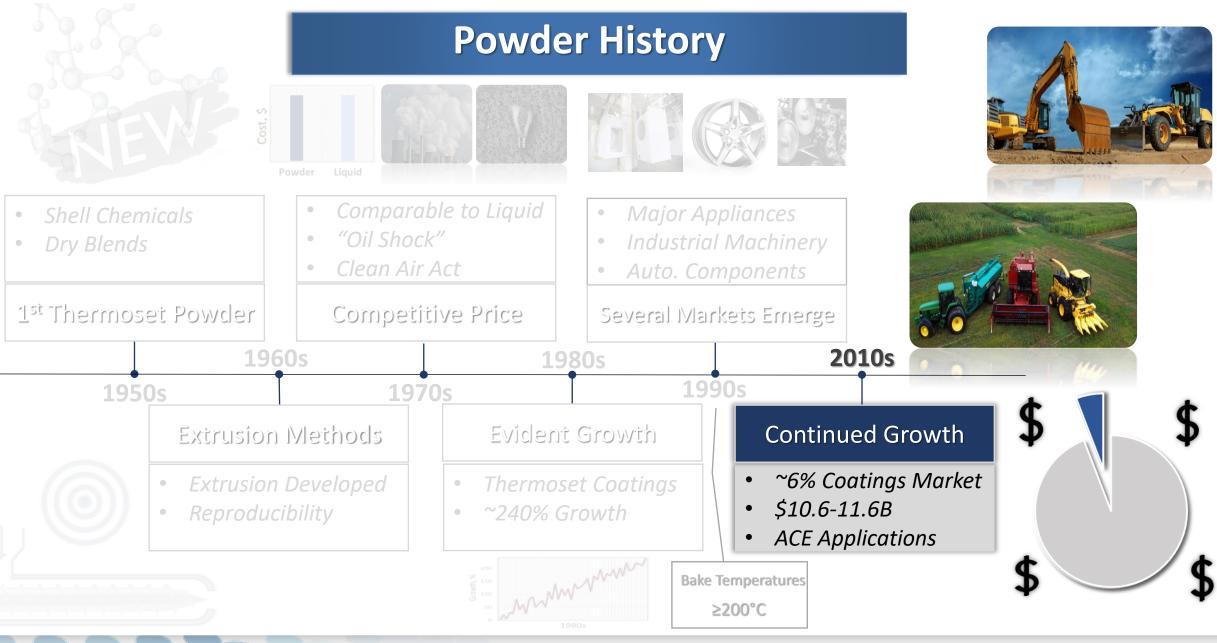




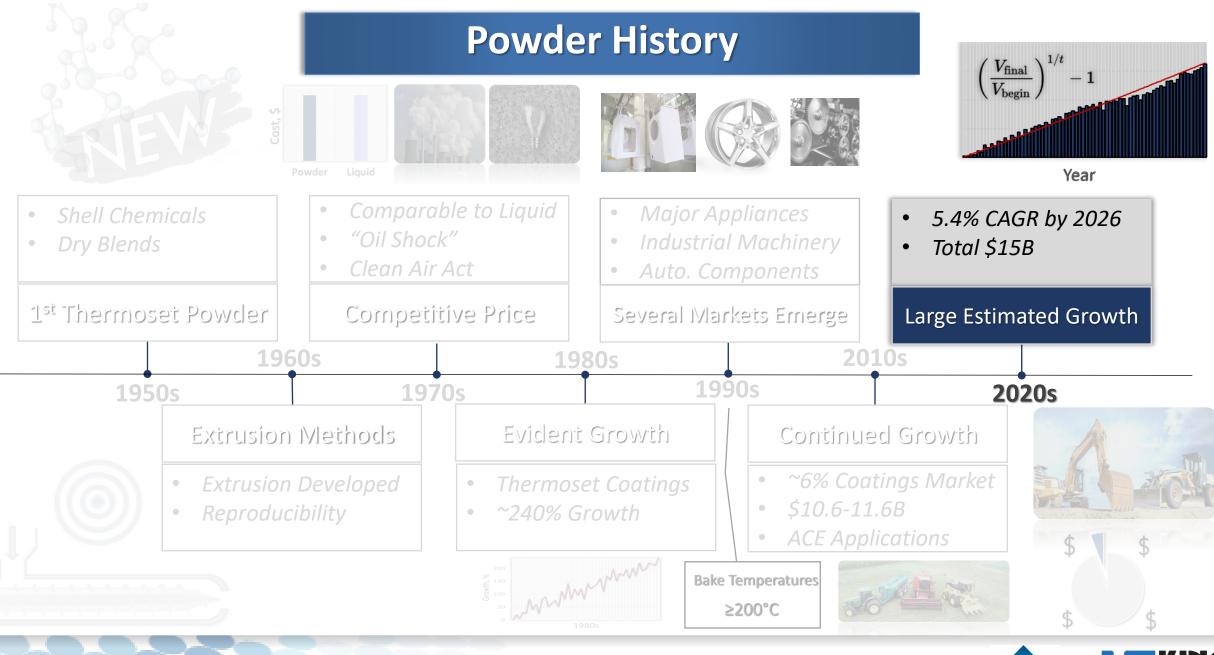




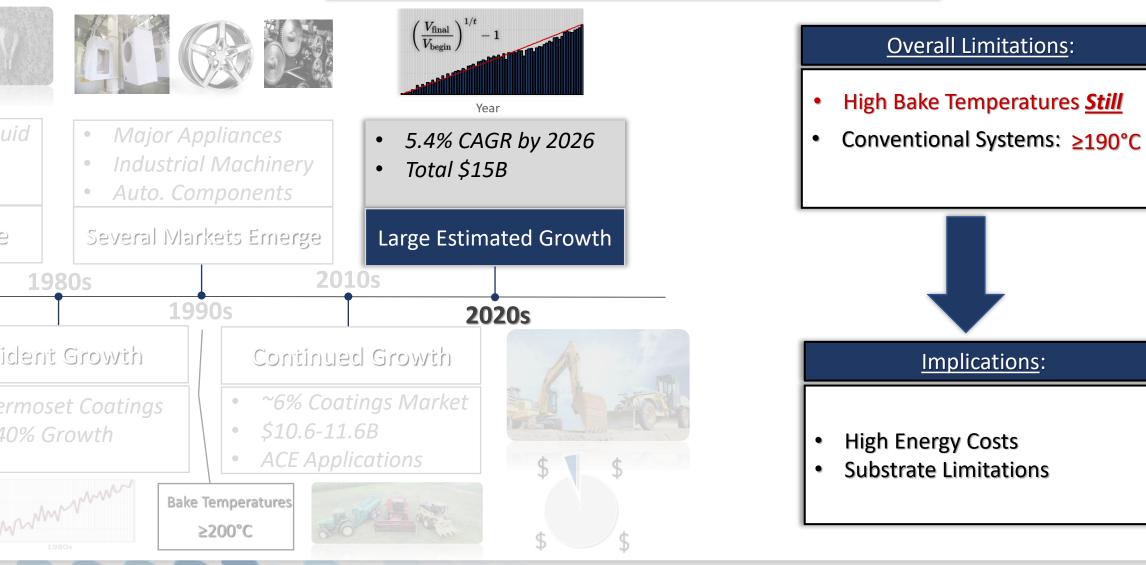




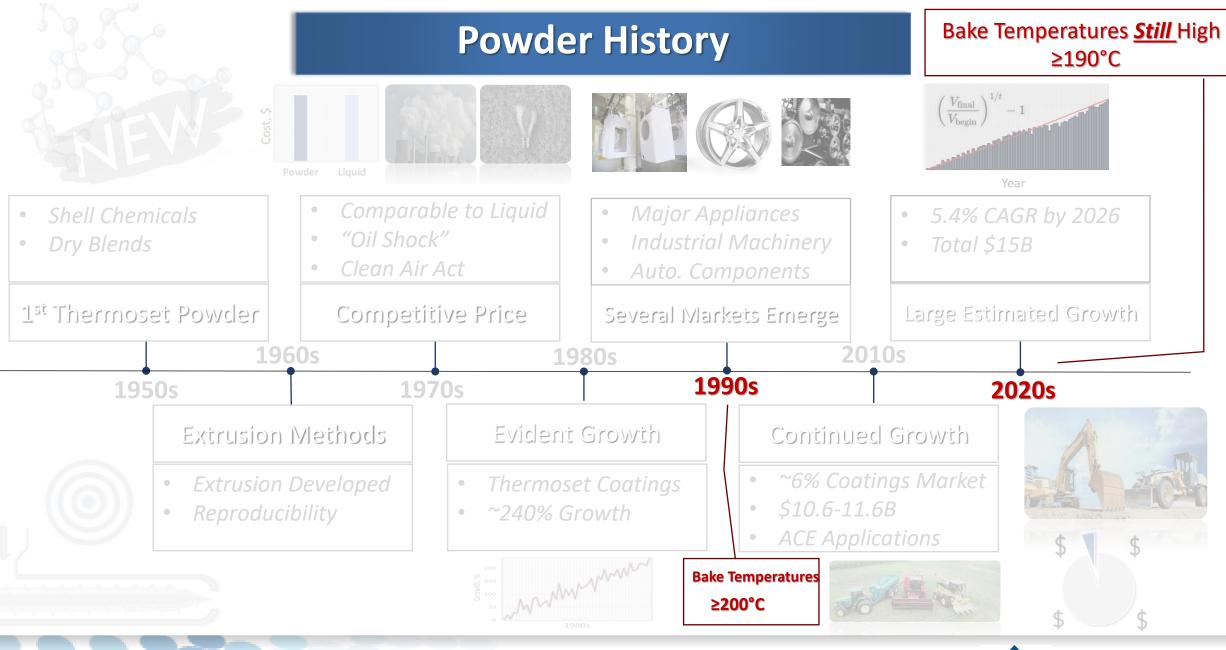




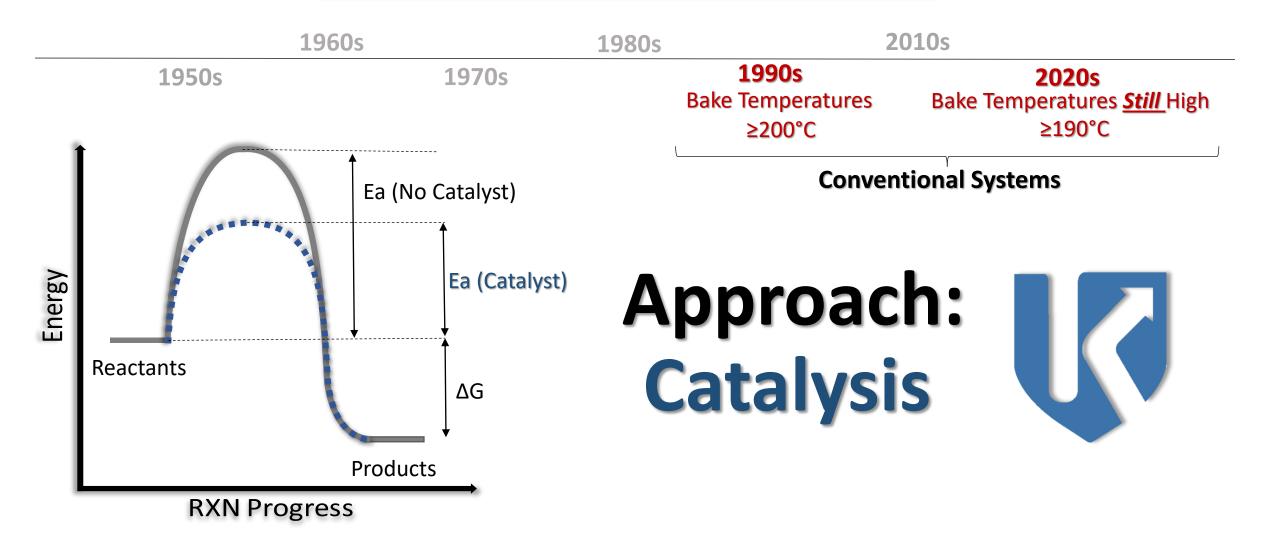








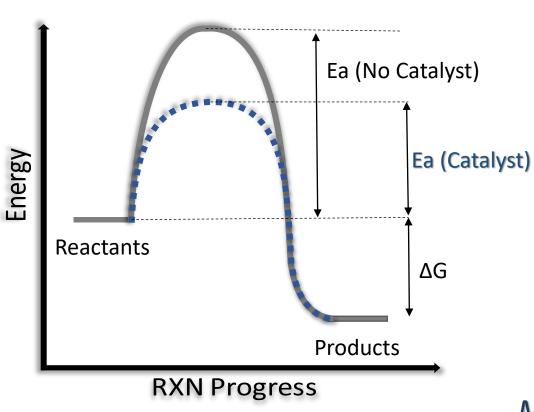








Overall Objectives



Approach: Catalysis

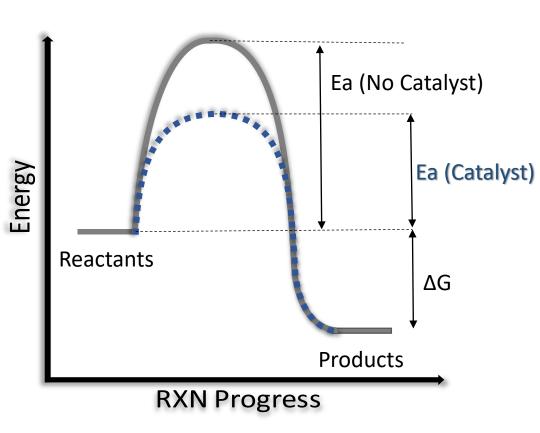


- Low Temperature Cure (LTC):
 - Increase Efficiency
 - Reduce Energy Costs
 - Environmental Awareness
 - Heat Sensitive Substrates

Maintain Growth of Powder Coatings Market



Overall Objectives

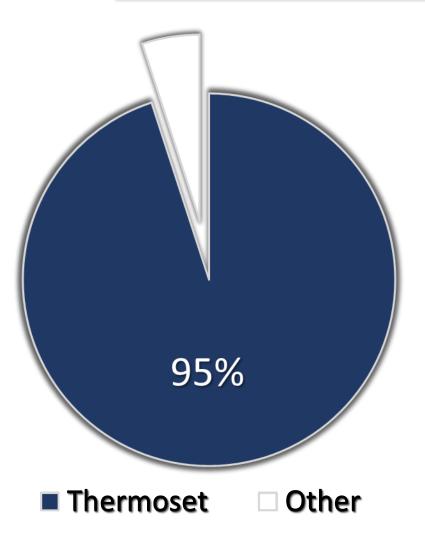


Approach: Catalysis



Naming Convention	%Active	Appearance
Catalyst LC	80	Clear, Light Straw- color Liquid
Catalyst PC	56	White, Free- Flowing Powder

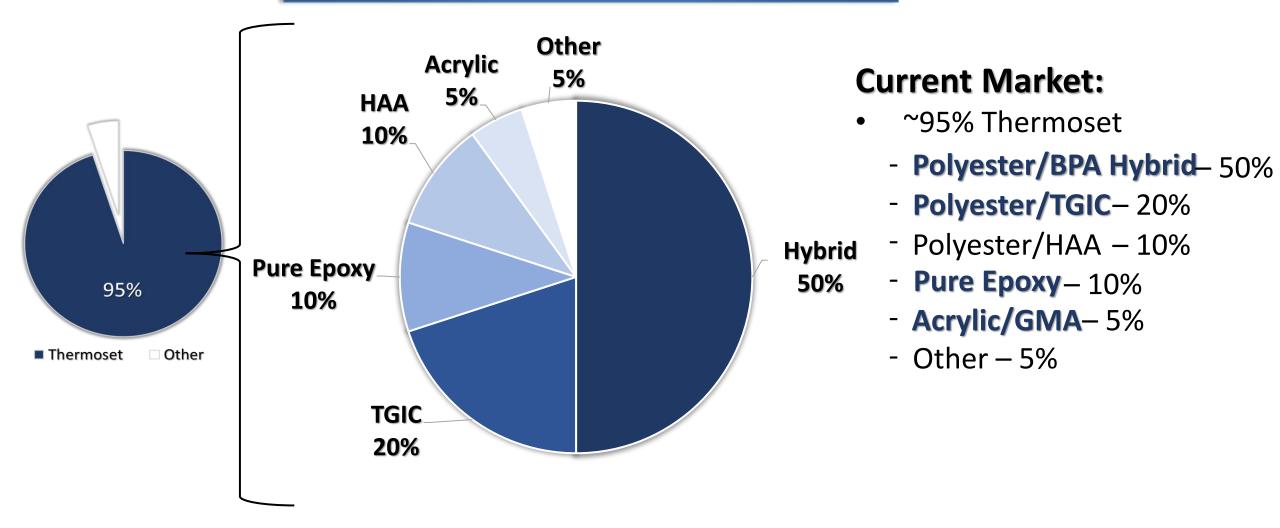




Current Market:

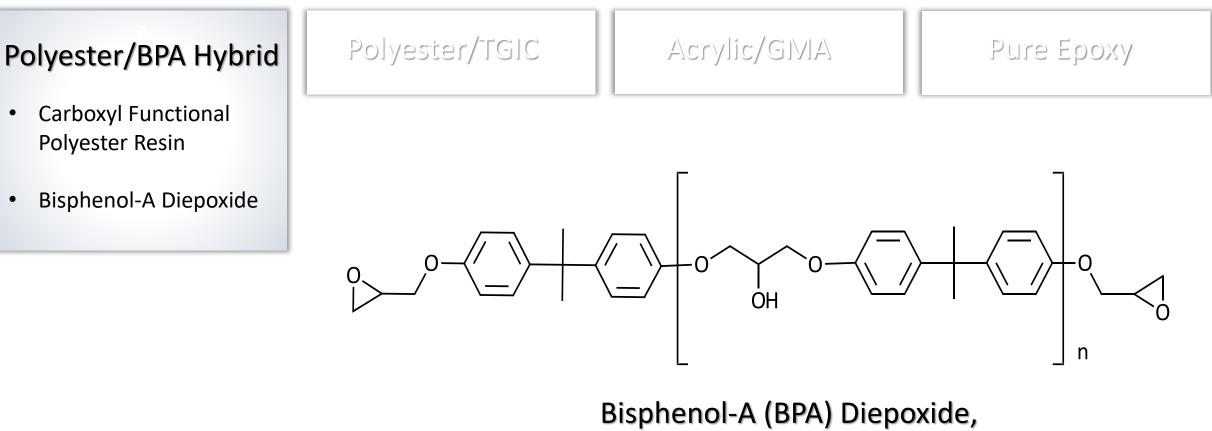
• ~95% Thermoset











n ≥ 0



Polyester/BPA Hybrid

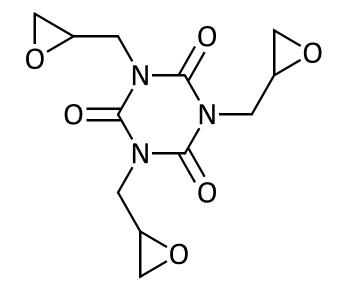
Bisphenol-A (BPA) Diepoxide, $n \ge 0$

Polyester/TGIC

- Carboxyl Functional Polyester Resin
- Trifunctional Epoxide Crosslinker

Acrylic/GMA

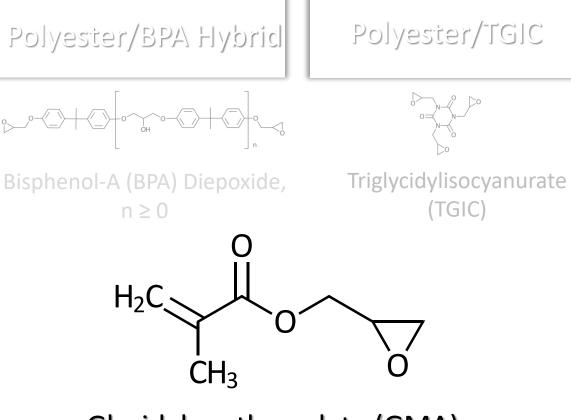
Pure Epoxy



Triglycidylisocyanurate (TGIC)







Glycidyl methacrylate (GMA) monomer

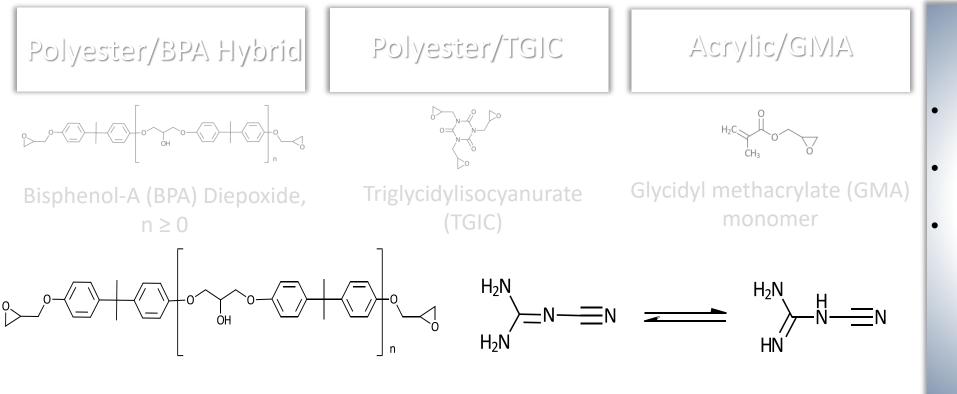


Acrylic/GMA

- Carboxyl Functional Acrylics
- Epoxy Functional Acrylics
 - Glycidyl
 - methacrylate (GMA) Acrylics

Pure Epoxy





Pure Epoxy

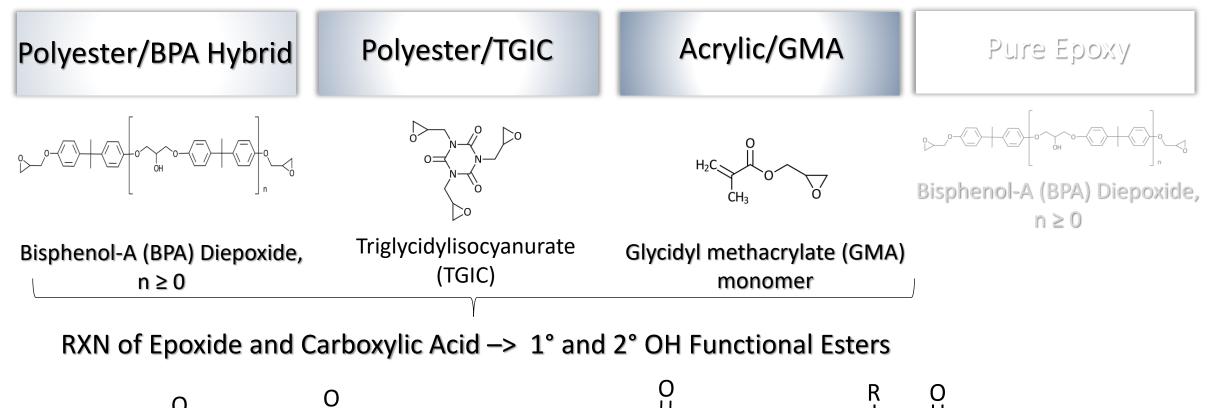
- BPA Epoxy
- No Acrylic or Polyester
- Amine Functional Hardeners
 - DICY
 - Dihydrazide
 - Benzoguanamine

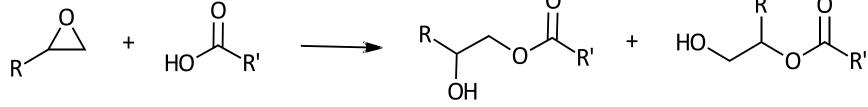
Bisphenol-A (BPA) Diepoxide, $n \ge 0$

Dicyandiamide (DICY)

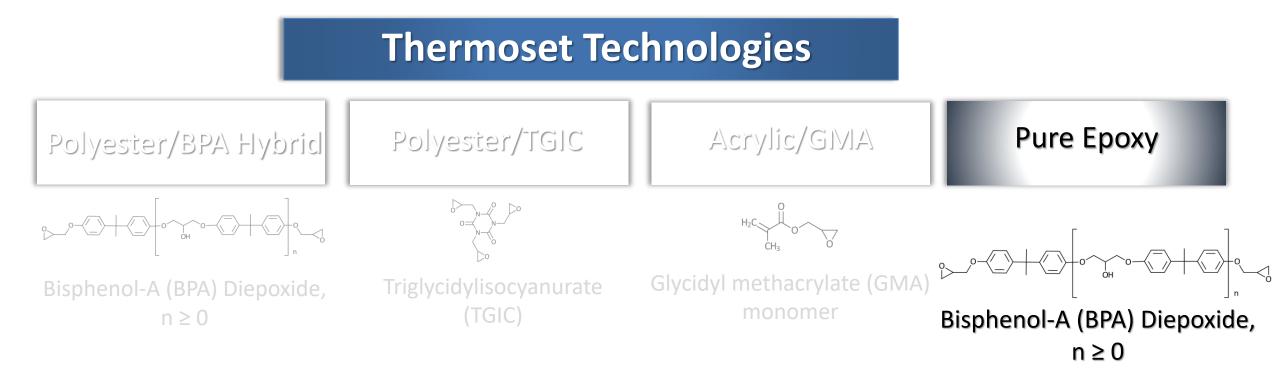


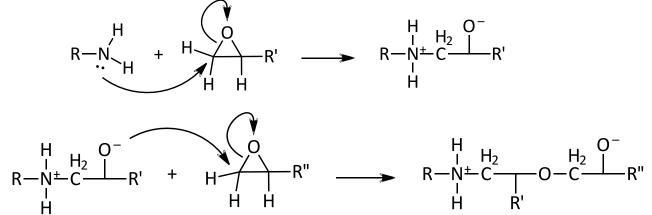






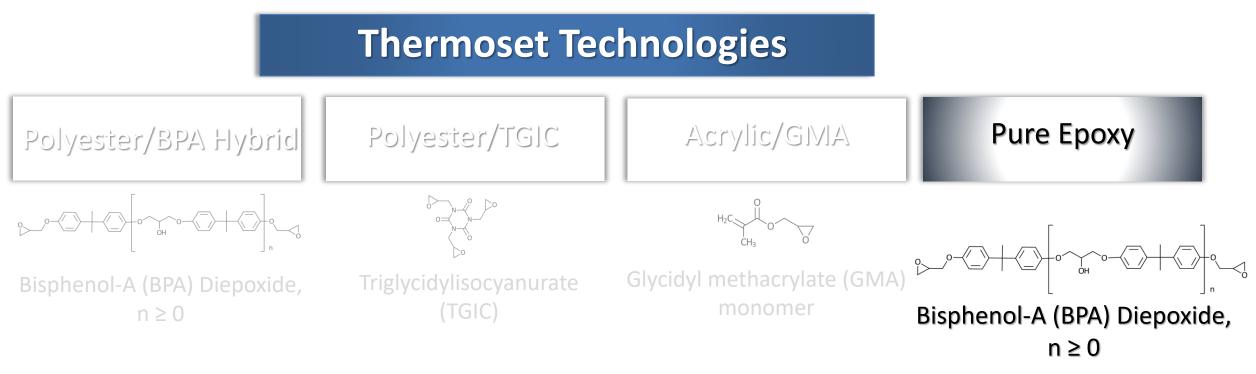


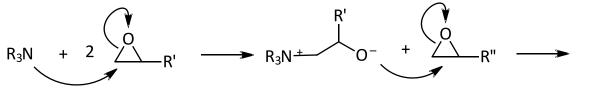


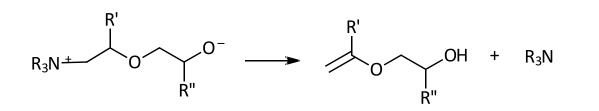


• Epoxy/Amine Polymerization



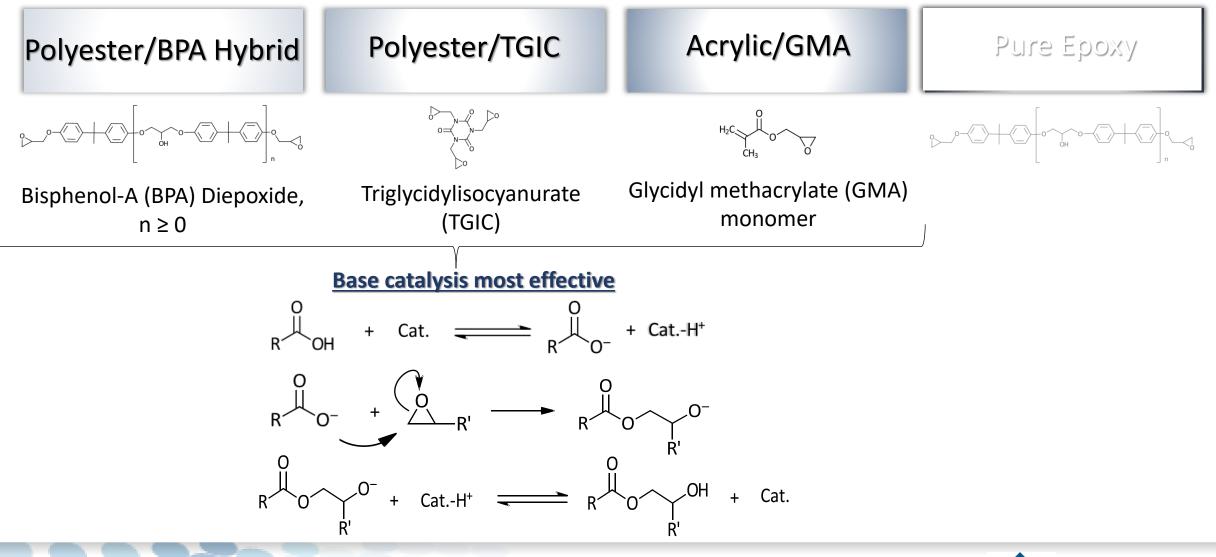






- Epoxy/Amine Polymerization
- Epoxy Homopolymerization
 - Often Catalyzed with 3° Amine







Suitable Catalysts for Epoxy/Carboxy RXN

Base catalysis most effective

Family	Chemical	
	Benzyldimethylamine (BDMA)	
Tertiary amines	2-methylimidazole (2-MI)	
	1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU)	
	Tetramethyl Guanidine (TMG)	
	Octyldimethylamine (ODMA)	
	Decyldimethylamine (DDMA)	
Quaternary bases (Ammonium & Phosphonium)	Benzyl trimethylammonium bromide (BTAB)	
	Tetrabutyl ammonium bromide (TBAB)	
	Tetrabutyl phosphonium bromide (TBPB)	
Metal compounds	Zinc chelates	
	Zinc-Amine	
	Zinc octoate	
	Bismuth-Amine	







Suitable Catalysts for Epoxy/Carboxy RXN

Base catalysis most effective

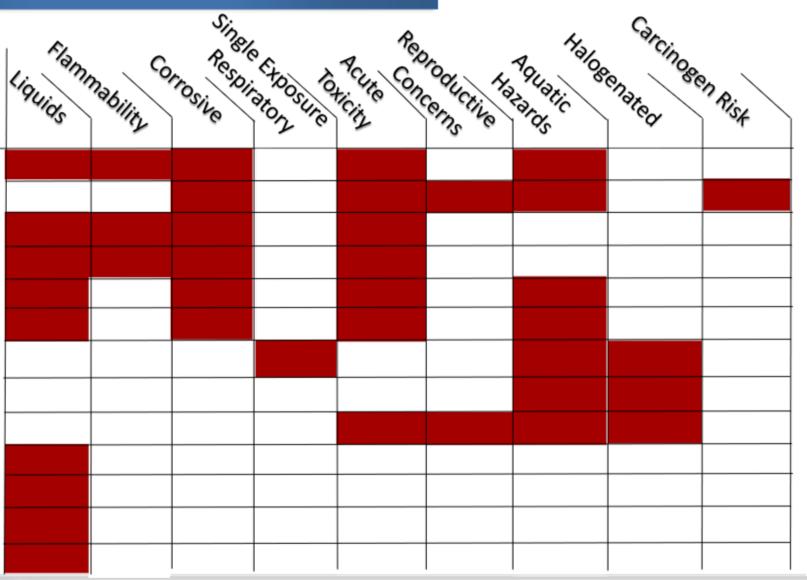
Family	Chemical	
Tertiary amines	Benzyldimethylamine (BDMA) 2-methylimidazole (2-MI) 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) Tetramethyl Guanidine (TMG) Octyldimethylamine (ODMA) Decyldimethylamine (DDMA)	Limitations/Issues: Performance: • Appearance • Yellowing • Storage Stability
Quaternary bases (Ammonium & Phosphonium)	Benzyl trimethylammonium bromide (BTAB) Tetrabutyl ammonium bromide (TBAB) Tetrabutyl phosphonium bromide (TBPB)	Handling, Safety, and Regulatory:Several Concerns
Metal compounds	Zinc chelates Zinc-Amine Zinc octoate Bismuth-Amine	



Limitations/Issues:

Handling, Safety, and Regulatory

Benzyldimethylamine (BDMA) 2-methylimidazole (2-MI) 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) Tetramethyl Guanidine (TMG) Octyldimethylamine (ODMA) **Decyldimethylamine** (DDMA) Benzyl trimethylammonium bromide (BTAB) Tetrabutyl ammonium bromide (TBAB) Tetrabutyl phosphonium bromide (TBPB) Zinc chelates Zinc-Amine Zinc octoate **Bismuth-Amine**





Catalyst LC & PC

Naming Convention	%Active	Appearance
Catalyst LC	80	Clear, Light Straw- color Liquid
Catalyst PC	56	White, Free- Flowing Powder

Catalysts for Epoxy Powder Coatings:

- Safe and Easy to Handle
- LTC Capabilities
- Achieve Good Chemical Resistance and Impact Resistance
- Better Film Appearance than Conventional Materials



Catalyst LC

Catalyst PC



Experimental







Experimental

Experiment I – Epoxy Homopolymerization

> Experiment II – Acrylic/GMA

Experiment III – Polyester/BPA

Experiment IV – Polyesteramide/TGIC



Experimental

Experiment I – Epoxy Homopolymerization

Experiment II – Acrylic/GMA

Catalyst LC

• Demonstrate Capabilities of Accelerating Homopolymerization of BPA-type Epoxy.

Experiment III – Polyester/BPA

Experiment IV – Polyesteramide/TGIC • Liquid Materials

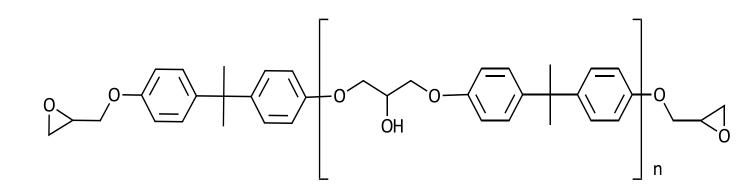
Bisphenol-A (BPA) Diepoxide, n ≥0

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Formulation

Material	Description	%
Epoxy Resin	BPA type resin, EEW 182- 192 g/eq	100.00
TOTAL		100.00
%Total resin solids (TRS)	100	

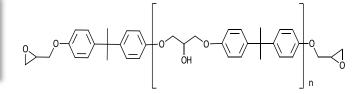


Bisphenol-A (BPA) Diepoxide, n = 0



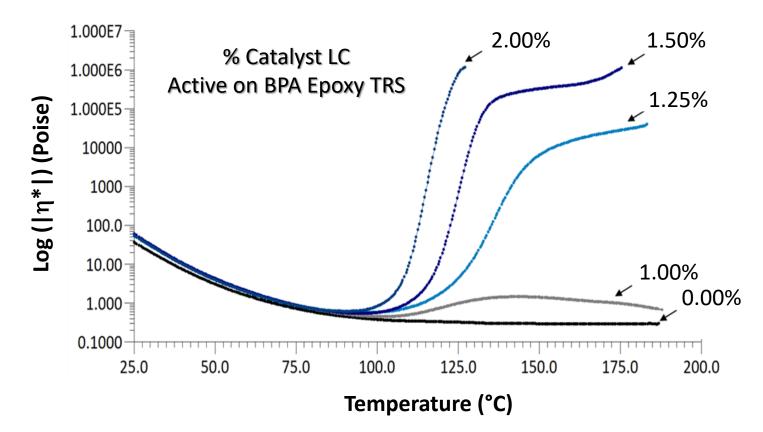
Experiment I – Epoxy Homopolymerization

Gel Temperatures



AR 2000 Rheometer – Pelteir Plate – 20mm Steel Plate

Temperature Ramp: 2.5°C / min – 25-188°C

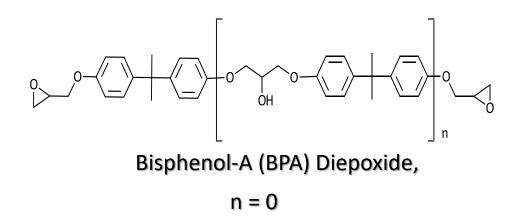


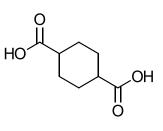


Experiment I – Epoxy Homopolymerization

Gel Temperatures

AR 2000 Rheometer – Pelteir Plate – 20mm Steel Plate Temperature Ramp: 5°C / min – 25-188°C + Isotherm





1,4-Cyclohexanedicarboxylic Acid (CHDA) Nucleophile

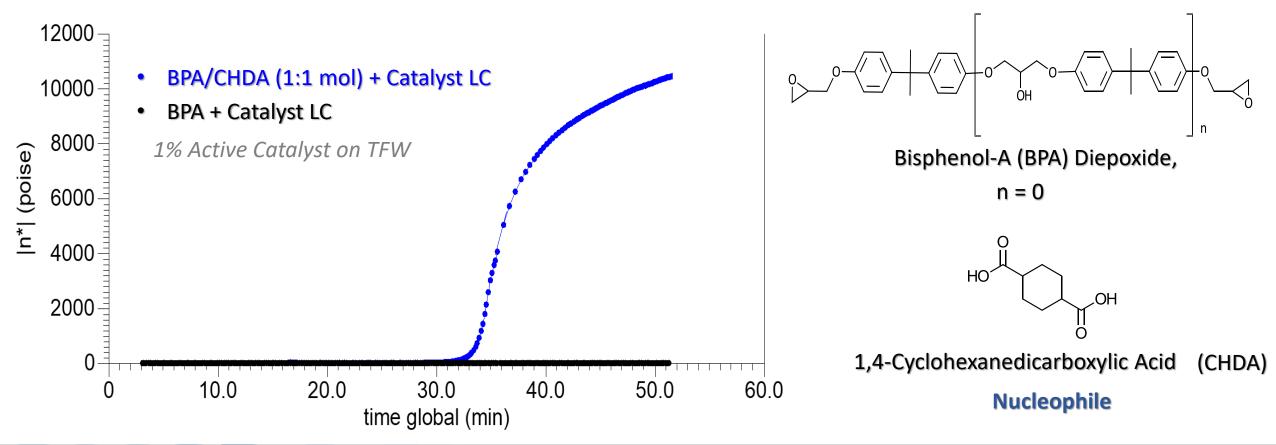




Experiment I – Epoxy Homopolymerization

Gel Temperatures

AR 2000 Rheometer – Pelteir Plate – 20mm Steel Plate Temperature Ramp: 5°C / min – 25-188°C + Isotherm





Experiment I – Epoxy Homopolymerization

– Il ±meriment II Acrylic/GMA

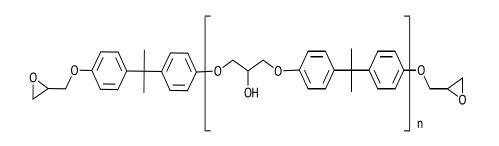
Conclusions:

- Catalyst Accelerates Epoxy Homopolymerization of BPA-Type Epoxy
- Useful for Pure Epoxy Systems

Experiment III – Polyester/BPA

More Effectively Promotes Epoxy/Carboxy RXN

Experiment IV – Polyesteramide/TGIC



Bisphenol-A (BPA) Diepoxide, n = 0

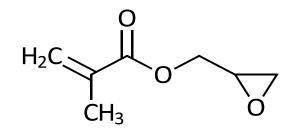


Experiment I – Epoxy Homopolymerization Experiment II – Acrylic/GMA

- Catalyst LC
- Carboxyl Functional Acrylic Resin with GMA-Type Epoxy

Experiment III – Polyesteramide/TGIC

- SB and Powder Systems
- Gel Temperature / Cure Evaluations



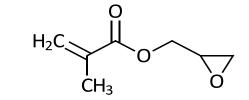
Glycidyl methacrylate (GMA) monomer



Experiment IV – Polyester/BPA



Formulation



2K SB Clear Acrylic/GMA

Component	Material	Description	%
	Acrylic resin	Carboxyl functional acrylic, AV 148 mg KOH/g	31.10
Acid	Xylene	Solvent	15.10
Acid	PM acetate	Solvent	15.10
Component	n-Butyl acetate	Solvent	7.50
	Silane flow additive	Polyester modified dimethylsiloxane	0.20
	Epoxy resin	Glycidyl methacrylate (GMA), EEW 300 - 350 g/eq	14.00
Ероху	Xylene	Solvent	6.80
Component	PM acetate	Solvent	6.80
	<i>n</i> -Butyl acetate	Solvent	3.40
TOTAL			100.00

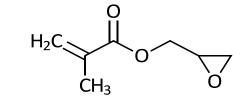
Total Resin Solids (TRS) = 45%

Acrylic/GMA on TRS = 69/31









Powder Acrylic/GMA

Material	Material Description	
Acrylic resin	Carboxyl-functional acrylic, AV 148 mg KOH/g	69.00
Epoxy resin	Glycidyl methacrylate (GMA), EEW 300 - 350 g/eq	31.00
	100.00	

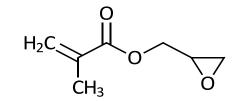
Total Resin Solids (TRS) = 100% Acrylic/GMA on TRS = 69/31







Powder Rheology Method



Powder Acrylic/GMA

Powder Disc Prepared using Cylindrical Pellet Press (left)



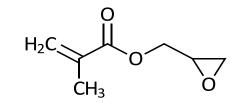








Powder Rheology Method



Powder Acrylic/GMA

Powder Disc Prepared using Cylindrical Pellet Press (left)

-3 Piece Press

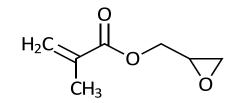








Powder Rheology Method



Acrylic/GMA Powder

Powder Disc Prepared using Cylindrical Pellet Press (left)

-3 Piece Press

1) Fine Powder Poured into Press

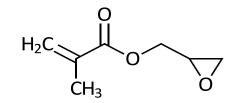




10,000 N



Powder Rheology Method



Acrylic/GMA Powder

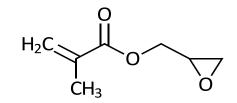
Powder Disc Prepared using Cylindrical Pellet Press (left)

- -3 Piece Press
- 1) Fine Powder Poured into Press
- 2) Powder Pressed with 10,000 N Force





Powder Rheology Method

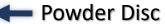


Acrylic/GMA Powder

Powder Disc Prepared using Cylindrical Pellet Press (left)

- -3 Piece Press
- 1) Fine Powder Poured into Press
- 2) Powder Pressed with 10,000 N Force
- 3) Disc Ejected From Bottom of Pellet Press

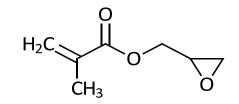








Powder Rheology Method



Acrylic/GMA Powder

Powder Disc Prepared using Cylindrical Pellet Press (left)

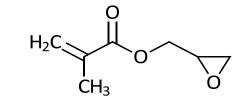
- -3 Piece Press
- 1) Fine Powder Poured into Press
- 2) Powder Pressed with 10,000 N Force
- 3) Disc Ejected From Bottom of Pellet Press
- 4) Disc Placed Between Parallel Plate Geometry and Evaluated for Gel Time via Oscillation Tests





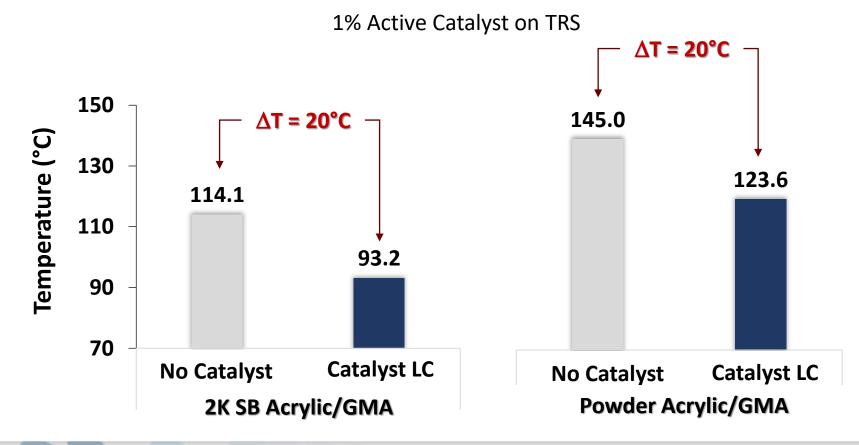


Gel Temperatures



AR 2000 Rheometer

Temperature Ramp = 1°C / min





Experimental

- I fnemireqx3 Epoxy Homopolymerization

Experiment II -Acrylic/GMA

Conclusions:

- Catalyst is Highly Active in GMA-Type Acrylic Systems ۲
 - Accelerates Crosslinking Reaction
 - Carboxyl Functional Acrylic/GMA-Type Diepoxide

– III tnemineqxE Polyesteramide/TGIC

-VI triemined IV

Polyester/BPA

- Significantly Reduces Gel Temperature: ۲
 - Acrylic SB and Powder Systems

 H_2

Glycidyl methacrylate (GMA) monomer



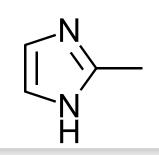


Experiment I – Epoxy Homopolymerization

Catalyst PC

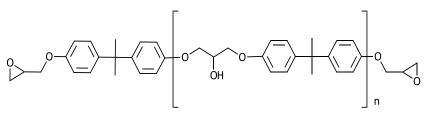
– Il inenineqxE Acrylic/GMA

- White Polyester/BPA Hybrid (70/30)
- Gel Times
- Film Performance & LTC Capabilities:
 - 170°C and 140°C PMT
- Comparisons vs. 2-MI



Experiment III –

Polyester/BPA



Bisphenol-A (BPA) Diepoxide, $n \ge 0$

Experiment IV– Polyesteramide/TGIC

> POWDER COATING SUPVICER 09,2022



Formulation

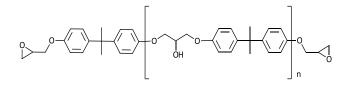
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Material	Description	%
Polyester resin	Carboxyl-functional polyester, AV 35 mg KOH/g	45.50
Epoxy resin	BPA type resin, EEW 182 - 192 g/eq	19.50
TiO ₂	Titanium dioxide	17.38
BaSO ₄	Barium sulfate extender	15.82
Surface agent	Polyacrylate surface agent	1.50
Benzoin	Degassing agent	0.30
	TOTAL	100.00
%Total resin solids (TRS)	65	
Polyester/BPA on TRS	70 / 30	





Formulation



Material	Description		
Polyester resin	Carboxyl-functional polyester, AV 35 mg KOH/g	45.50	
Epoxy resin	BPA type resin, EEW 182 - 192 g/eq	19.50	
TiO ₂	Titanium dioxide	17.38	
BaSO ₄	Barium sulfate extender	15.82	I
Surface agent	Polyacrylate surface agent	1.50	I
Benzoin	Degassing agent	0.30	
	TOTAL	100.00	
%Total resin solids (TRS)	65		
Polyester/BPA on TRS	70 / 30		

- No catalyst
- 2-Methylimidazole
 - 1% as Supplied = 1% Active

Catalyst PC

- 1% as Supplied = 0.56% Active
- 1.79% as Supplied = 1% Active



Coating Preparation

Processing

- Raw Materials were premixed for 180 seconds:
 5 Kg Batch/Formulations
- Premix was added to extruder hopper
 - Extruded under standard conditions.
 - Maximum Zone 3 temperature of 105°C.
- Extrudate was flaked and ground using ACM
- Optimum particle size and distribution achieved using Ultrasonic Sieve (No. 140 Mesh)





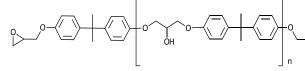


Film Preparation

- Coatings Sprayed over ZnPO₄ CRS
 - Spray Gun: Gema Optiflex Pro
 - Gun Voltage: 65 kV
- Films Cured in Conventional Oven
 - Temperatures: 170°C & 140°C
 - Dwell Time: 15 min PMT
 - **DFT =** ~2.8 mil



Gel Temperatures



AR 2000 Rheometer – ETC – Parallel Plates

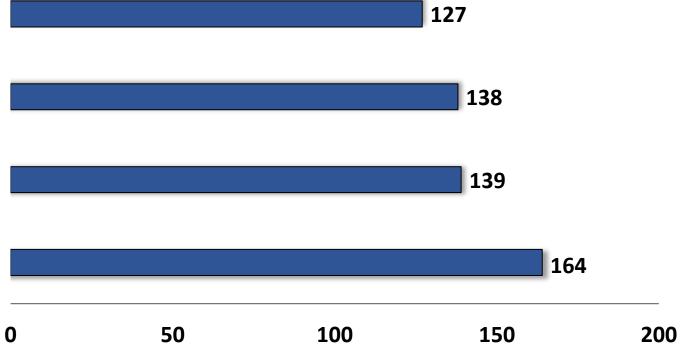
Temperature Ramp: 5°C / min – 20 - 200°C

Catalyst PC (1.79% as supplied; 1% active)

Catalyst PC (1% as supplied; 0.56% active)

2-Methyl imidazole (2-MI) (1% as supplied; 1% active)

No catalyst (0% as supplied; 0% active)

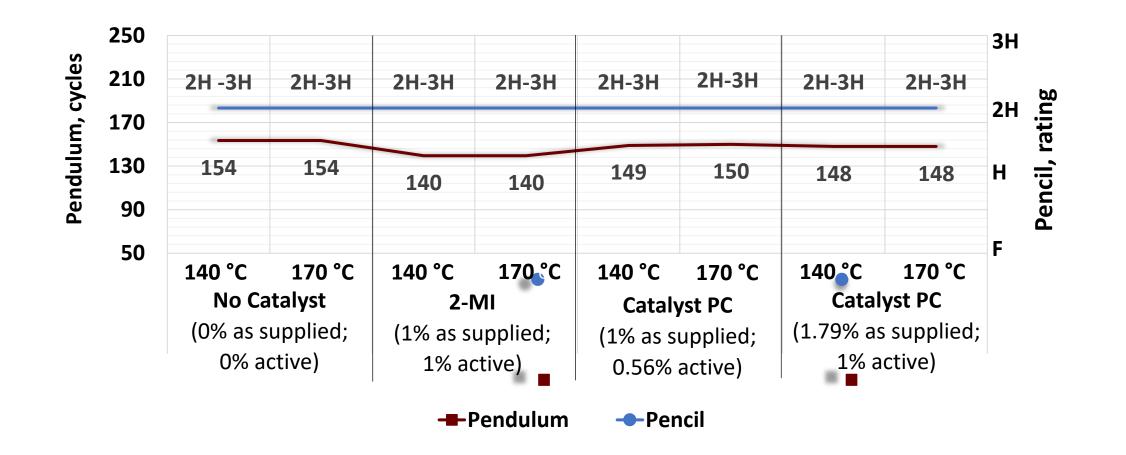


Temperature (°C)



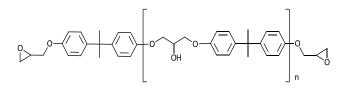
Film Hardness

Experiment III – Polyester/BPA





Cure Response: *MEK Resistance*



Catalyst PC (1.79% as supplied; 1% acti

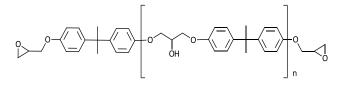
Catalyst PC (1% as supplied; 0.56% act

No Catalyst (0% as supplied; 0% active

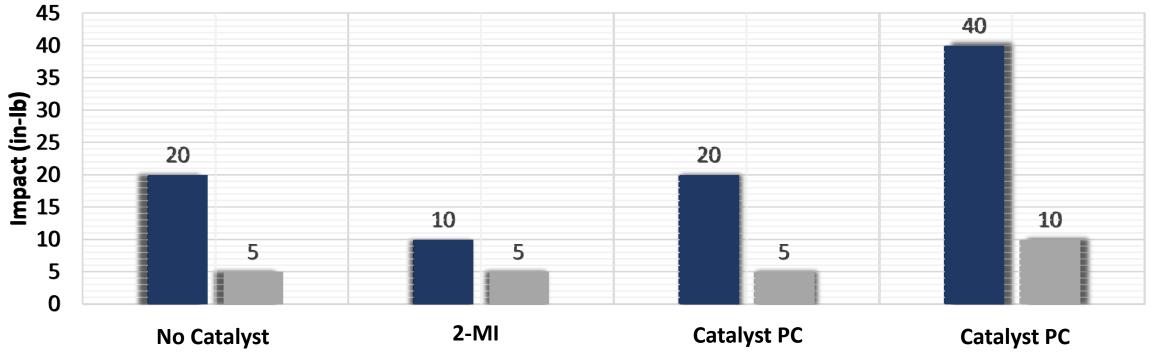
Catalyst PC	> 200				
79% as supplied; 1% active)	>200				
	_				
Catalyst PC	> 200)			
% as supplied; 0.56% active)	148				
2-Methyl imidazole (2-MI)	> 200				
1% as supplied; 1% active)	45				
No Catalyst	> 200)			
0% as supplied; 0% active)	16				
	0	50	100	150	200
			MEK 2X		
Bake Temperature / 15 mi	n.	■ 170 °C	140 °C		



Impact Resistance



140°C/15min



Indirect

(0% as supplied; 0% active) 2-MI (1% as supplied; 1% active)

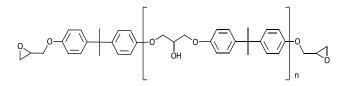
Direct

Catalyst PC (1% as supplied; 0.56% active)

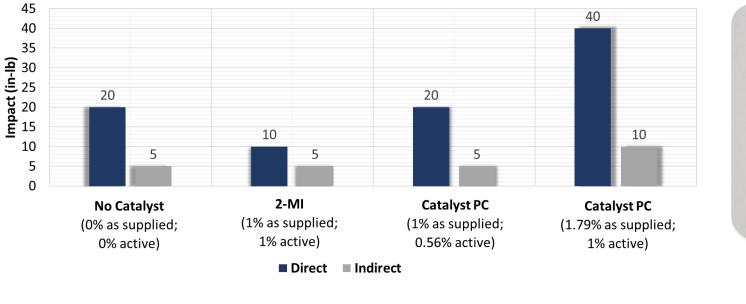
Catalyst PC (1.79% as supplied; 1% active)



Impact Resistance



140°C/15min



Fail @ 20 in-lb

1% 2-MI

(1% Active)

Pass @ 40 in-lb

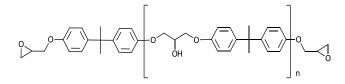


1.79% Catalyst PC (1% Active)

140°C Cure



Mandrel Bend



Mandrel Bend

Fail



1% 2-MI (1% Active)

Pass

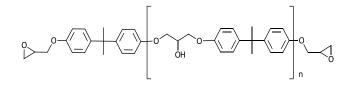
1.79% Catalyst PC (1% Active)

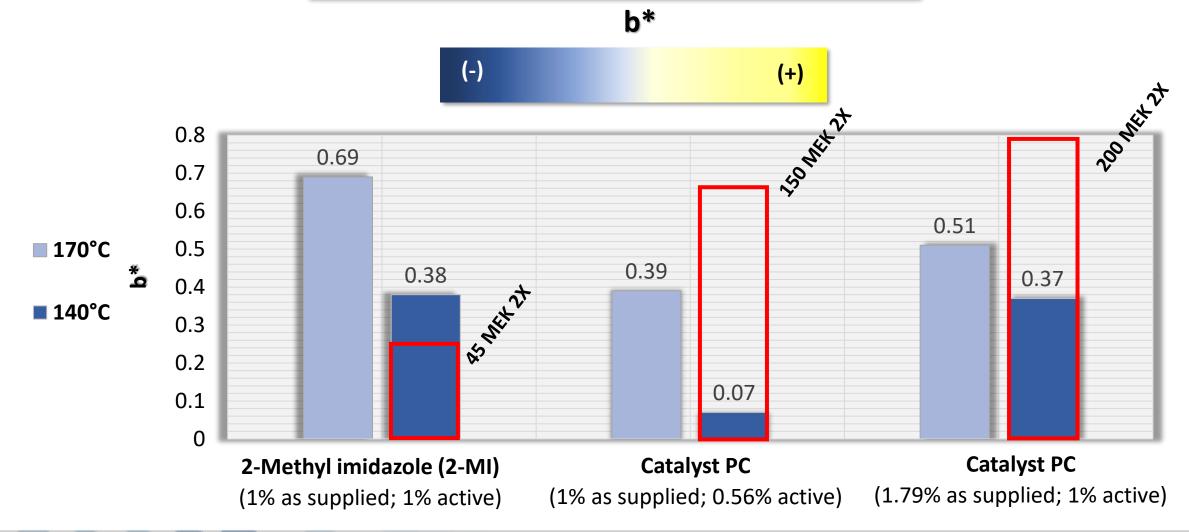
140°C Cure





Color: Yellowing







NEW STUDIES: 60/40 Hybrid

Color: Yellowing

0.68% 2-Methyl Imidazole

1	50°C/10min
	150°C/20min
	200°C/10min
0	200°C/20min
	3

0.68% Catalyst PC

150°C/10min	
150°C/20min	
200°C/10min	
200°C/20min	
C	

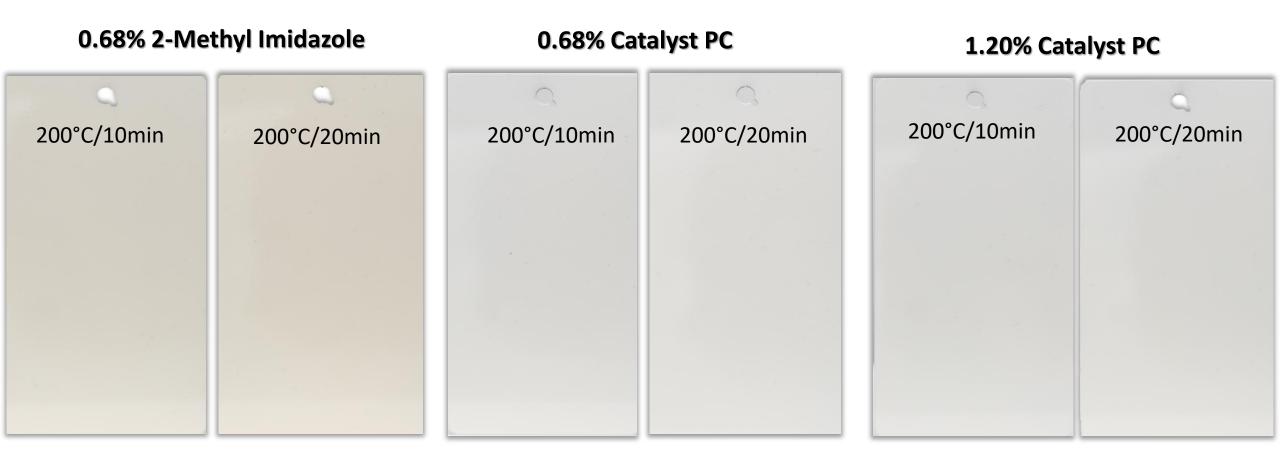
1.20% Catalyst PC

1	50°C/10min	
	150°C/20min	
(200°C/10min	
	200°C/20min	
	C	



NEW STUDIES: 60/40 Hybrid

Color: Yellowing



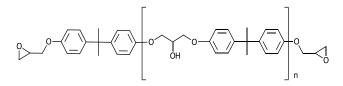








Heat Aged Stability



Storage Stability

50°C Storage

Formulation	Initial	1 Month+
No Catalyst (0% active; 0% as supplied)	Free-flowing powder	Free-flowing powder
2-Methyl Imidazole (1% as supplied; 1% Active)	Free-flowing powder	Free-flowing powder
Catalyst PC (1.79% as supplied; 1% active)	Free-flowing powder	Free-flowing powder
Catalyst PC (1% as supplied; 0.56% active)	Free-flowing powder	Free-flowing powder





Experimental

Experiment I – Epoxy Homopolymerization

> – II fnemiregx3 Acrylic/GMA

Conclusions:

- **Catalyst PC is Highly Active in BPA Hybrids**
 - Accelerates Crosslinking Reaction
 - Carboxyl Functional Polyester/BPA-Type Diepoxides.

Experiment III -

Polyester/BPA

- 70/30 White Polyester/BPA Hybrid
- Superior to 2-MI
 - Compared on Equal Active and Equal as Supplied
 - Superior LTC
 - Less Discoloration
 - **Better Gloss Properties**
 - Cleaner SDS \rightarrow Safer \rightarrow Less Labeling in Manufacturing —



Experiment IV-Polyesteramide/TGIC

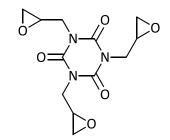
Experiment I – Epoxy Homopolymerization

Catalyst PC

– Il źneninegx Acrylic/GMA

Experiment III – Polyester/BPA

- White Polyesteramide/TGIC
 - -Biobased Polyesteramide (soybean oil)
 - Melt-Flow Rheology
 - Film Performance & LTC Capabilities:
 - 135°C and 125°C PMT
- Comparisons vs. 2-heptadecyl-1H imidazole ('C17 Imidazole')



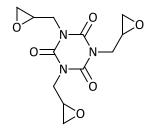
Triglycidylisocyanurate (TGIC)



 $C_{17}H_{35}$

Experiment IV – Polyesteramide/TGIC





Material	Description	%
Polyester-amide resin	Carboxyl-functional resin, AV 35 mg KOH/g	61.55
TGIC	Triglycidyl isocyanurate, EEW 100 g/eq	6.84
Surface agent Flow additive		1.00
Benzoin	Degassing agent	0.50
TiO ₂	Titanium dioxide	
	TOTAL	100.00
%Total resin solids (TRS)	68.2	
Polyester/TGIC on TRS	90 / 10	







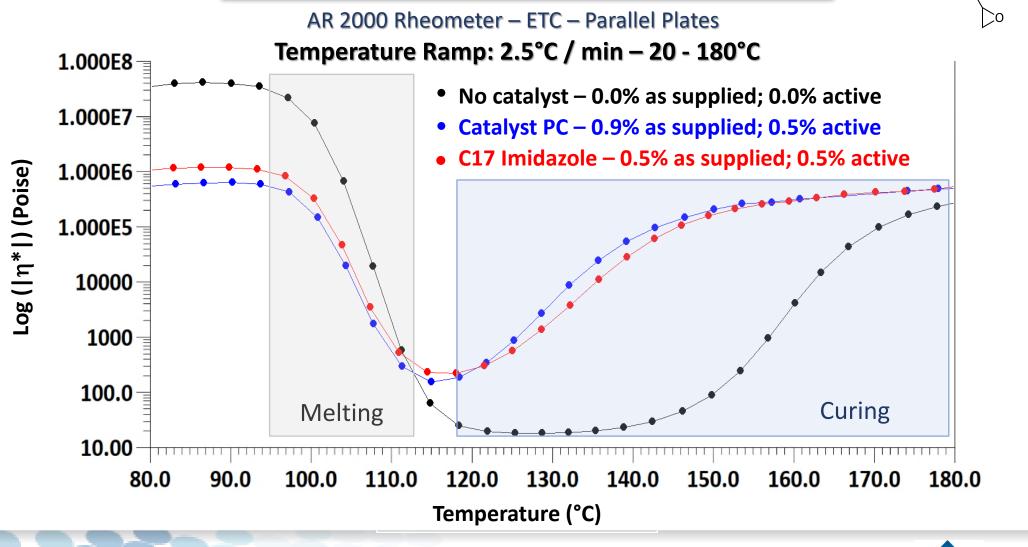
Formulation & Film Preparation

- Extruded, Pulverized, & Classified
- Coatings Electrostatically Sprayed over Bare CRS
- Films Cured in Conventional Oven
 - **Temperatures:** 135°C & 125°C
 - **Dwell Time:** 15 min 25 min PMT
 - **DFT =** ~3.0-4.0 mil

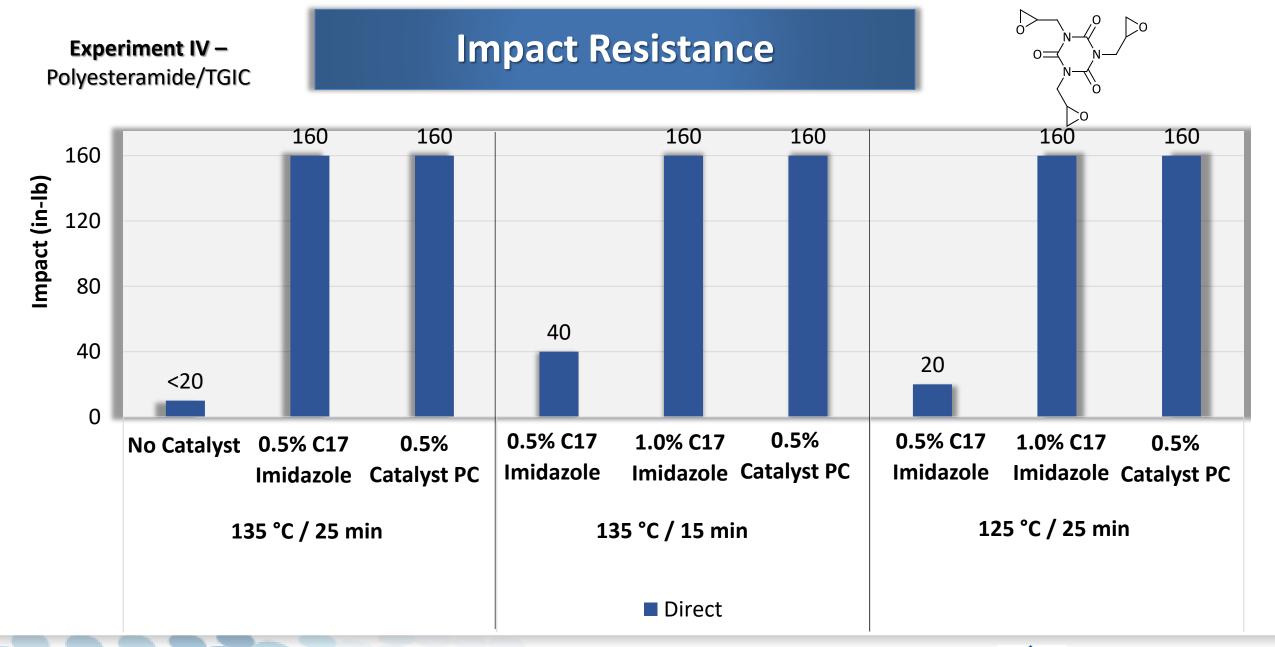


Experiment IV – Polyesteramide/TGIC

Melt-Flow Rheology Profile



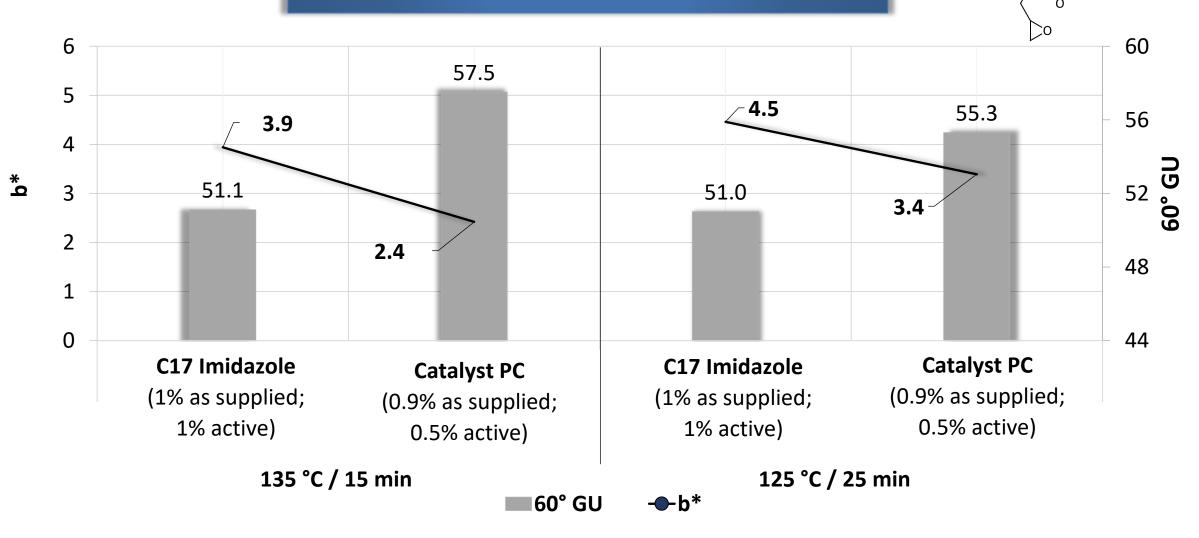






Experiment IV – Polyesteramide/TGIC

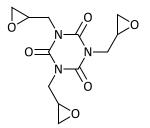
Appearance: Color and Gloss





Experiment IV – Polyesteramide/TGIC

Heat Aged Stability



Storage Stability

50°C Storage

Formulation	Initial	1 Month+	
No Catalyst	Free-flowing powder	Free-flowing powder	
(0% active; 0% as supplied)			
2-Methyl Imidazole	Free flowing powder	Free flowing pourder	
(1% as supplied; 1% Active)	Free-flowing powder	Free-flowing powder	
Catalyst PC	Free flowing neudor	Free flowing nouder	
(0.9 as supplied; 0.5% active)	Free-flowing powder	Free-flowing powder	





Experiment I – Epoxy Homopolymerization

> – Il transmeri Experiment II Acrylic/GMA

Conclusions:

- Catalyst PC is Highly Active in TGIC Systems
 - Accelerates Crosslinking Reaction
 - Carboxyl Functional Resins/TGIC Crosslinkers

Experiment IV –

Polyesteramide/TGIC

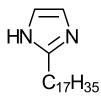
• White TGIC Powder Coating

Experiment III – Polyester/BPA

• Good Melt-Flow Profile with Catalyst PC

- Superior to 2-Heptadecyl-1H-imidazole ('C17 Imidazole')
 - LTC with Lower Active Catalyst
 - Less Active Catalyst = Better Appearance
 - Less Discoloration
 - Better Gloss Properties

o N N V O Triglycidylisocyanurate (TGIC)





Experiment I – Epoxy Homopolymerization Experiment II – Acrylic/GMA Experiment III – Polyester/BPA **Experiment IV –** Polyesteramide/TGIC

Conclusions

Catalyst PC & LC can be Used to Achieve LTC in a Variety of Epoxy Coatings.

- Accelerates Epoxy Homopolymerization
 - BPA-Type Epoxies
 - Pure Epoxy Formulations
- Promotes Nucleophilic Addition:
 - Carboxylic Acid + Epoxide
- Highly Active for Crosslinking RXN of Carboxyl Groups with:
 - GMA Epoxy Resins
 - Epoxidized BPA Resin
 - TGIC Crosslinkers





Experiment I – Epoxy Homopolymerization Experiment II – Acrylic/GMA

Experiment III – Polyester/BPA **Experiment IV –** Polyesteramide/TGIC

Conclusions

Catalyst PC & LC can be Used to Achieve LTC in a Variety of Epoxy Coatings.

White Polyester/BPA Hybrid (70/30)

- Superior to 2-MI
- LTC Response
 - Less Discoloration
 - Better Gloss Properties
- Equal Active and As Supplied

White TGIC Crosslinked Coating

- Superior to 2-heptadecyl-1H-imidazole
- LTC Response with Lower Active Catalyst
 - Less Discoloration
 - Better Gloss Properties



Experiment I – Epoxy Homopolymerization Experiment II – Acrylic/GMA Experiment III – Polyester/BPA

Experiment IV – Polyesteramide/TGIC

Implications

- Reduce Energy Consumption
- Improve Productivity
- Lower Active Catalyst Levels
- Better Performance
- Heat Sensitive Substrates

Continue Growth of Powder Coatings Market





Acknowledgements

Contributions in Product Development

- Dr. Ravi Ravichandran
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- Dr. Steven Woltornist
- Dan Miller

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- Atman Fozdar (Fozdar Dymanics)
- Jeff Cafmeyer (Battelle)

Supporting Development of Bio-Based Resin

• United Soybean Board

For Permission to Present

King Industries, Inc Norwalk CT 06852 203 - 866 - 5551

Opportunity to Present









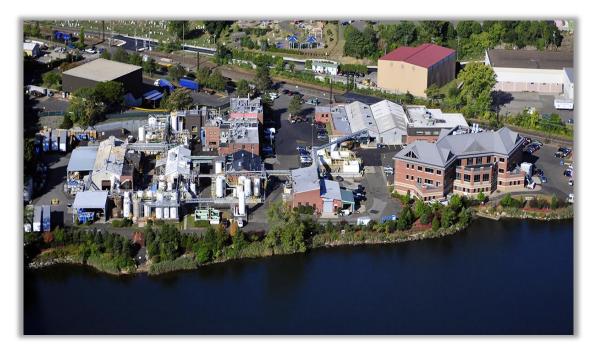
Questions

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