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An Investigation into High-Temperature Epoxy Powder Coatings Formulated Using Benzophenone Tetracarboxylic Dianhydride (BTDA)

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Research study:
BTDA-based epoxy powder coatings

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To understand the development of high crosslink densities

(which lead to **high-temperature performance**)

vs...

- Formulation variables
- Cure process

Co-contributors:

- Dr. Jeff Dimmit
  - Jayhawk Fine Chemicals Corp
- Mr. Kevin Biller & team
  - ChemQuest Powder Coating Research
- Mr. Nikola Bilic
  - Kansas Polymer Research Center

Acknowledgements:

- Dr. Lingyun He, Olin Corporation
  - solid epoxy resin samples & advice
- Dr. Pritesh Patel, Evonik Crosslinkers
  - imidazole accelerator samples

Contributor groups

Jayhawk Fine Chemicals Corporation

- Kansas-based global leader in
  - Dianhydrides
  - Specialty crosslinkers
  - Custom-manufacturing
- 50+ year history
  - Prior ownership by Gulf Chemical, AlliedSignal, Evonik Industries
  - Now part of CABB Group GmbH
  - Experts in dianhydride chemistry and applications

ChemQuest Powder Coating Research

- Powder coatings experts
  - Columbus, OH
  - Independent lab & consulting
  - 40+ years experience in powder coatings
- Producers of
  - Ask Joe Powder "powdcast",
  - PC Kitchen: powder formulator's short course.
  - Co-producer: annual Powder Coating Summit

KANSAS POLYMER RESEARCH CENTER

- Part of Pittsburg State Univ.
  - Pittsburg, Kansas
  - Known for industry-academia collaboration
- Experts in
  - Polymer chemistry & material science
  - Bio-based chemistries
  - Polyurethanes & Foams
  - Electroactive materials

BTDA: a versatile dianhydride

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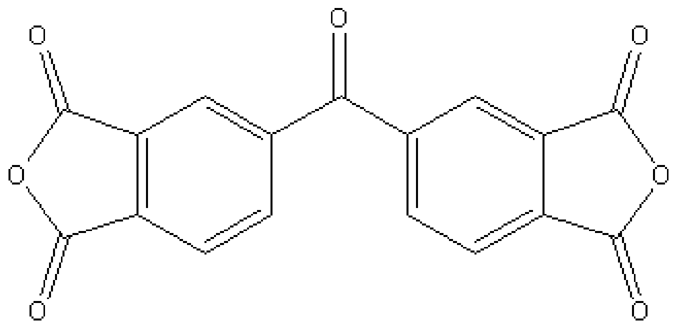
BTDA = 3,3',4,4'-Benzophenone Tetracarboxylic Di-Anhydride		
Melt pt. = 220-230^{0}C (neat)	MW = 322 g/mol	AEW = 161 g/eq
Thermal curing agent for epoxy resins (high temperatures, sustainable properties, electrical insulation)		
Co-monomer for polyimide synthesis (optimal adhesion and dielectric properties)		

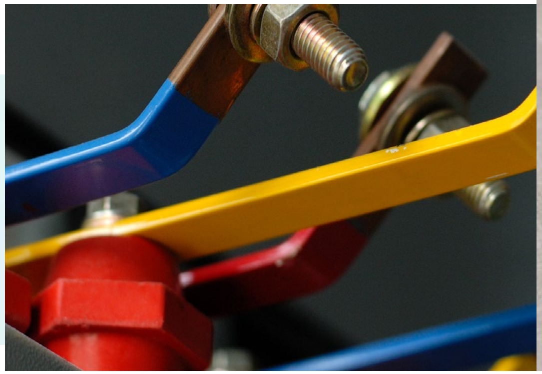


Grades for epoxy use	Form	Median particle size (PSD50), µm	Comments
BTDA Polymer Fine	Fine powder	10-22	Workhorse & used in this study
BTDA Microfine	Finer powder	2-5	Preferred by some customers

BTDA-based epoxy powder coatings

- Achieve high crosslink densities & superior properties…
  - Heat-resistance
  - Thermo-oxidative stability
  - Sustained dielectric performance at high-temperature
  - Superior barrier properties and chemical resistance

- … leading to success in advanced applications:
  - Coating powders for insulation in electric motors, busbars
  - Molding powders for electrical encapsulation
  - FBE coatings for pipe & rebar (infrastructure)

Dianhydrides will cure any epoxy compound

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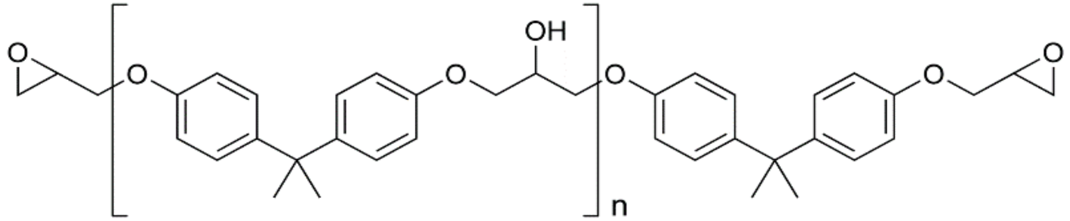
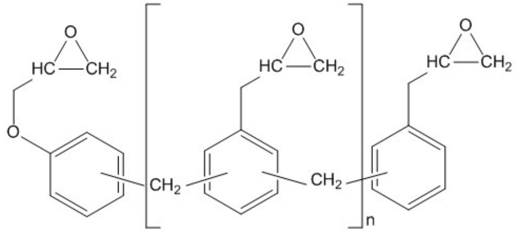
Standard resins based on bisphenol A:
liquid or solid epoxy resins, F~2.0
usually most cost-effective

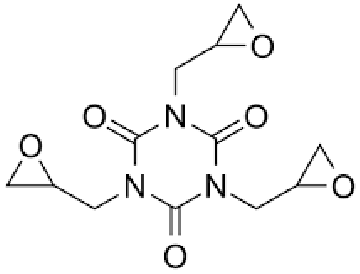


BTDA allows using simple bisphenol-A resins even in demanding applications

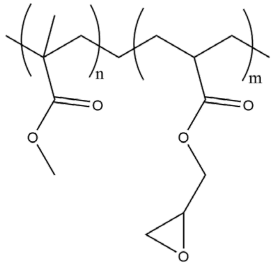
Epoxy novolac resins:
epoxide functionality > 2.0
solids or semi/solids



TGIC:
i.e., triglycidyl isocyanurate
Workhorse ingredient for
powder coating industry



GMA acrylic resins:
i.e., glycidyl-functional
acrylic polymers, e.g.:



Epoxy-anhydride cure chemistry

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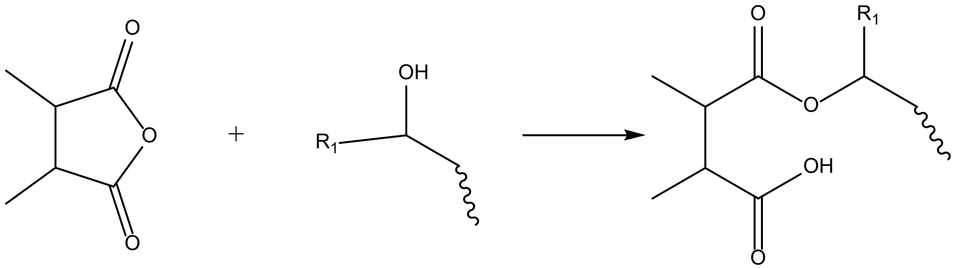
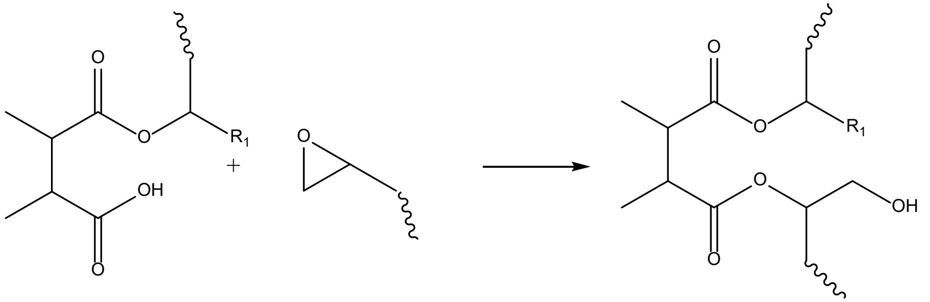
Step 1:



- **Reaction 1** is first of two steps for curing reaction

Step 2:



- **Reaction 2** is the critical step for polymerization and network formation

BTDA-epoxy formulations: stoichiometry + art

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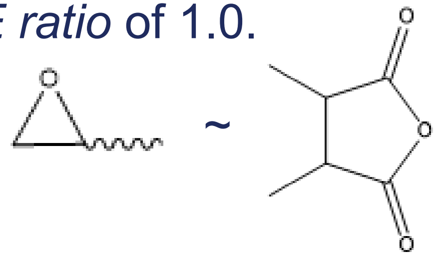
Key terms:

(1) Formulation's **<u>A/E Ratio</u>** = $\dfrac{\textbf{Anhydride}\text{ equivalents}}{\textbf{Epoxide}\text{ equivalents}}$

(2) Epoxide Equivalent Wt., **EEW** = use supplier provided values

(3) BTDA's Anhydride Eq. Wt., **AEW** = **161 g/eq.** (MW/functionality = 322/2)

- In theory, one **epoxide** group ***completely consumes*** one **anhydride** group, …implying a *theoretical A/E ratio* of 1.0.



- **However, best performance is obtained at <u>A/E ratios << 1.0</u>**

$$\textbf{BTDA usage (phr) with epoxy resin} = \frac{\textbf{100 x 161 x (A/E)}}{\textbf{resin EEW}} \text{ (parts per 100g of epoxy resin)}$$

BTDA usage with epoxy resins: Suggested stoichiometric ratios (A/E)

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Epoxy resin EEW (g/eq)	Example resin grades	Suggested * A/E ratios
< 200	Liquid epoxy resins (BPA, BPF, cycloaliphatics, multifunctional) epoxy novolac resins	0.5 – 0.6
500 – 700	**Solid BPA resin, Type 1-2**	**0.6 – 0.7**
700 – 900	**Solid BPA resin, Type 3-4**	**0.7 – 0.8**
> 900	Solid BPA resin, Type 5 & higher	0.8 – 1.0

Relevant for most epoxy powder coatings

* Initial suggestions, based on the resin EEW
A/E = anhydride/epoxide equivalent ratio in the formulation

Design of experiments

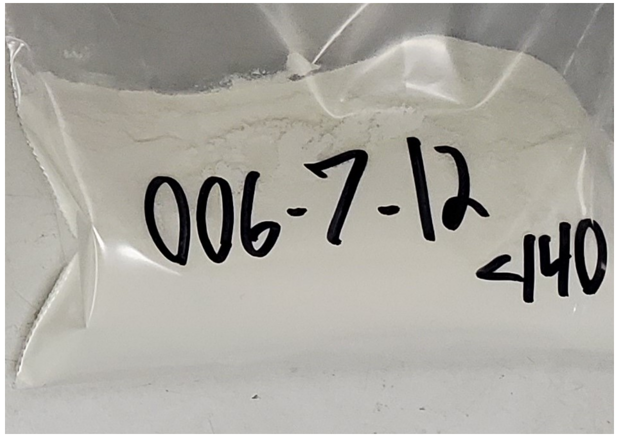
Formulation No.:	1	2	3	4	5	6	7	8	9	10	11	12
Formulation A/E Ratio →	*0.5*	*0.6*	*0.7*	*0.8*	*0.5*	*0.6*	*0.7*	*0.8*	*0.5*	*0.6*	*0.7*	*0.8*
Formulations:	***grams***				***grams***				***grams***			
2.5-Type Bis-A SER, EEW ~700, softening pt ~95°C	62.5	61.2	60.0	58.8								
4-Type Bis-A SER, EEW ~900, softening pt.~105°C					63.9	62.9	61.9	60.9				
7-Type Bis-A SER, EEW ~1800, softening pt.~130°C									66.6	66.1	65.5	64.9
BTDA PF (AEW 161)	7.2	8.4	9.7	10.8	5.7	6.8	7.8	8.7	3.0	3.6	4.2	4.7
Cat. 2-MI (0.5% of resin system)	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
Acrylic polymer (flow agent)	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Benzoin (degassing agent)	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Rutile TiO_2 (pigment)	28.5	28.5	28.5	28.5	28.5	28.5	28.5	28.5	28.5	28.5	28.5	28.5
Total Batch, g =	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

Processing conditions

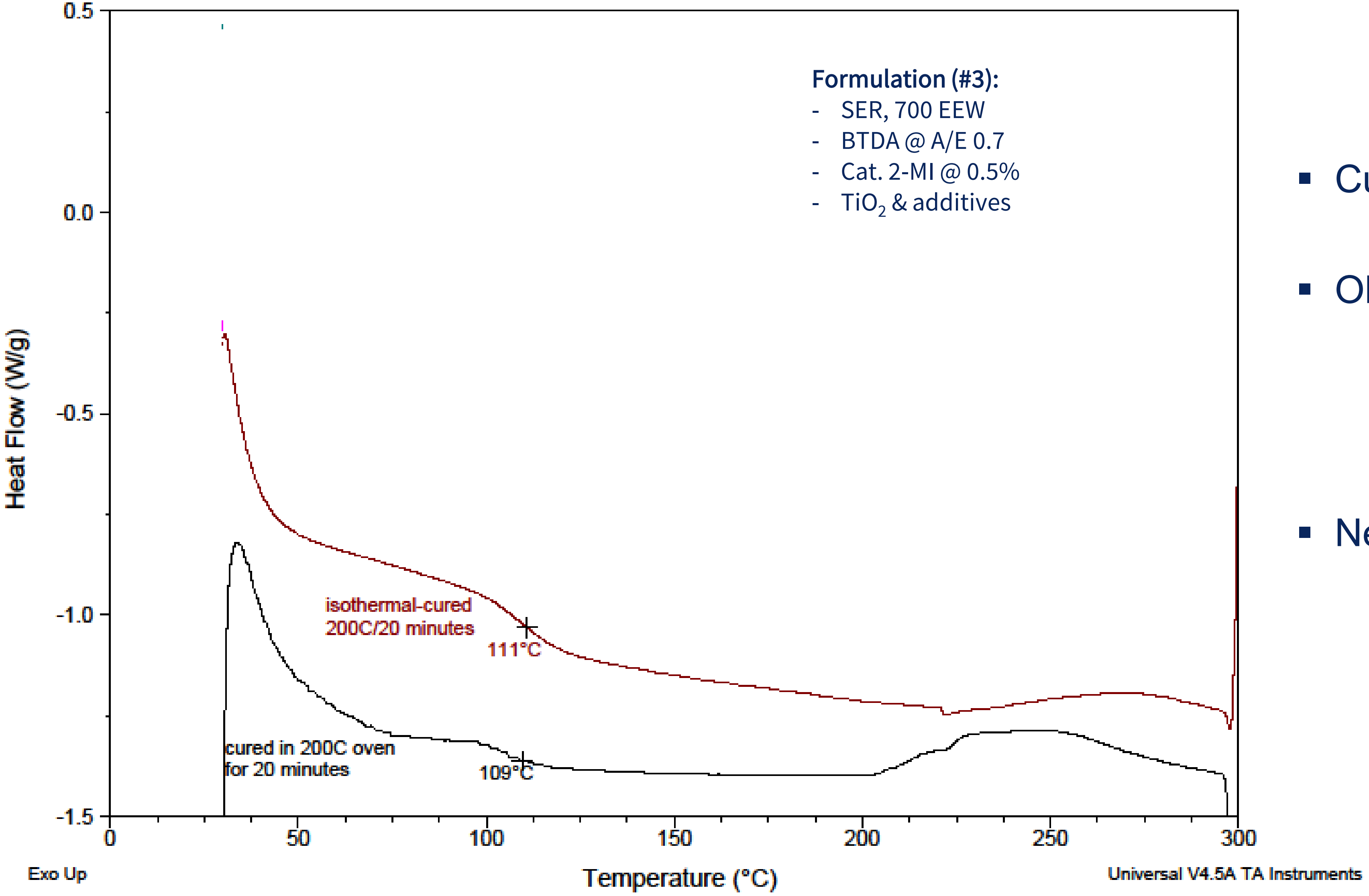
- Extrusion melt-processing conditions
  - Twin-screw extruder
  - Residence time ~15 secs
  - Barrel temps
    - ~ melt points for the resins ~ 100, 110, 130°C

- Spray applied on Q-panels

- Basic cure profile
  - 200°C for 20 minutes in oven



DSC T_g for cured coating



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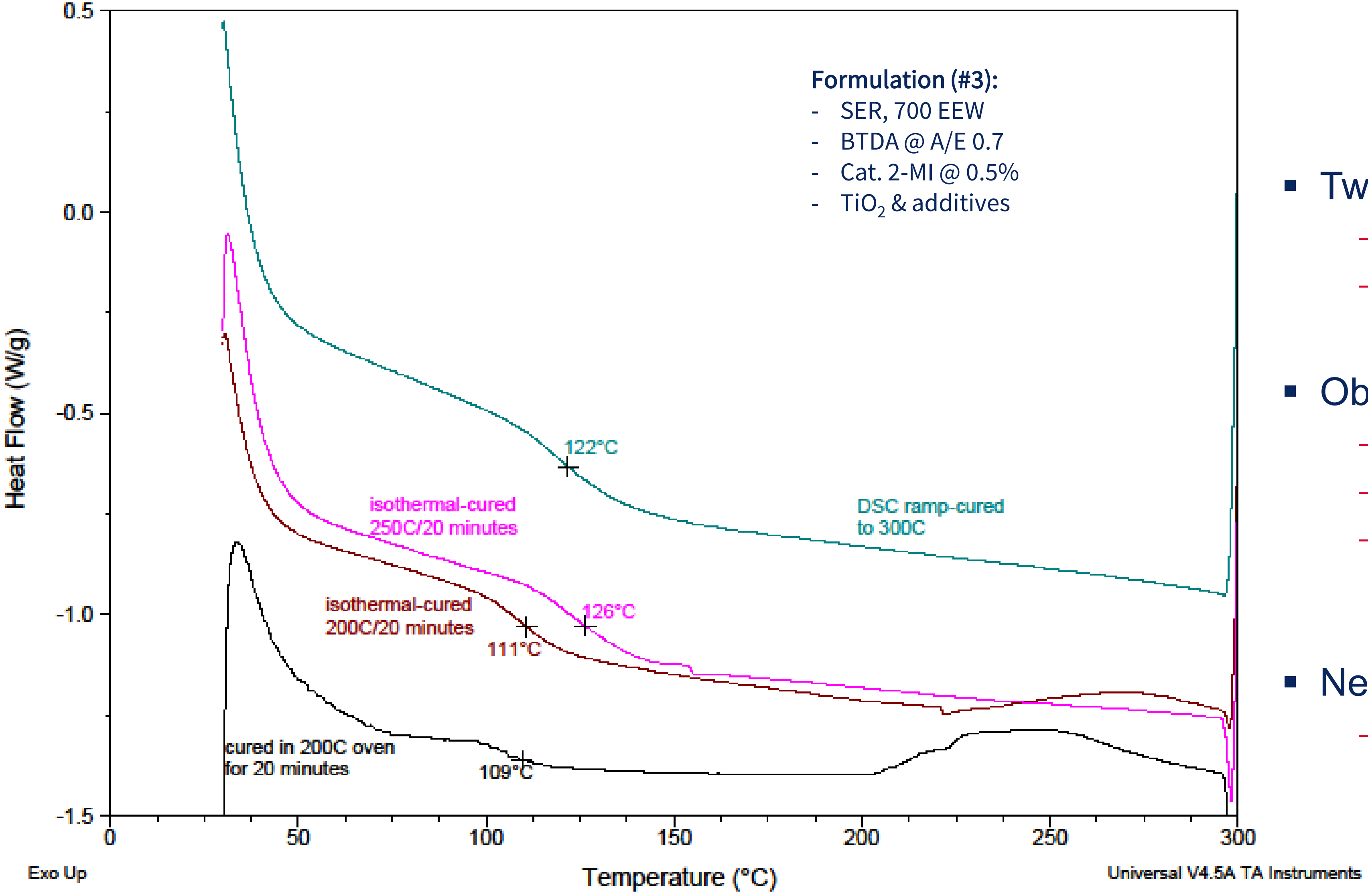
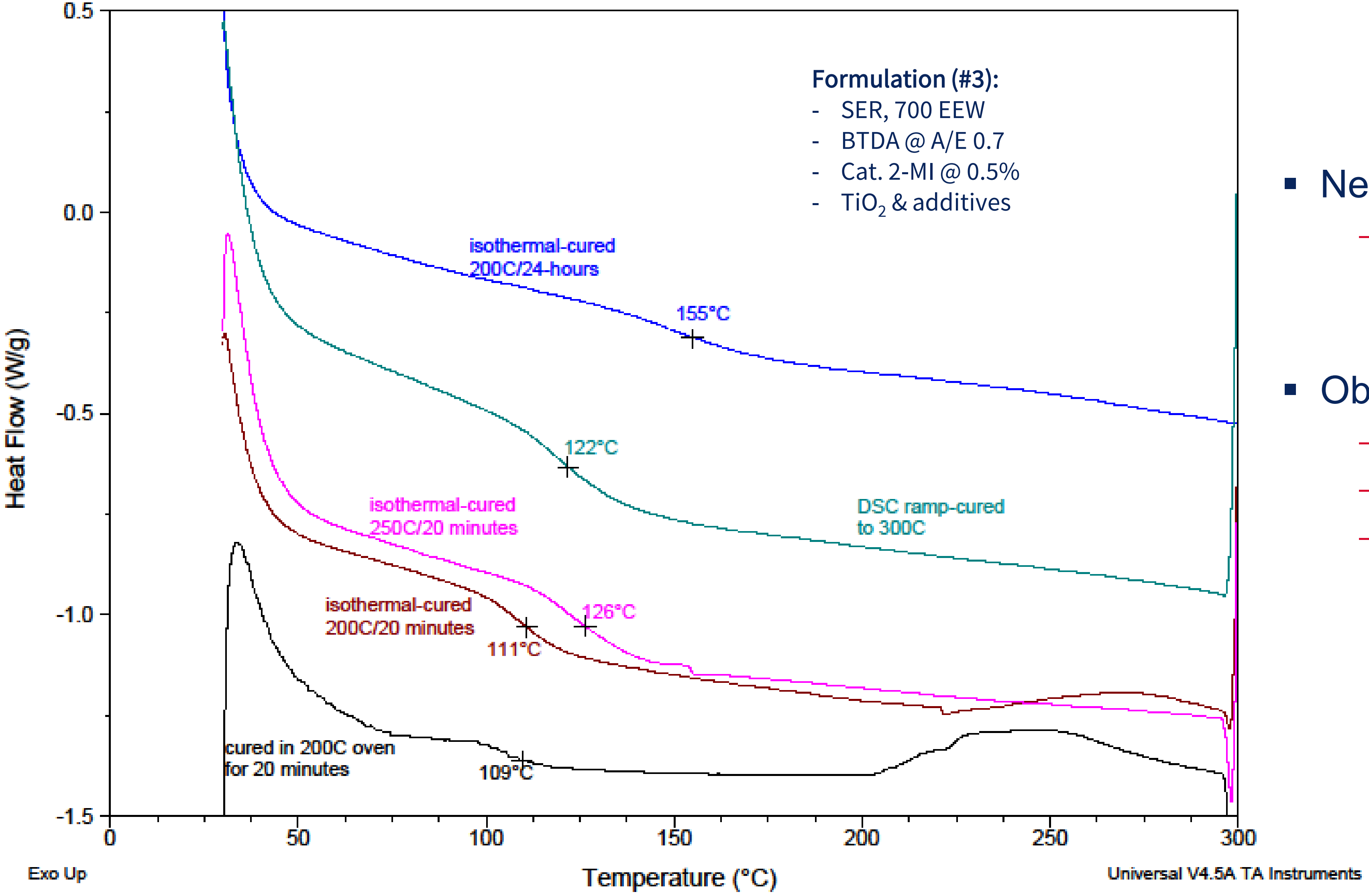
- Cured @ 200C ~ 20 mins.
- Observations:
  - Tg: 109C, 111C
  - Residual cure-exotherm is substantial
- Next:
  - Raise cure temperature

Higher cure-temperatures improve Tg



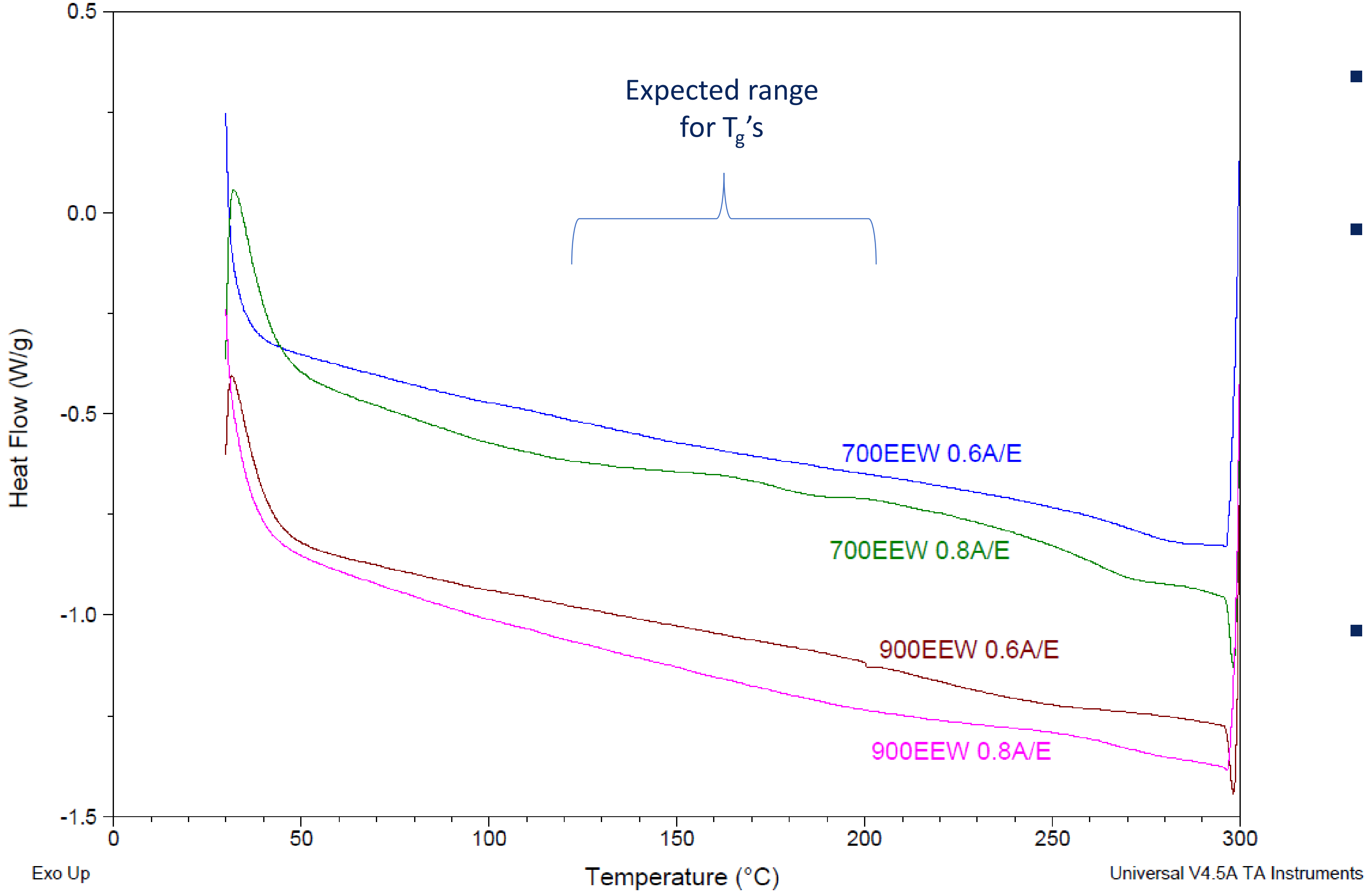
- Two new cure-conditions:
  - Isothermal 250°C/20', or
  - DSC ramp to 300°C
- Observations (for both):
  - Tg rises to 122°C, 126°C
  - Residual exo disappears
  - suggesting full-cure, but wait…!
- Next:
  - Raise cure time

Longer cure-times show marked Tg increase



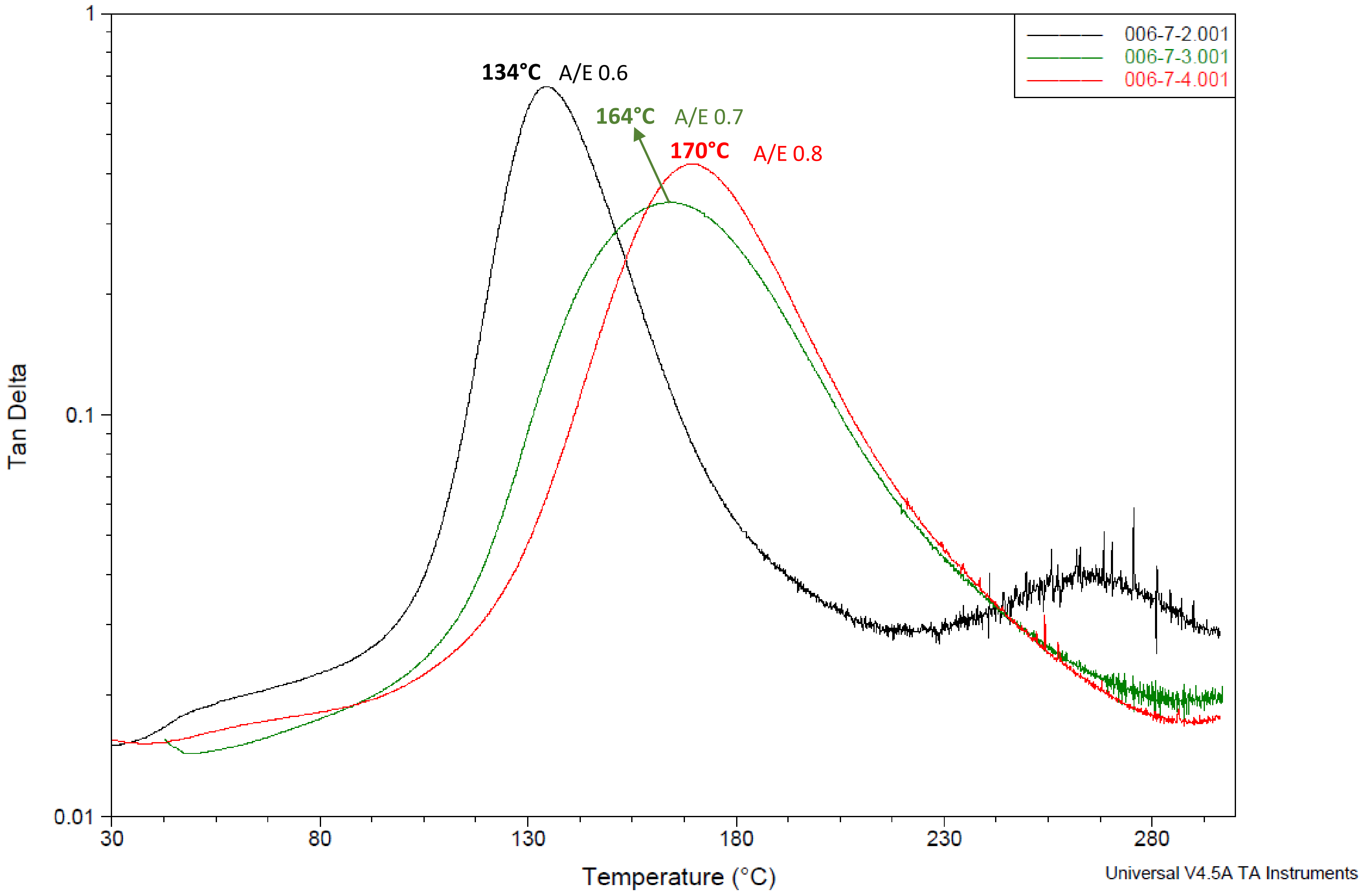
- New cure condition:
  - Longer cure time
    24 hr @ 200C
- Observations:
  - Tg rises to 155C
  - Tg magnitude suppressed
  - Indicates:
    additional x-linking & tightening of network!

Some formulations:
T_g too faint for detection by DSC



- Cure condition:
  - Long cure-time, 24-hr @200C
- Observations:
  - T_g too faint for detection via DSC
    - Some unusually high thermal transitions noted, but not expected to be T_g's
- Next steps:
  - Dynamic mechanical analysis (DMA) for Tg determination

Tg via DMA (loss tangent, tanδ)



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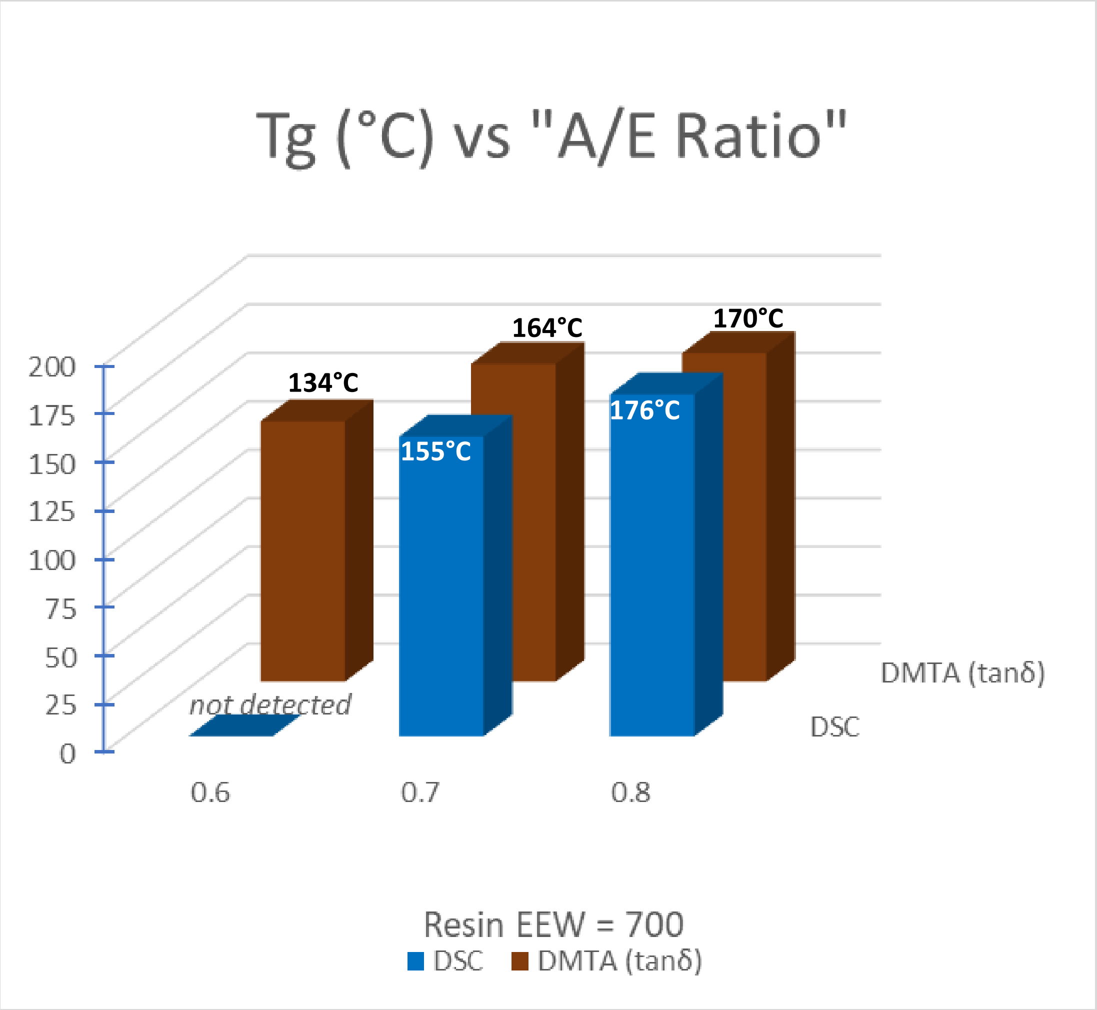
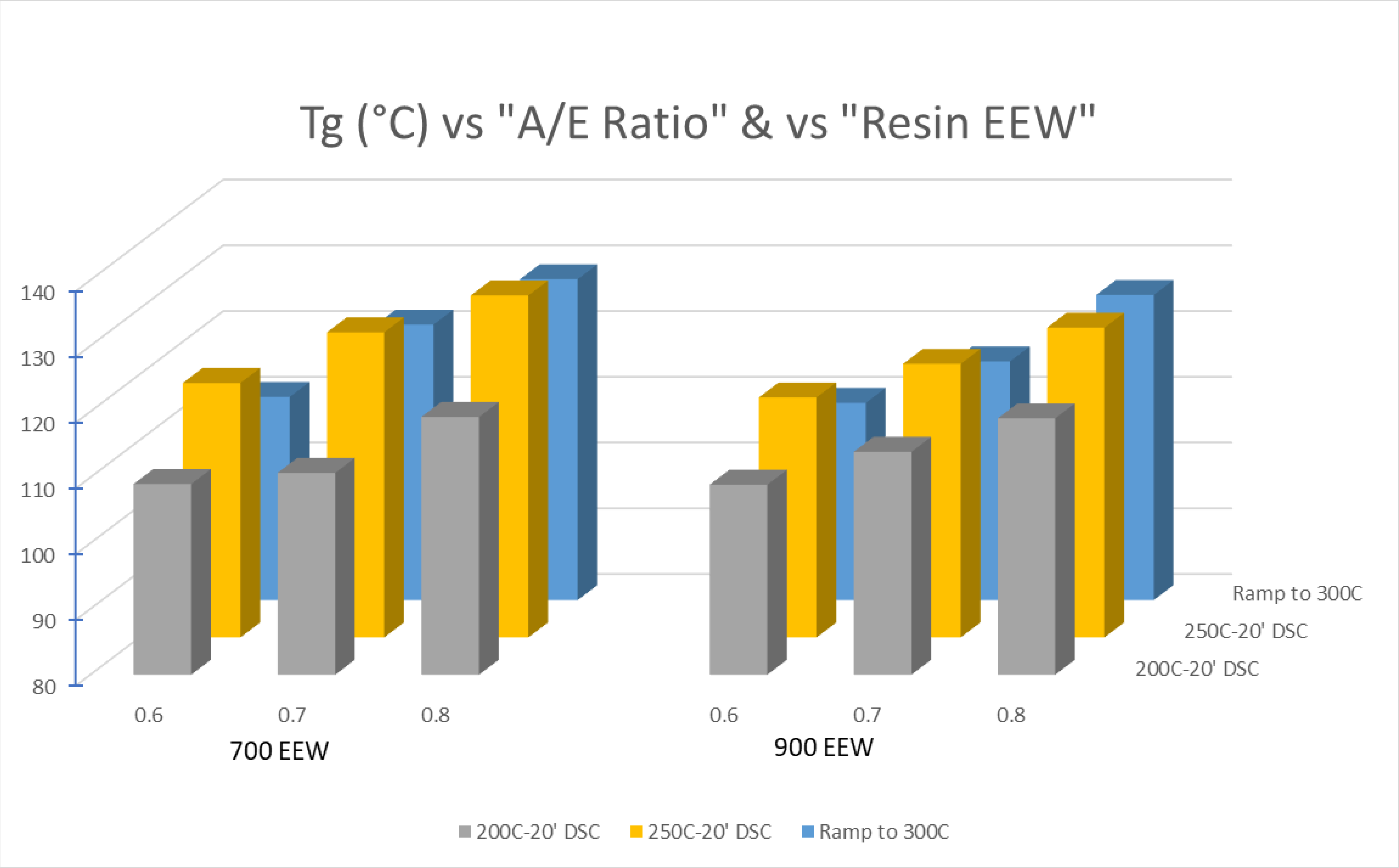
- Formulation
  - SER 700 EEW
  - Catalyst AMI-2 at 0.5%
- Cure condition:
  - 24-hr @ 200C
- Test:
  - TA 800, 3-pt bending
  - 3°C/min
- Observations:
  - Tg increases with A/E ratio

DMA vs DSC: Good correlation on Tg



- Tg increases with A/E ratio
  - Noted 170's °C
- Good correlation (DSC vs DMA)
- Formulation
  - SER 700-EEW
  - Catalyst AMI-2 at 0.5%
- Cured:
  - 24-hr @ 200C

Dialing in T_g via formulation & process variations



- T_g rises with A/E
- T_g's are higher for resin with lower EEW

Cure enthalpy release vs time (@200°C)

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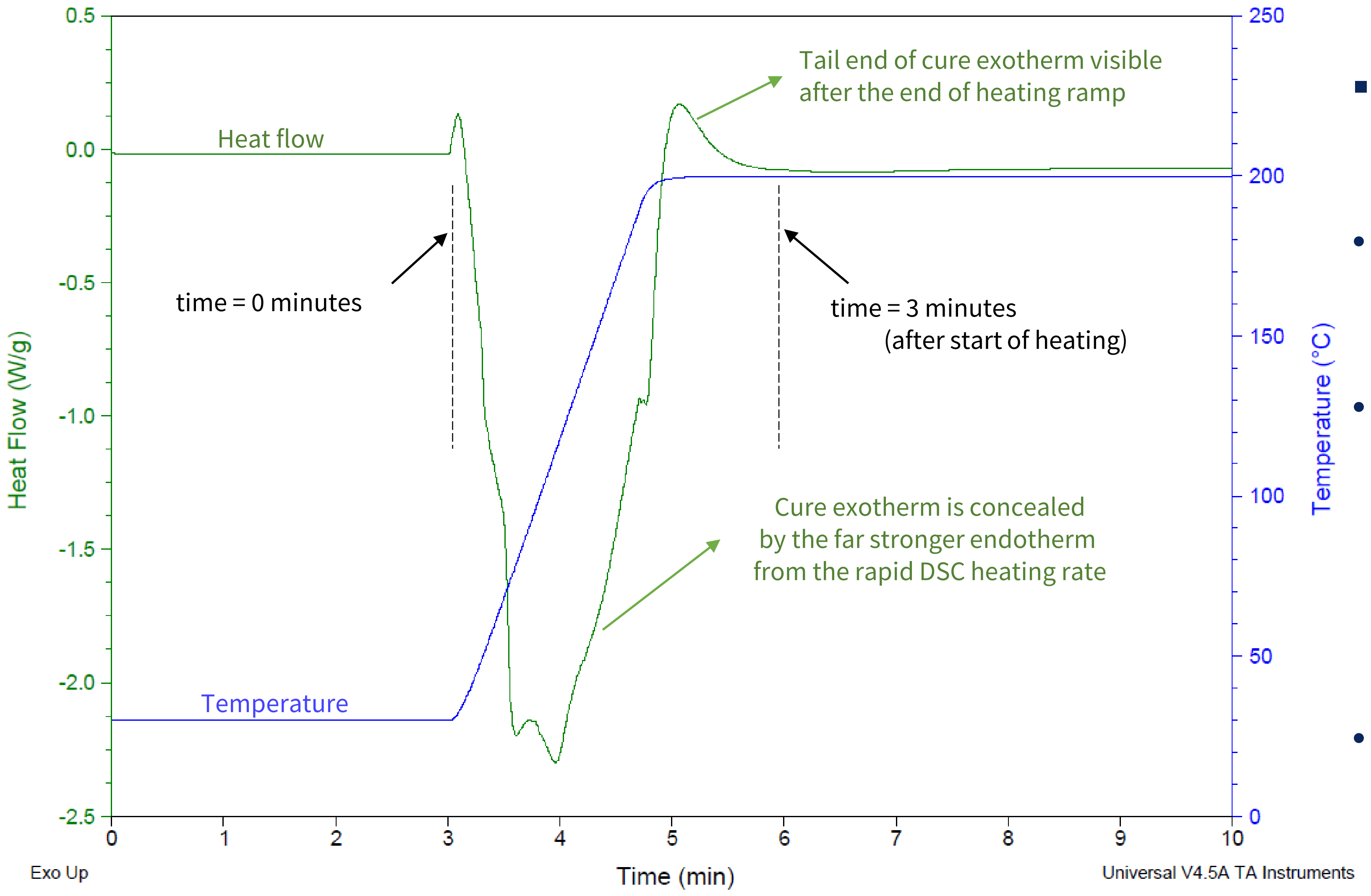

- DSC thermal ramp:
  - 100°C/min from 30°C to 200°C
- Sample (uncured):
  - SER, 700 EEW
  - BTDA @ A/E 0.7
- Observation:
  - Measurable cure (in DSC) completed within 1 minute of reaching 200°C
  - But we know Tg continues to build with time!
- Key takeaway: **Slower reactions play a role!**

SUMMARY:
BTDA-cured epoxy powder coatings

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- High T_g's achieved, up to 170°C, using difunctional epoxy resin
  - using *simplest* epoxy resins, but due to high crosslink densities
- With highest T_g's, the transitions are very faint, indicating:
  - reduced changes in properties around T_g
  - superior performance at high temperatures
- Cure conditions are key!
  - Slower reactions play significant role
- To maximize T_g:
  - Increase A/E ratio (stoich.), i.e., usage level of BTDA
  - Use lower EEW resins
  - Increase cure time
  - Increase cure temperature

Questions?

Contact:

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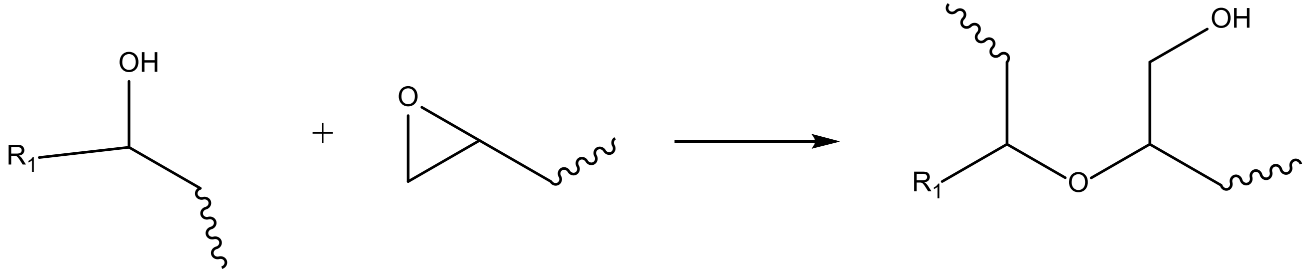
Checkout new technical community website:

www.dianhydrides.com

Why A/E << 1.0 helps…

Lower than stoichiometric amount of anhydride…

1. Addresses the epoxide homopolymerization
   - Side reaction consumes epoxides but not anhydrides



2. Controls extent of crosslinking for optimum performance
   - Avoids vitrification, and unreacted anhydride groups
   - Avoids over-crosslinking; leads to improved mechanical properties

Formulations

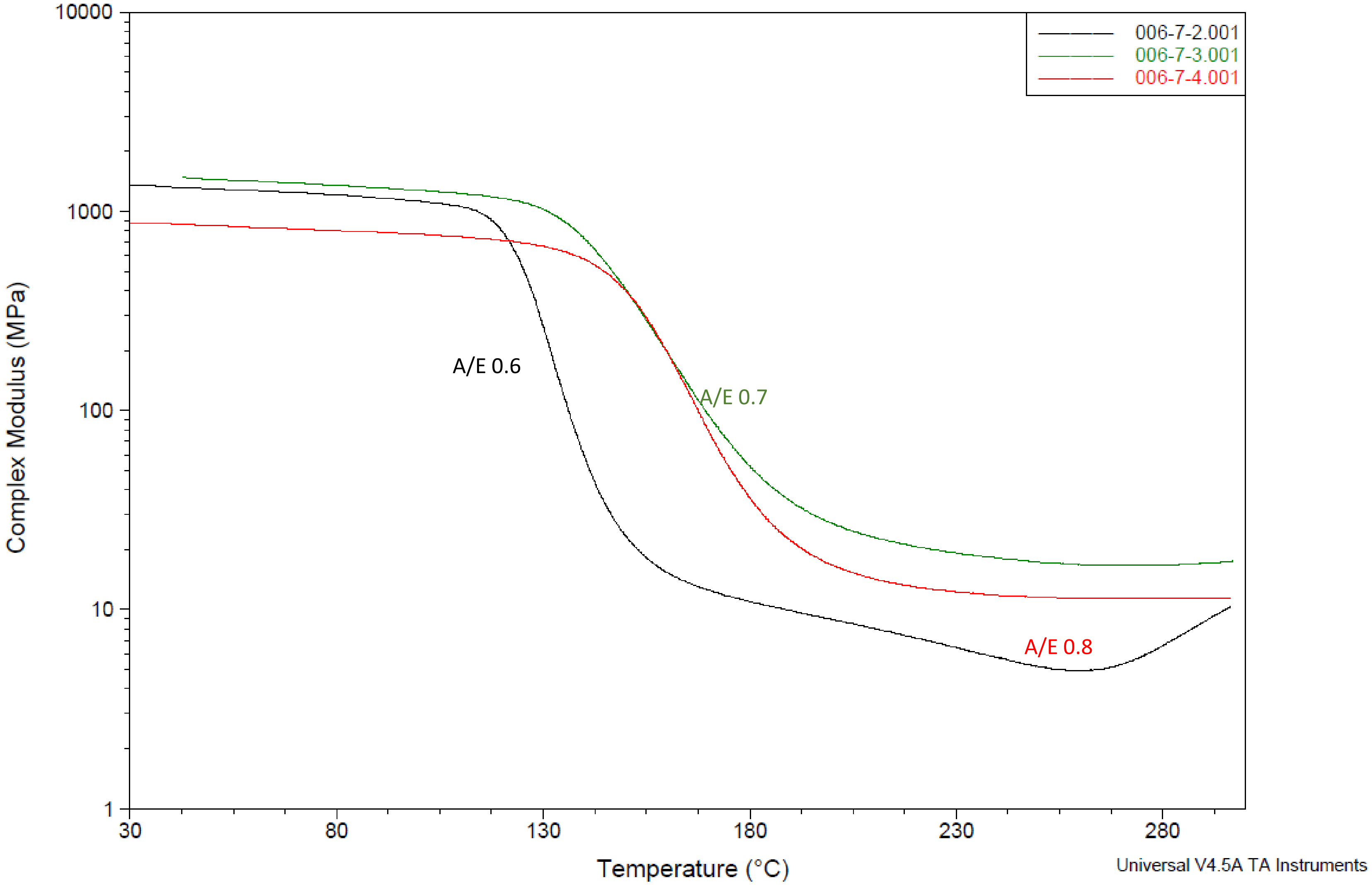
- Difunctional solid epoxy resins (SER) based on Bisphenol A:
  - 2.5-Type EEW ~ 700 softening point ~ 95°C
  - 4-Type EEW ~ 900 softening point ~105°C
  - 7-Type EEW ~1800 softening point ~130°C

- Curing Agent: BTDA Polymer Fine (BTDA-PF)
  - Using stoich. A/E* ratios: 0.5, 0.6, 0.7, 0.8

- Catalyst type and level
  - 2-methylimidazole (2-MI), 140°C m.p.
    - @ 0.5% (in 'resin + curative' mix)

* A/E = Anhydride/Epoxide equivalent ratio

Tg via DMA (complex modulus, G*)



Jayhawk Fine Chemicals

- Formulation
  - SER 700 EEW
  - Catalyst 2-MI at 0.5%
- Cure condition:
  - 24-hr @ 200C
- Test:
  - TA 800, 3-pt bending
  - 3°C/min
- Observations:
  - Tg increases with A/E ratio
  - Smaller drop in G* at Tg at higher A/E => higher crosslink density