SAND2016-8221PE

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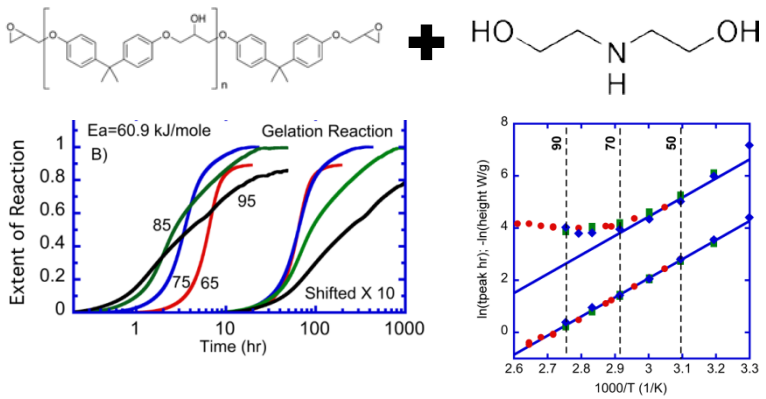
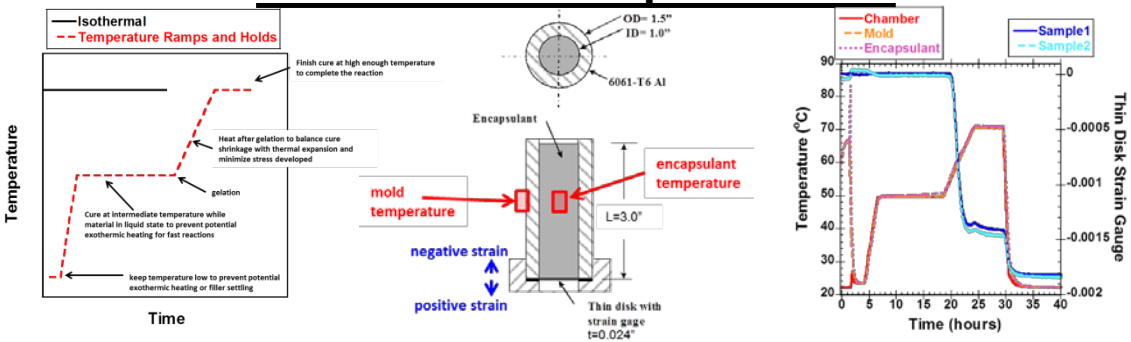
Polymerization Kinetics



Cure Schedule Optimization



Understanding and Predicting the Evolution of Thermosetting Polymers During Reaction: A Necessary Capability in Order to Predict the Cradle-to-Grave Performance of Polymer Packaged Electronic Devices

Jamie Kropka

August 2016 Material Science Seminar

U.S. DEPARTMENT OF ENERGY | NNSA National Nuclear Security Administration

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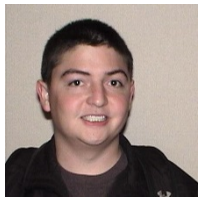

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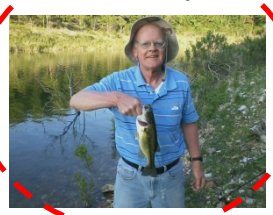


Kevin Long

Brenton Elisberg

Kevin Troyer

Kurtis Ford

Matthew Neidigk

John McCoy (NM Tech)

Main Contributors to Today's Topics

National Nuclear Security Administration

Sandia National Laboratories

What We Do

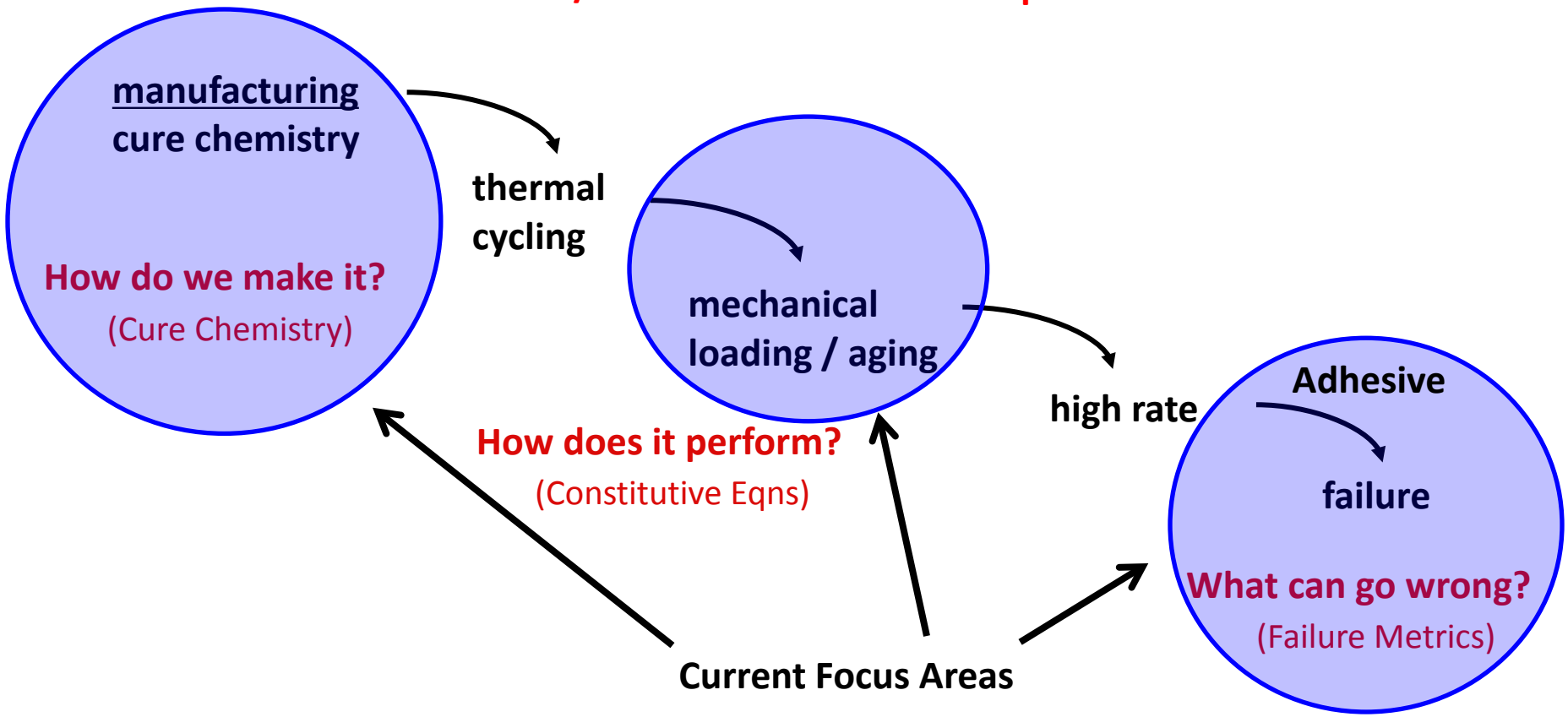
1. Capability Development (relevant to Encapsulation and Bonding)
    a. Understanding of Polymer Material Structure-Processing-Properties Relationships
    b. Understanding of Stress in Polymers
2. Material Properties Analysis
3. Problem Solving

Our Vision: Validated Model-Based Lifecycle Engineering for Packaging Design

J.M. Caruthers, et al., *Polymer*, 2004, 45, 4577
D.B. Adolf, et al., *Polymer*, 2004, 45, 4599
D.B. Adolf, et al., *Polymer*, 2009, 50, 4257

Polymer Nonlinear Viscoelastic (NLVE) Model

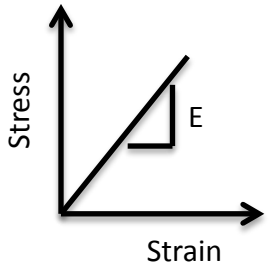
Current talk **Predict Stress/Strain and Understand Impact on Performance**



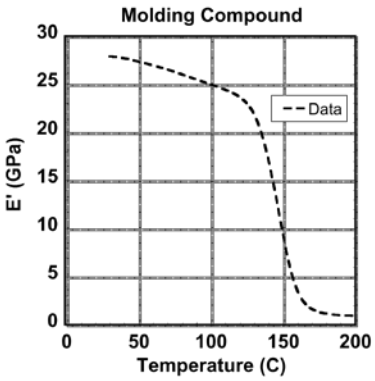
Capability Development: Evolution of Constitutive Representation of Polymers

Linear Elasticity → **Linear Viscoelasticity** → **Nonlinear Viscoelasticity**

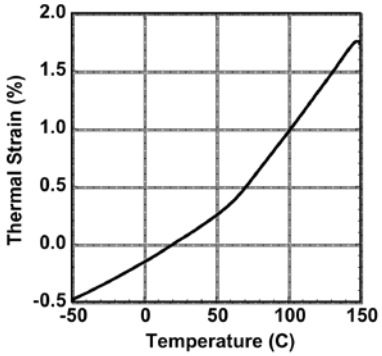
E, ν, α



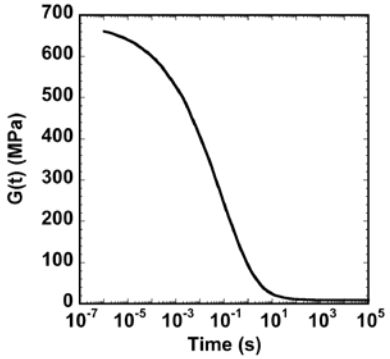
+ temperature dependencies



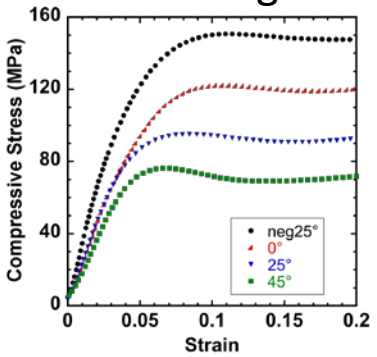
Glass Transition



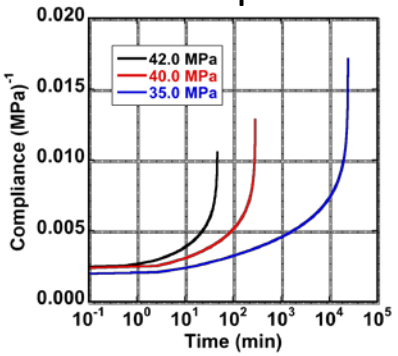
Stress Relaxation



Yielding



Creep



+ manufacturing
+ aging
+ failure metrics

Hierarchy of Polymer Material Characterization for Modeling Nonlinear Viscoelasticity (NLVE)

Other Options not Possible

Bare Bones Approach

Measure:

1. calorimetric Tg
2. filler volume fraction

Model Parameterization:
Estimate NLVE response based on universal properties and rule of mixtures approach

Limitations/Potential Errors:

- Must be rigid fillers (e.g., alumina, silica, mica…)
- Breadth of relaxation spectra
- Nonlinear material clock

Material Evaluations

Quick and Dirty Approach

Measure:

1. filler volume fraction
2. thermal strain versus temperature
3. elastic shear modulus versus temperature

Model Parameterization:
Estimate NLVE response based on universal properties and rule of mixtures approach. Compare predictions to data. Ability to tweak relaxation spectra and prefactors to better match predictions to data.

Limitations/Potential Errors:
Lack definition of clock for nonlinear relaxations

Critical Encapsulants/Adhesives

The Whole Shebang

Measure:

1. filler volume fraction
2. thermal strain versus temperature
3. elastic shear modulus versus temperature
4. compressive stress-stain through yield at multiple temperatures
5. shear mastercurve
6. glassy volume relaxation
7. creep at multiple temperatures and stress levels

Model Parameterization:
Populate material specific SPEC NLVE model

Advantage:
Model can now predict yielding AND (physical) aging with more confidence

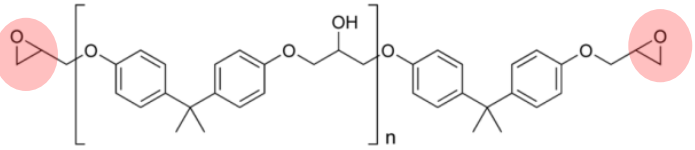
Polymer Thermoset Cure Stress Topics

1. Materials investigated
2. Characterization of material evolution associated with reaction
3. Structural response tests to design cure schedules and validate models
    a. Confined Cure
    b. Free-surface Cure

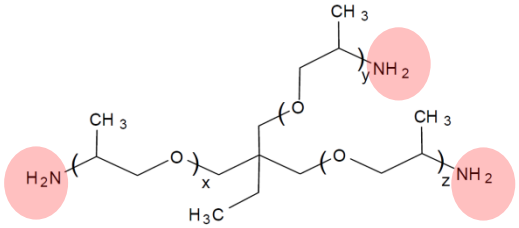
Materials

828/T403[1] and 828/GMB/T403

EPON® Resin 828
Diglycidylether of Bisphenol-A



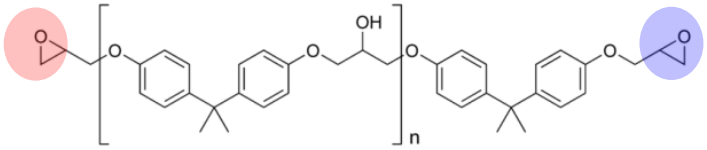
Jeffamine® T-403 Polyetheramine



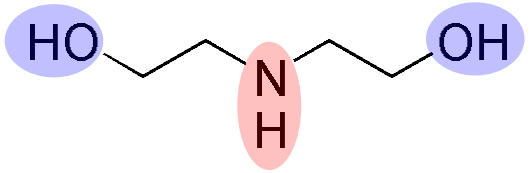
(x+y+z) = 5-6

828/DEA[2] and 828/GMB/DEA[3]

EPON® Resin 828
Diglycidylether of Bisphenol-A



Diethanolamine



3M D32 glass microballoons

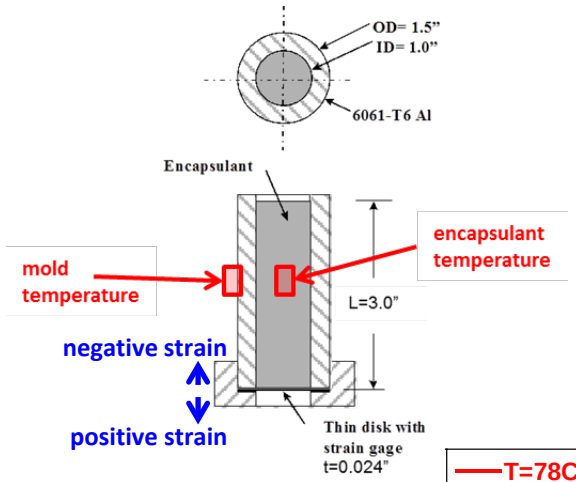
T_g ~ 80C
(when mixed stoichiometrically epoxy-amine)

T_g ~ 70C

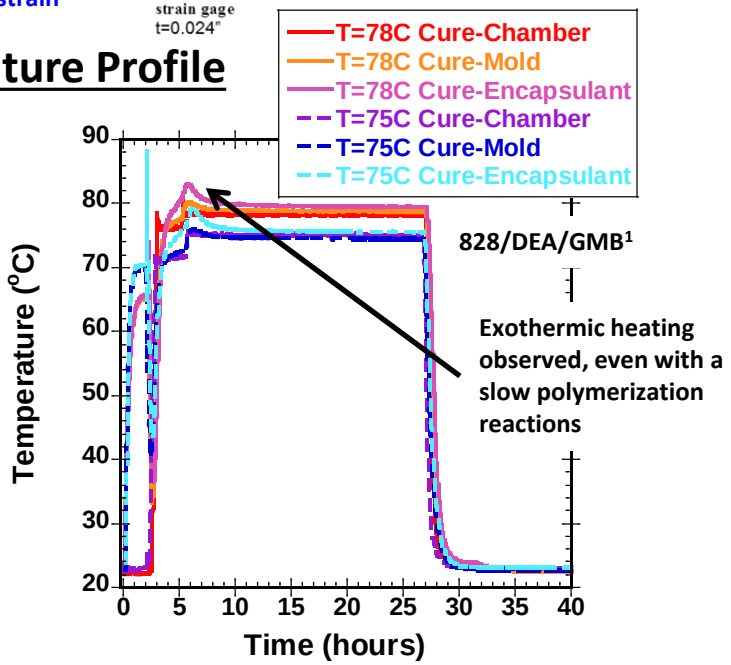
[1]Mix ratio, cure schedule, and more can be found in SAND2013-8681
[2]Mix ratio, cure and typical properties can be found at: http://www.sandia.gov/polymer-properties/828_DEA.html
[3]Mix ratio, cure and typical properties can be found at: http://www.sandia.gov/polymer-properties/828_DEA_GMB.html

Why is Cure Stress Important?

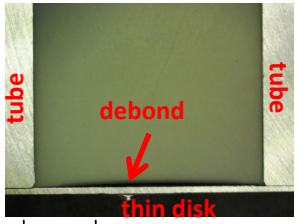
Geometry: Thin Disk on Cylinder

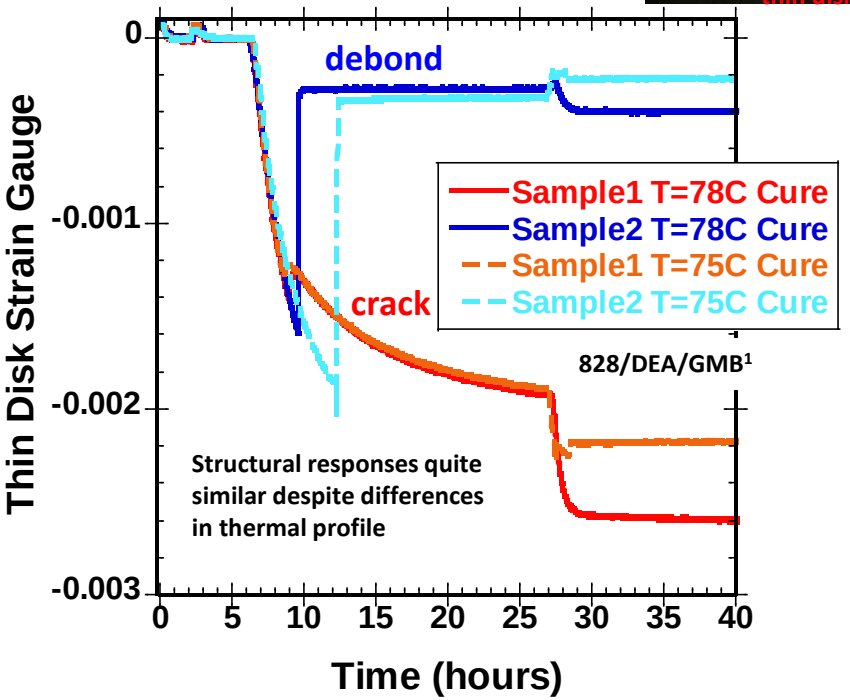


Temperature Profile

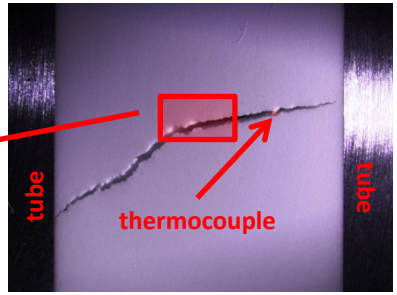


Structural Response





Rough crack surface consistent with "tearing" in rubbery state?



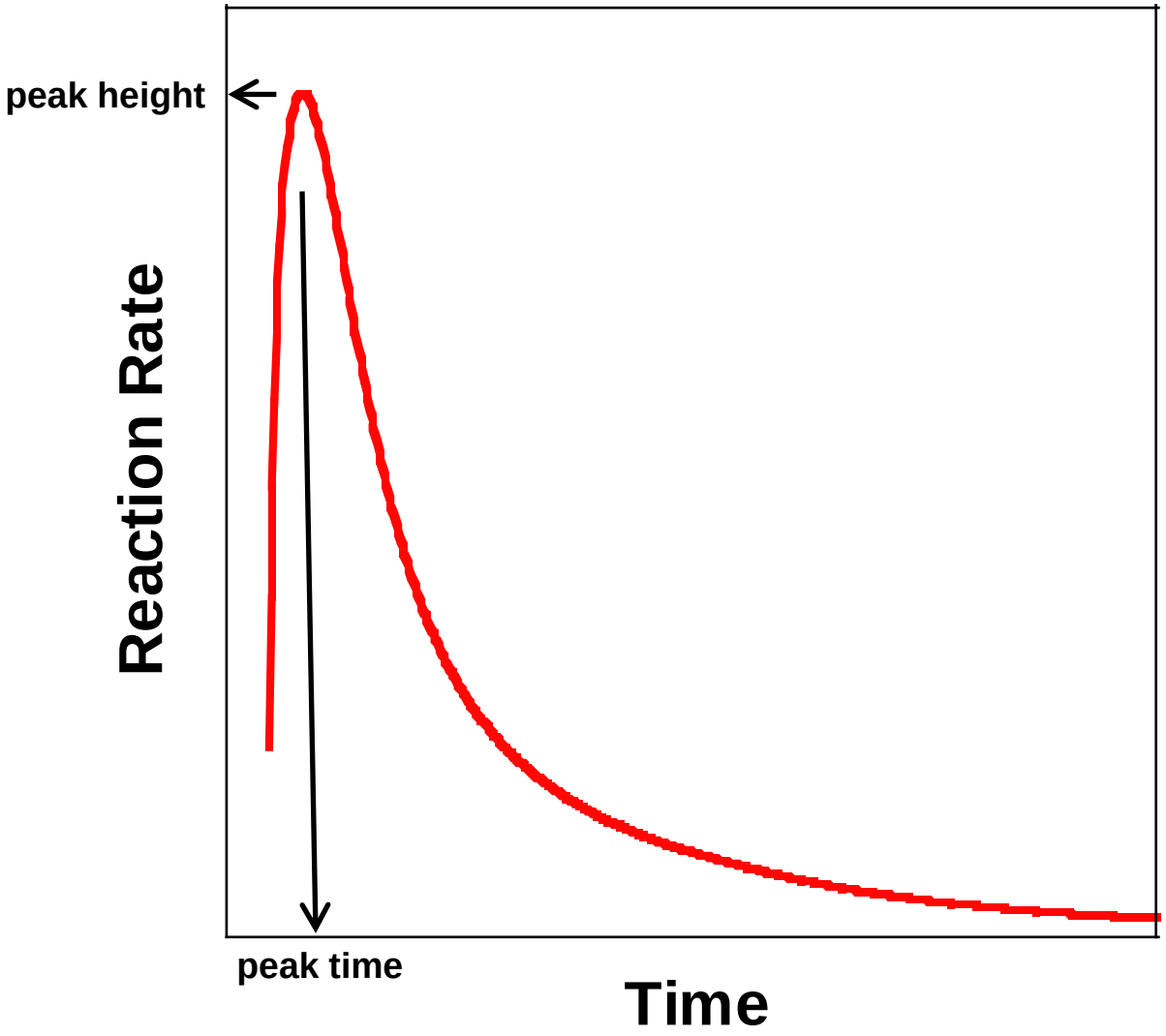
Failure can occur during cure!

[1]http://www.sandia.gov/polymer-properties/828_DEA_GMB.html

Kropka et al., SAND2016-5543

Reaction Kinetics

Autocatalytic Reaction Behavior



Mathematical Representation of the Autocatalytic Behavior

drives reaction rate to increase with reaction extent

$$\frac{dx}{dt} = \hat{k}\left(b + x^m\right)\left(1 - x\right)^n$$

Kamal, M. R. *Polym. Eng. Sci.* **1974,** 14, 231-239.

$$\hat{k} \equiv \frac{k}{\left(1 + w\,a\right)^{\beta}}$$

(phenomenological way to represent vitrification)

$$k = k_o\, e^{-\frac{E_a}{RT}}$$

(Arrhenius activation)

This framework works well for 828/T403

Kropka et al., SAND2013-8681

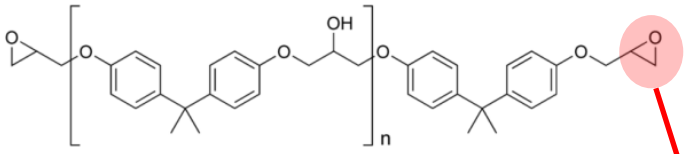
It is not sufficient for our favored 828/DEA!

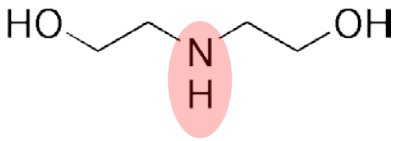
But why and what is needed to predict the behavior of this material?

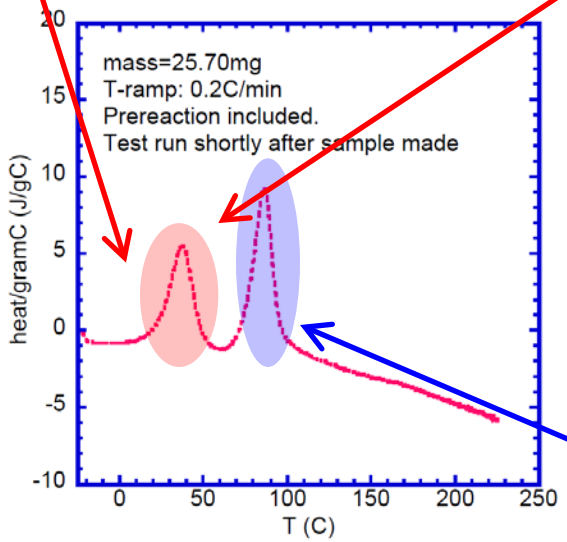
McCoy et al., *under review*

What Makes the Kinetics of 828/DEA so Interesting?

Simple Kinetics for the initial "Adduct-Forming Reaction"







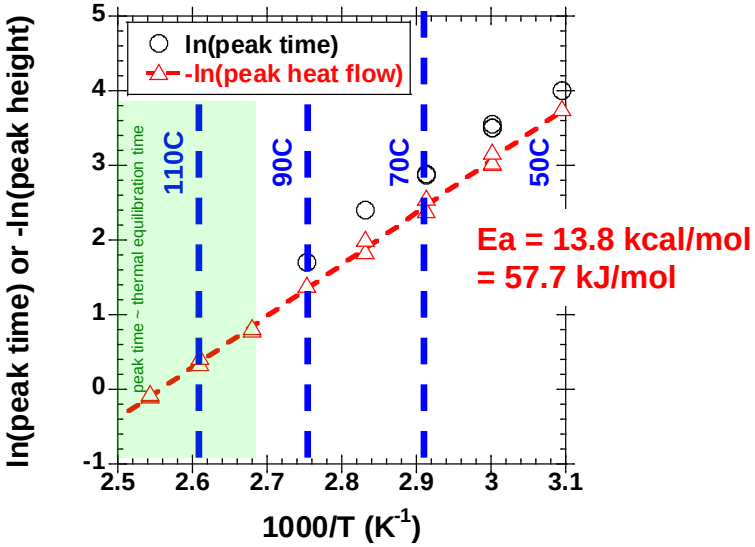
But what happens after that, during what we call the "Gelation Reaction"?

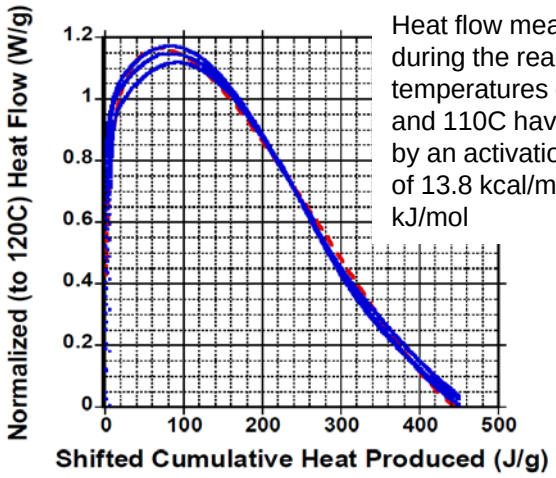
Epoxide-alcohol addition reaction?
Catalysis by the tertiary amine formed during the adduct-forming reaction?
Epoxy self-polymerization?
All of the above?

McCoy et al., *under review*

Temperature Dependence of Peak Location and Time-Temperature Superposition

Simple Kinetics for the "Model" 828/T403 Material

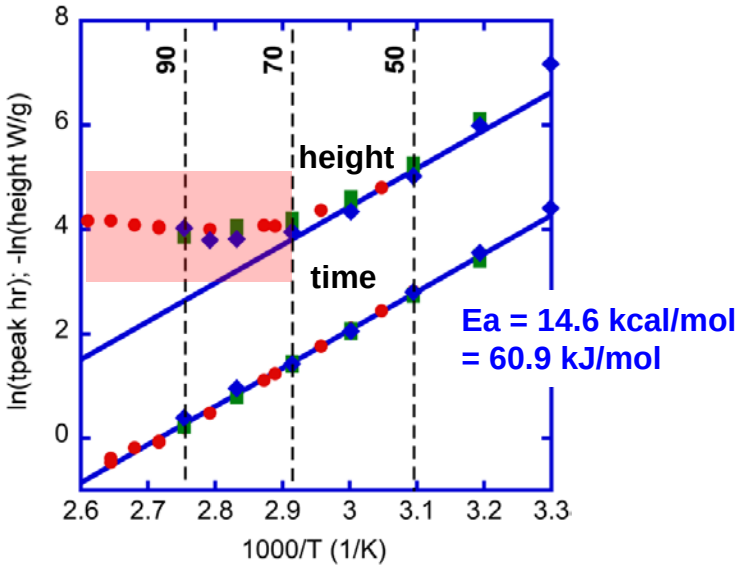


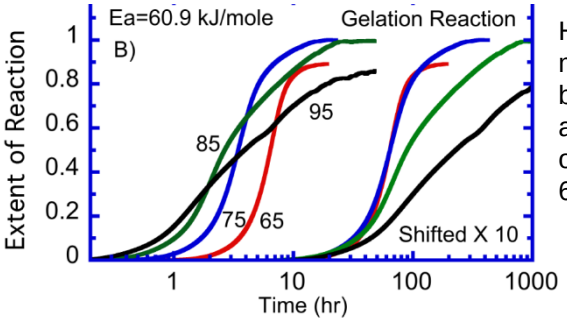


Heat flow measurements during the reaction at temperatures of 60, 70, 100, and 110C have been scaled by an activation energy, Ea, of 13.8 kcal/mol or 57.7 kJ/mol

Kropka et al., SAND2013-8681

Not So Simple Kinetics for the 828/DEA "Gelation Reaction"



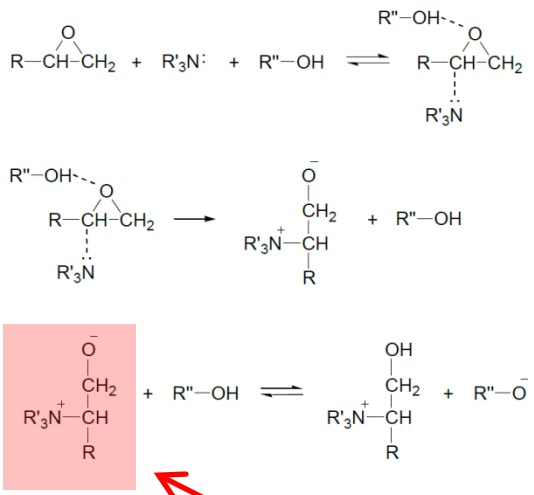


Heat flow measurements have been scaled by an activation energy, Ea, of 14.6 kcal/mol or 60.9 kJ/mol

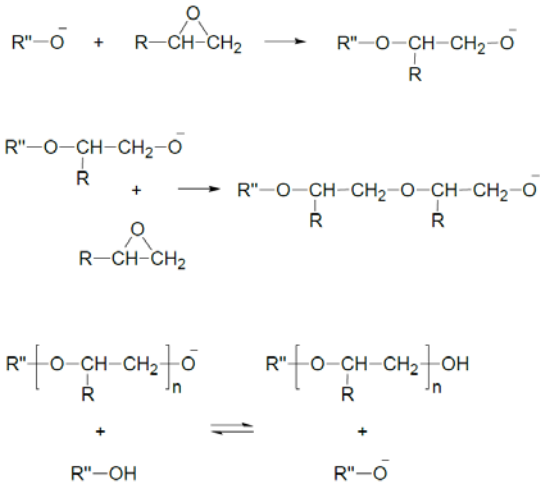
McCoy et al., *under review*

Proposed Mechanism for "Gelation Reaction" at Low Temperature

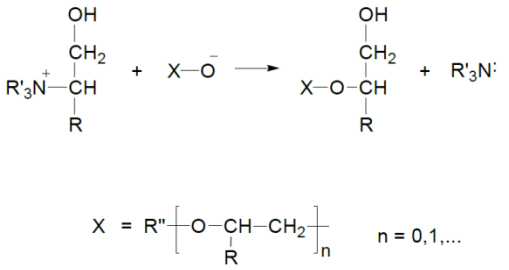
Initiation



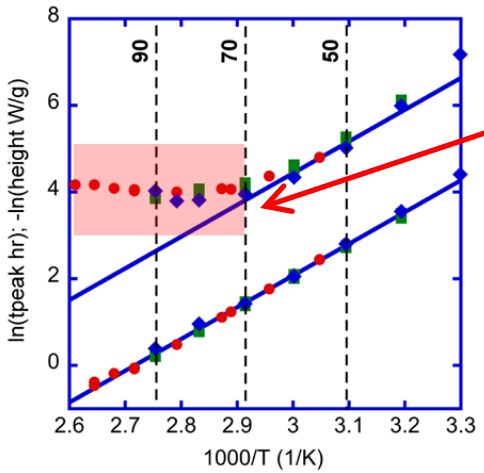
Propogation



Termination



The "weak" tertiary amine complex destabilizes at high temperature (~70C for 828/DEA)

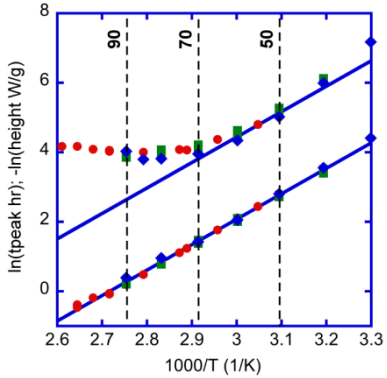


McCoy et al., *under review*

Challenges Representing 828/DEA Gelation Reaction Kinetics Mathematically

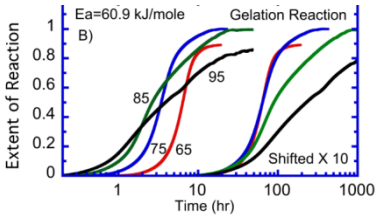
$$\frac{d\alpha}{dt} = ce^{\frac{-E_a}{RT}} f(\alpha)$$

no single activation energy



$$\frac{d\alpha}{dt} = f(T)f(\alpha)$$

no time-temperature superposition



$$\frac{d\alpha}{dt} = f(T, \alpha)$$

only works for isothermal reaction

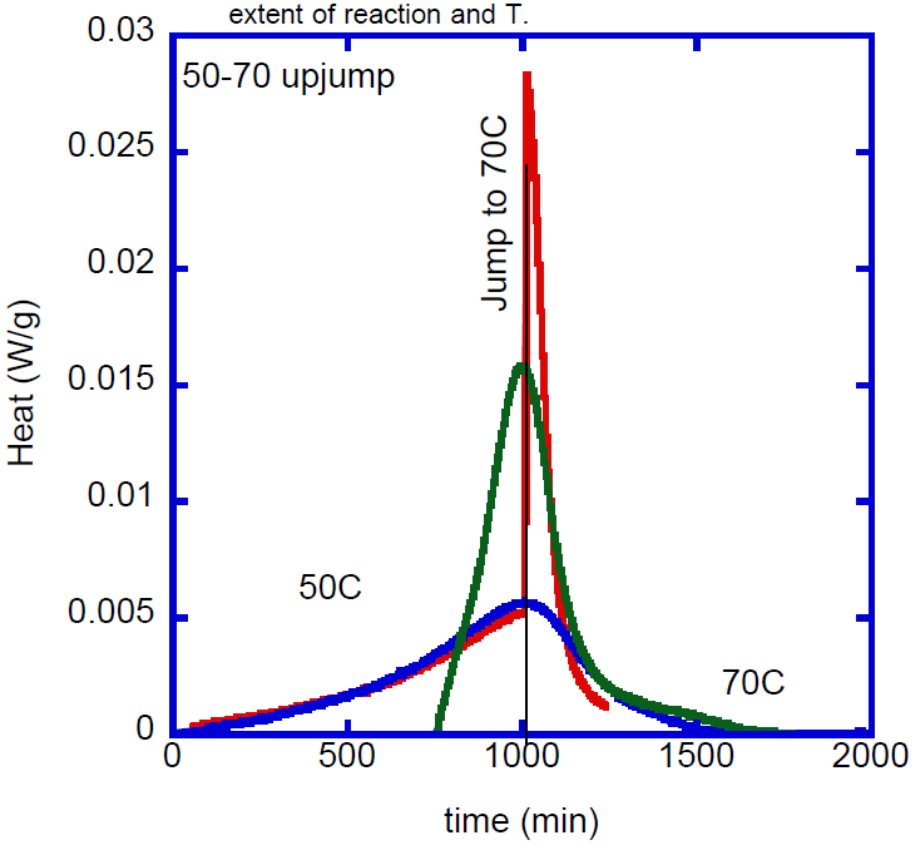
Concentration of the intermediates (e.g., X1, X2, X3…) of the subreactions (initiation, propagation, termination) must be taken into account

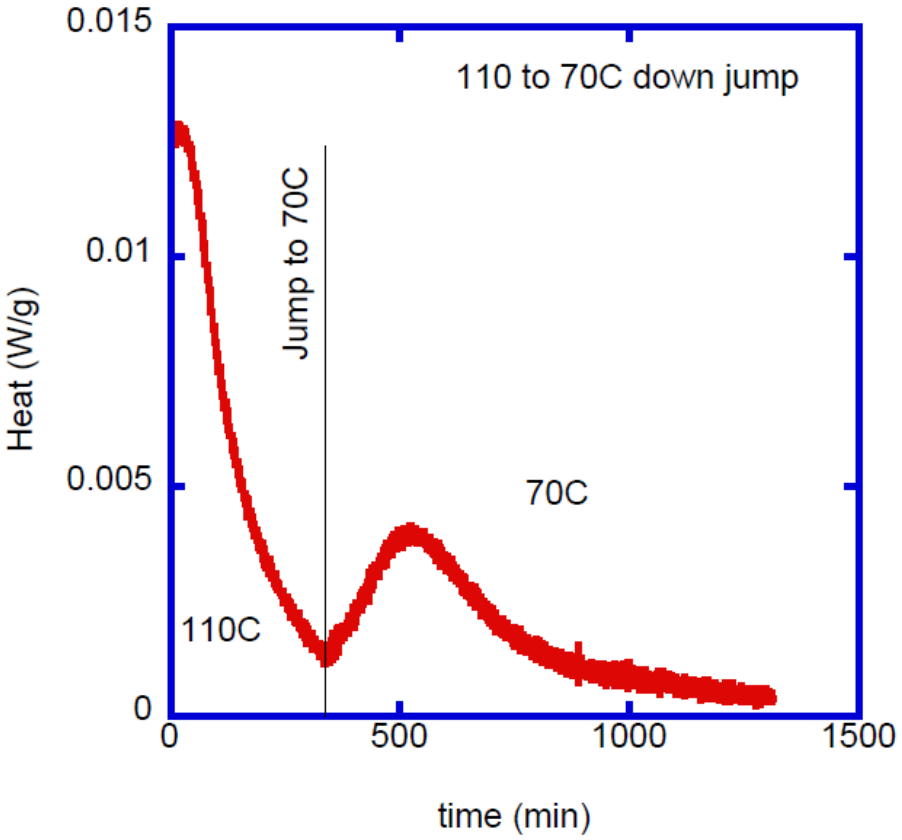
$$\frac{d\alpha}{dt} = f(T, \alpha, X1, X2, X3 \ldots)$$

McCoy et al., *under review*

Temperature Jump Experiments Showing Intriguing Behavior

Up Jump compared to full 50C and 70C runs the 70C run has been shifted in time since the jump happens at about the peak (150J/g) Notice that the reaction increases far beyond what it would be if it were only a function of extent of reaction and T.





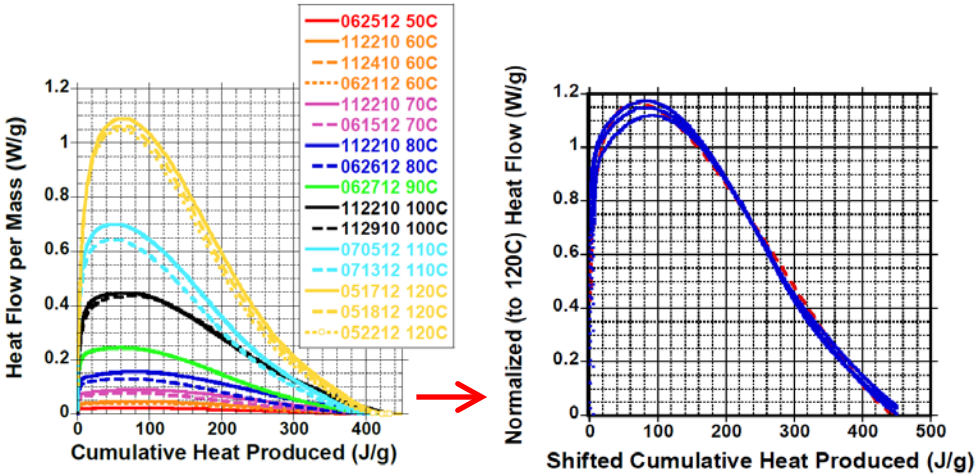
Jump up to T=70C generates a much higher reaction rate than ever seen during T=70C isothermal cure

Jump down to T=70C exhibits no activation energy for the reaction

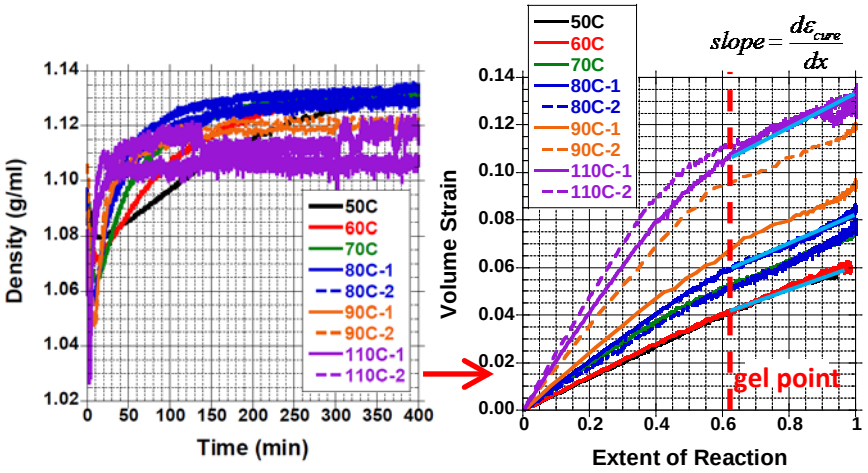
Material Evolution Associated with Reaction and Predictive Model Validation

828/T403 Material Evolution with Reaction

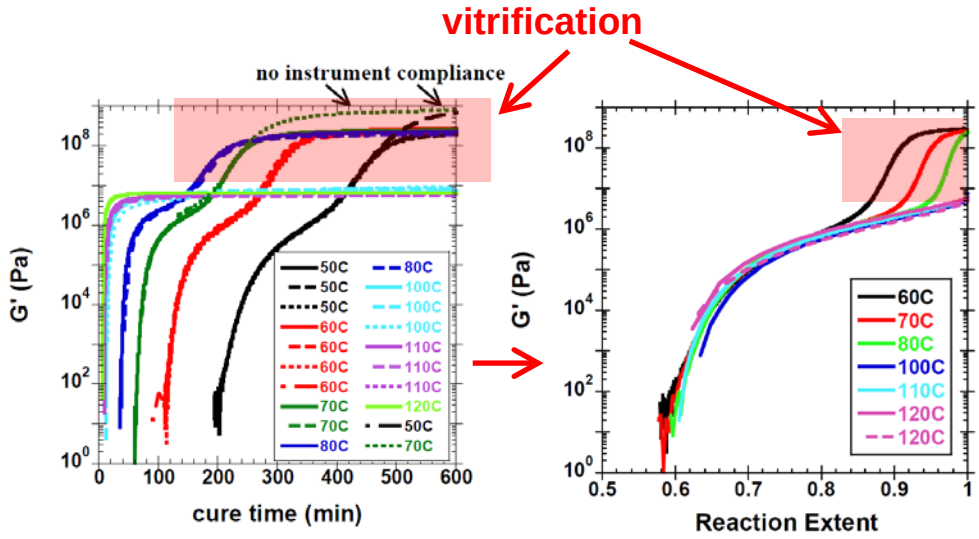
Reaction Kinetics



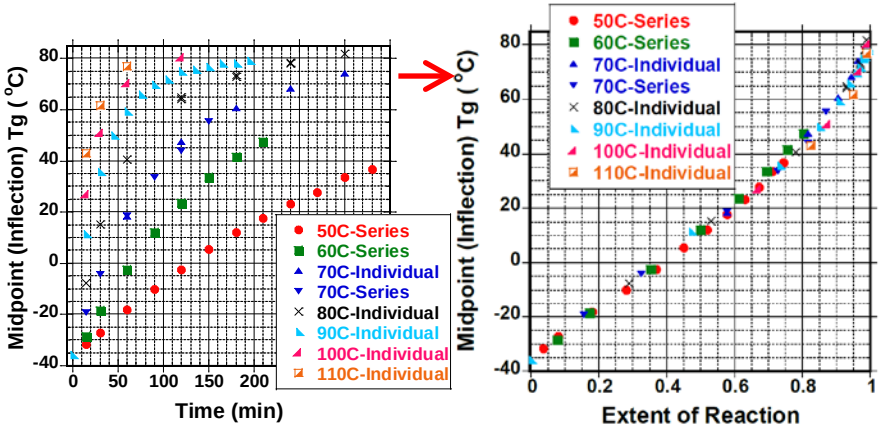
Cure Shrinkage



Modulus Evolution



Tg Evolution



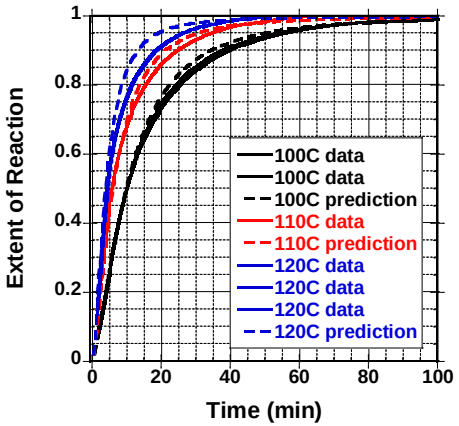
Kropka et al., SAND2013-8681

Predicting Cure Stress: Parameterizing the SPEC Cure Model

Reaction Kinetics

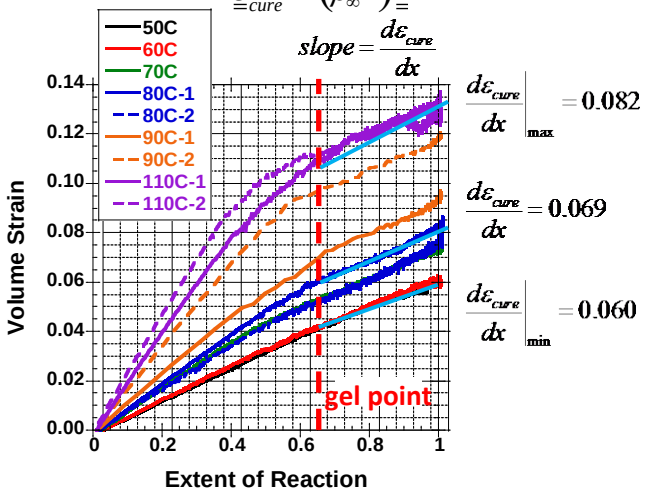
$$\frac{dx}{dt} = \hat{k}\left(b + x^m\right)(1-x)^n \qquad \hat{k} \equiv \frac{k}{\left(1 + w\,a\right)^\beta} \qquad k = k_o\, e^{-\frac{E_a}{RT}}$$

828/T403 Chemistry Limited Reaction Parameters	
Parameter	Value
E_a	13.8 kcal/mole
k_o	2.17x10^5 s^{-1}
b	0.17
m	0.33
n	1.37



Volumetric Cure Shrinkage

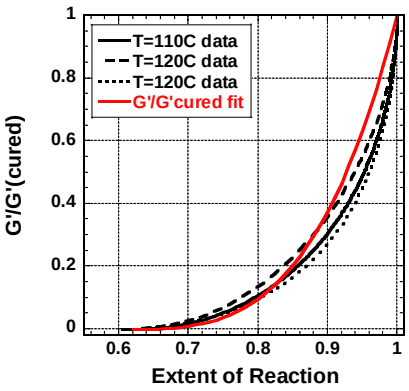
$$\underline{\underline{\varepsilon}}_{cure} = \left(\beta_\infty x\right)\underline{\underline{I}} \qquad slope = \frac{d\varepsilon_{cure}}{dx}$$



Evolution of Equilibrium Shear Modulus During Cure

$$\frac{G_\infty(x)}{G_\infty(1)} = \left[\frac{x^2 - x_{gel}^2}{1 - x_{gel}^2}\right]^{8/3}$$

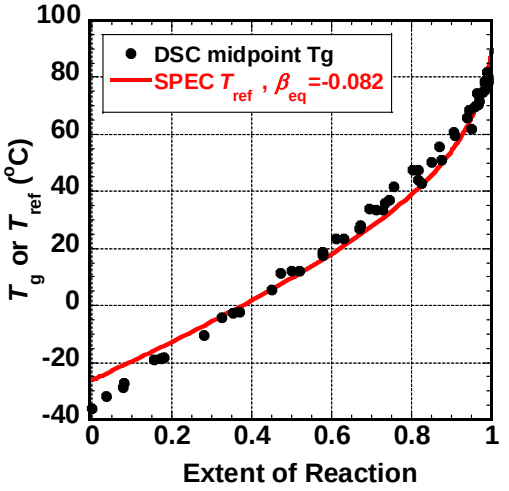
828/T403 $G_\infty(x)$ Parameterization	
Parameter	Value
x_{gel}	0.62



Evolution of Glass Transition Temperature During Cure

$$T_{ref}(x) = T_{ref} - \frac{\left[C_3\beta_\infty + C_5(x(t))\right]\left(x(t) - x_{ref}\right)}{\left(1 - C_3 \propto_\infty\right)} \qquad C_5(x(t)) = C_{5a} + \frac{C_{5c}}{\left(C_{5d} - C_{5b}x\right)^{C_{5e}}}$$

828/T403 T_{ref} Parameterization	
Parameter	Value
C_3	900 C
α_∞	500 ppm/C
C_{5a}	10 C
C_{5b}	0.97
C_{5c}	-105 C
C_{5d}	1.0088
C_{5e}	0.73



Kropka et al., SAND2013-8681

Predicting Cure Stress: Parameterizing the SPEC Cure Model

$$\underline{\underline{\sigma}} = \left[\Delta K \int_0^t ds\, \mathrm{f}_v(t^*-s^*) \frac{d\mathrm{I}_\varepsilon}{ds}(s) - \Delta(\mathrm{K}\alpha) \int_0^t ds\, \mathrm{f}_v(t^*-s^*) \frac{dT}{ds}(s) - \Delta(\mathrm{K}\beta) \int_0^t ds\, \mathrm{f}_v(t^*-s^*) \frac{dx}{ds}(s) \right] \underline{\underline{\mathrm{I}}}$$

$$+ 2\Delta G \int_0^t ds\, \mathrm{f}_s(t^*-s^*) \frac{\mathrm{d}\underline{\underline{\varepsilon}}_{dev}}{ds}(s) + \left[K_\infty I_\varepsilon - K_\infty \alpha_\infty \Delta T - K_\infty \beta_\infty \Delta x \right] \underline{\underline{I}} + 2 \int_0^t ds G_\infty(s) \frac{\mathrm{d}\underline{\underline{\varepsilon}}_{dev}}{ds}(s)$$

cure shrinkage terms

changing reference state term

Material time is computed by using a shift factor, a

$$t^* - s^* = \int_s^t \frac{dw}{a(w)} \qquad and \qquad \log a = -\hat{C}_1 \left(\frac{N}{\hat{C}_2 + N} \right)$$

The shift factor is a function of temperature, volume, deformation and reaction histories

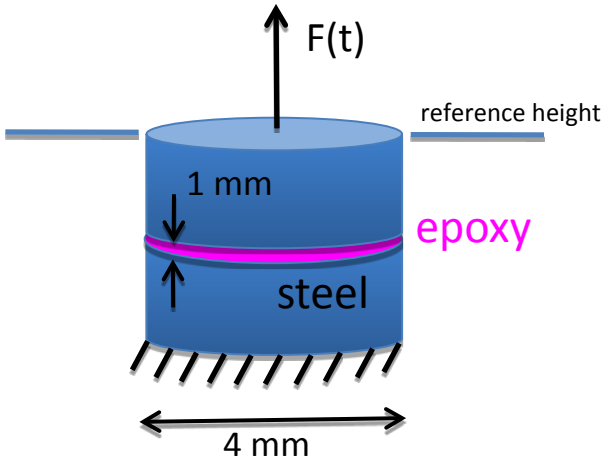
$$N = \left\{ \left[T(t) - T_{ref} \right] - \int_0^t ds\, \mathrm{f}_1(t^*-s^*) \frac{dT}{ds}(s) \right\} + C_3 \left\{ I_1(t)_{ref} - \int_0^t ds\, \mathrm{f}_1(t^*-s^*) \frac{d\mathrm{I}_1}{ds}(s) \right\}$$

$$+ C_4 \left\{ \int_0^t \int_0^t ds\, du\, f(t^*-s^*, t^*-u^*) \frac{d\underline{\underline{\varepsilon}}_{dev}(s)}{ds} : \frac{d\underline{\underline{\varepsilon}}_{dev}(u)}{du} \right\} + C_5(x(t)) \left\{ \left[x(t) - x_{ref} \right] - \int_0^t ds\, \mathrm{f}_1(t^*-s^*) \frac{dx}{ds}(s) \right\}$$

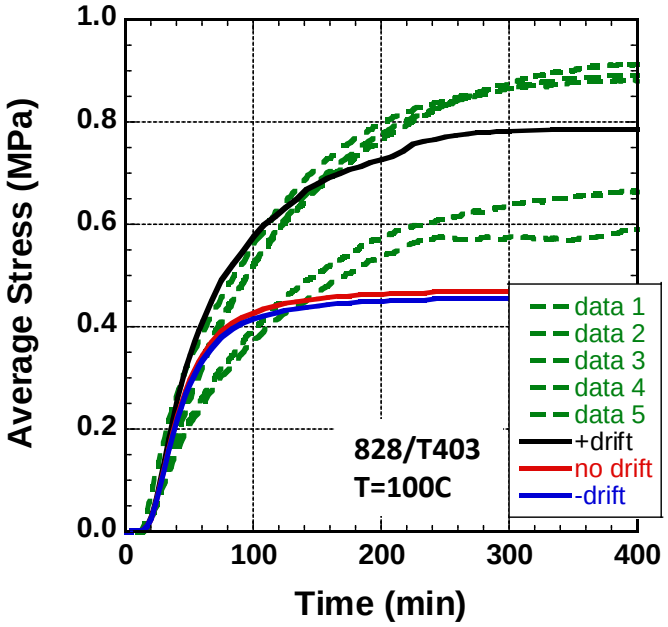
Kropka et al., SAND2013-8681

Predicting Cure Stress: Validation Tests

The Simple Test



Rubbery Cure Results



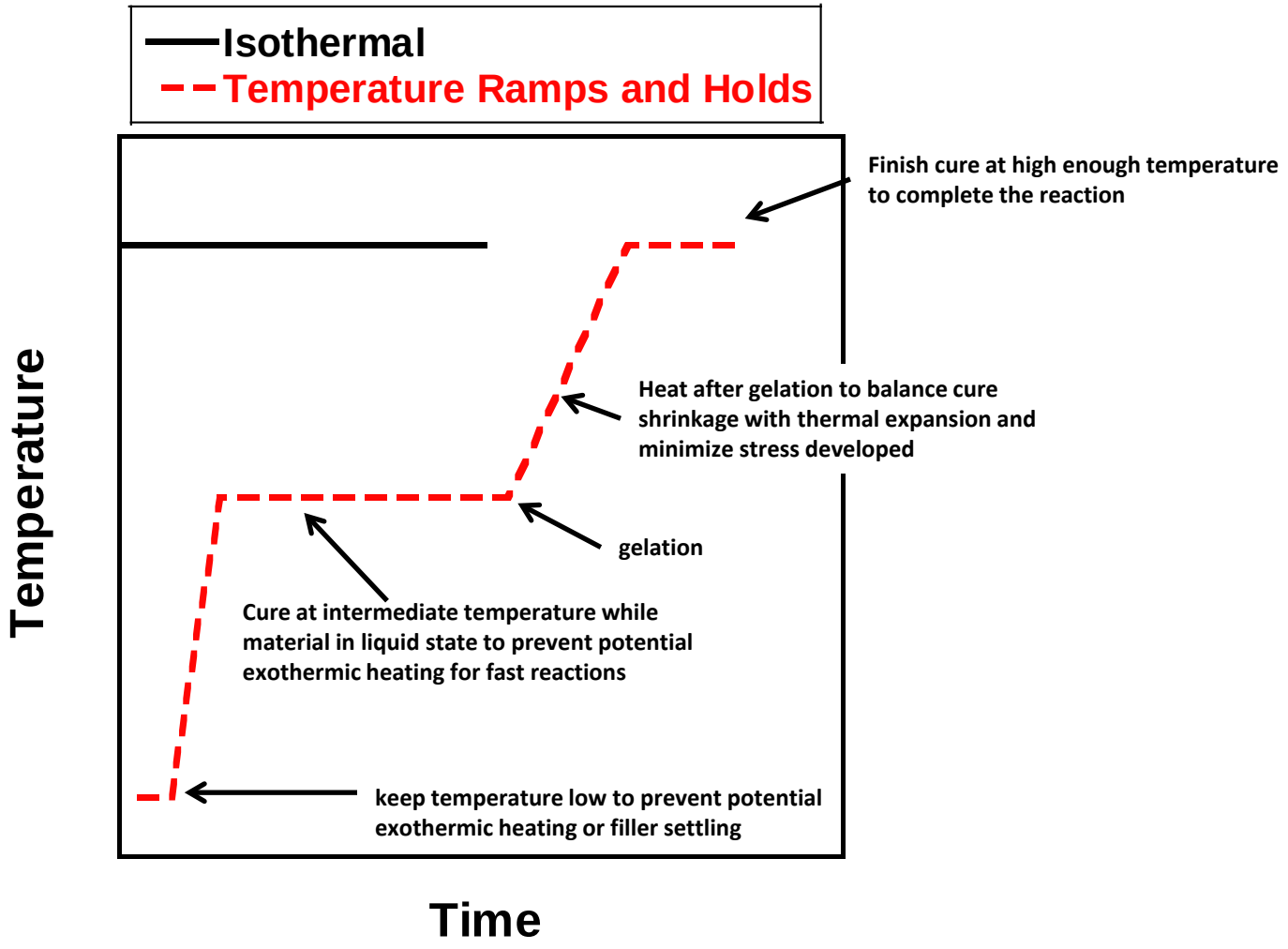
Good agreement between predictions and data, with known variations in boundary conditions during the test accounting for the spread in the data

This capability will enable the design of cure schedules to minimize stress

Kropka et al., SAND2013-8681

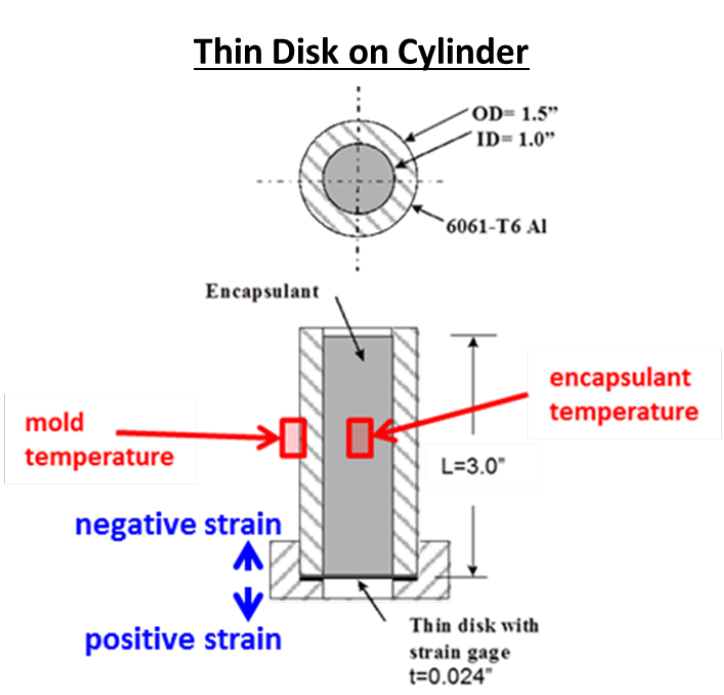
Structural Response Tests to Design Cure Schedules and Validate Models

Designing an Optimum Cure Schedule

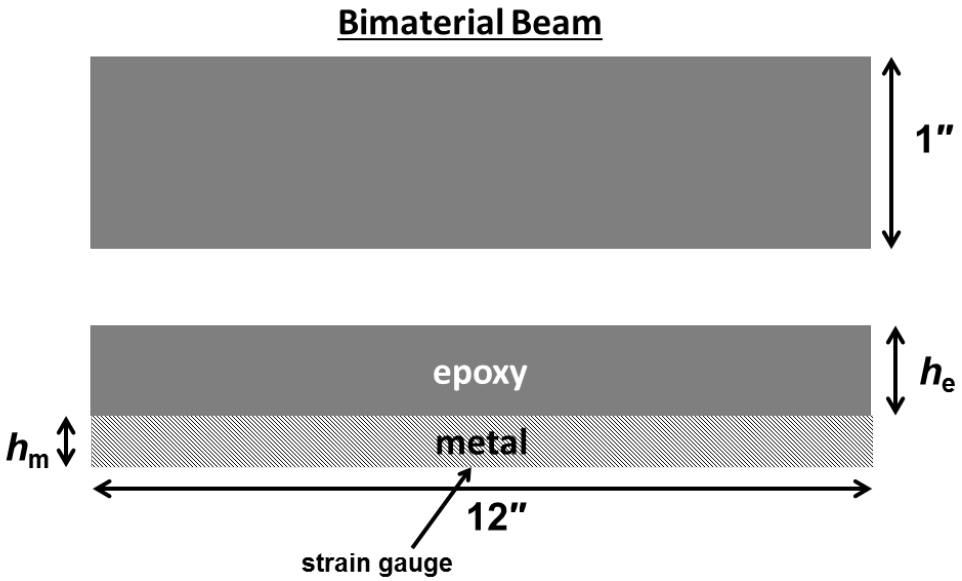


Isothermal reaction at a high temperature may be the fastest method to achieve complete cure, but other factors may drive the time-temperature profile in a different direction

Confined Cure



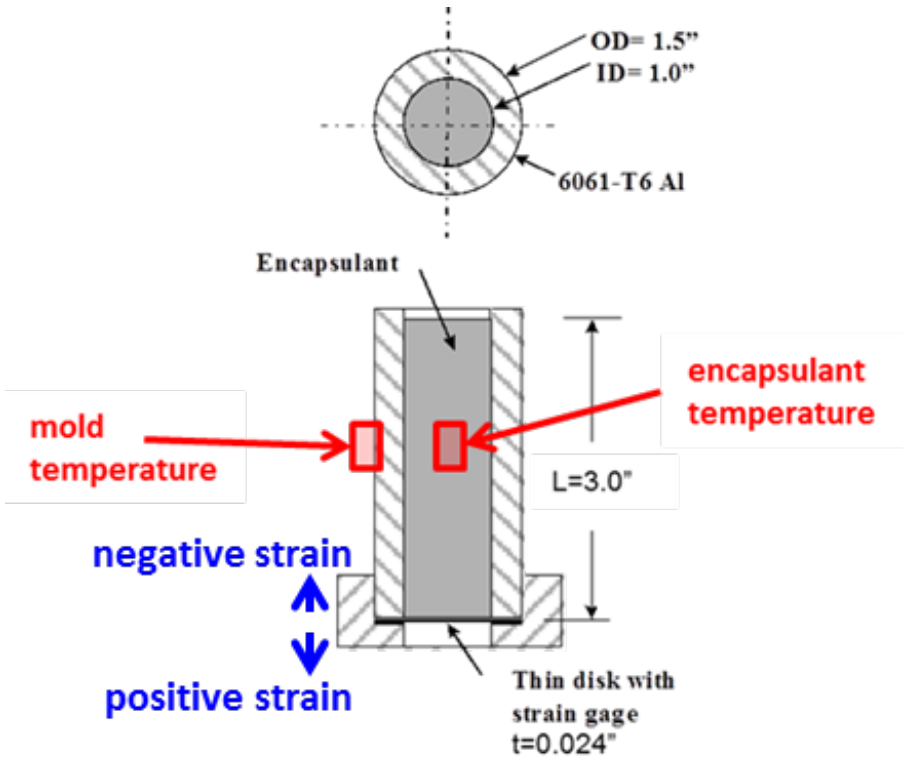
Free-surface Cure



h_e = thickness of epoxy
h_m = thickness of metal

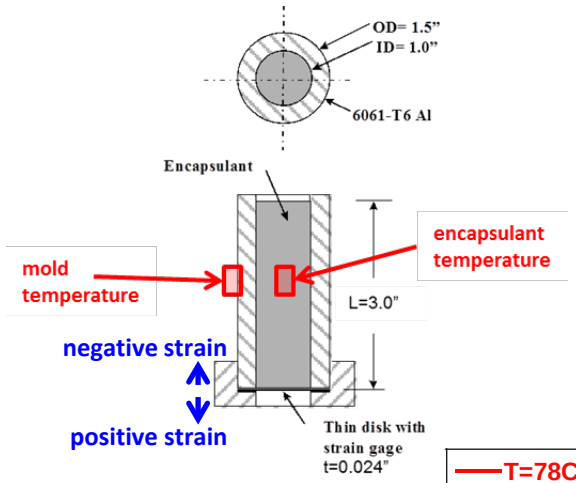
Confined Cure

Thin Disk on Cylinder

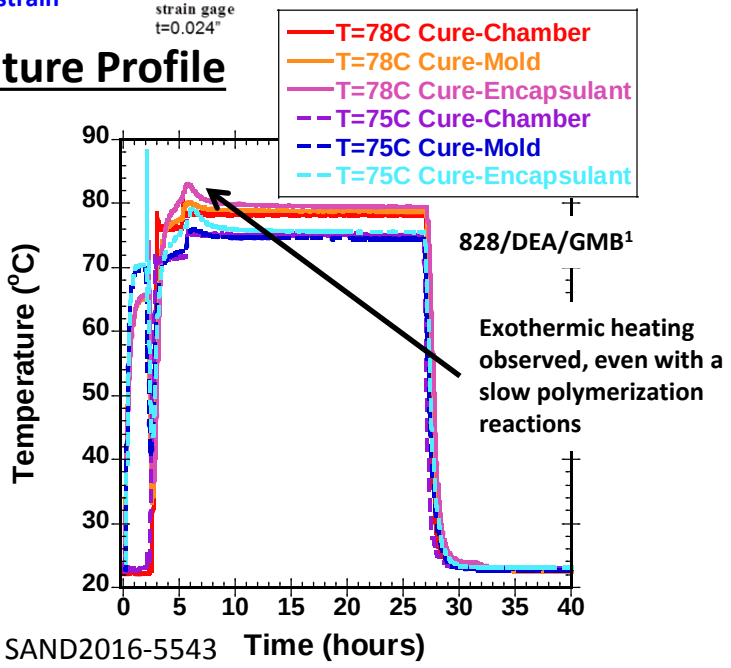


Isothermal Cure

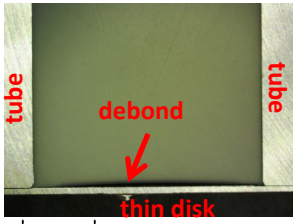
Geometry: Thin Disk on Cylinder

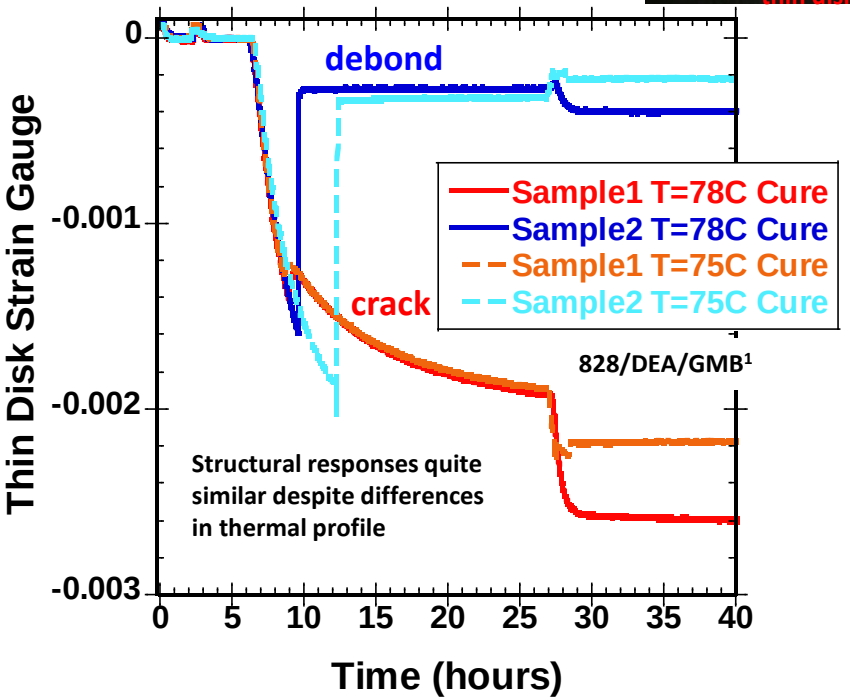


Temperature Profile

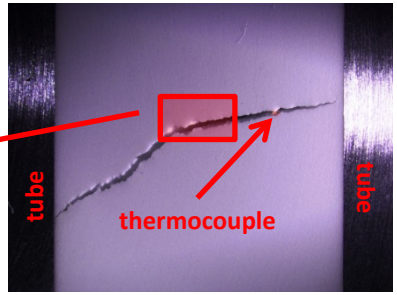


Structural Response





Rough crack surface consistent with "tearing" in rubbery state?



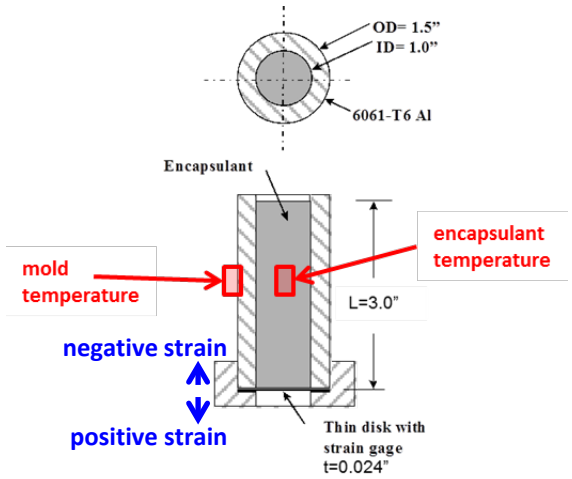
Kropka et al., SAND2016-5543

Failure can occur during cure…can it be avoided by minimizing stress?

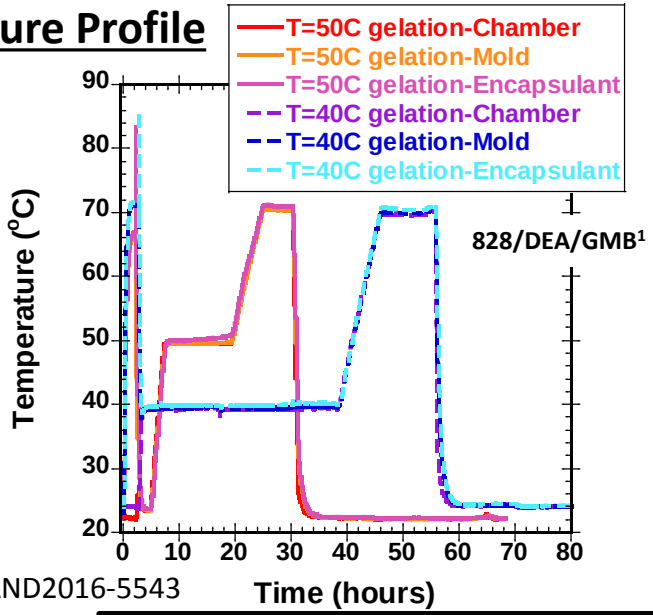
[1]http://www.sandia.gov/polymer-properties/828_DEA_GMB.html

Cure with Temperature Ramps and Holds

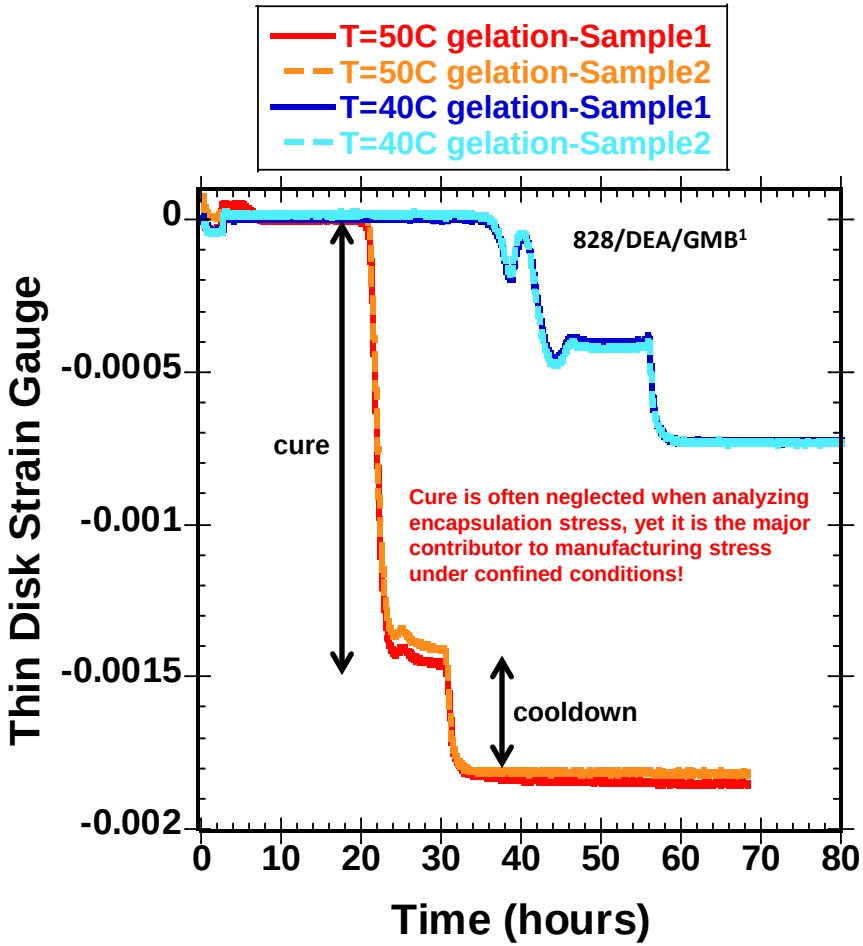
Geometry: Thin Disk on Cylinder



Temperature Profile



Structural Response

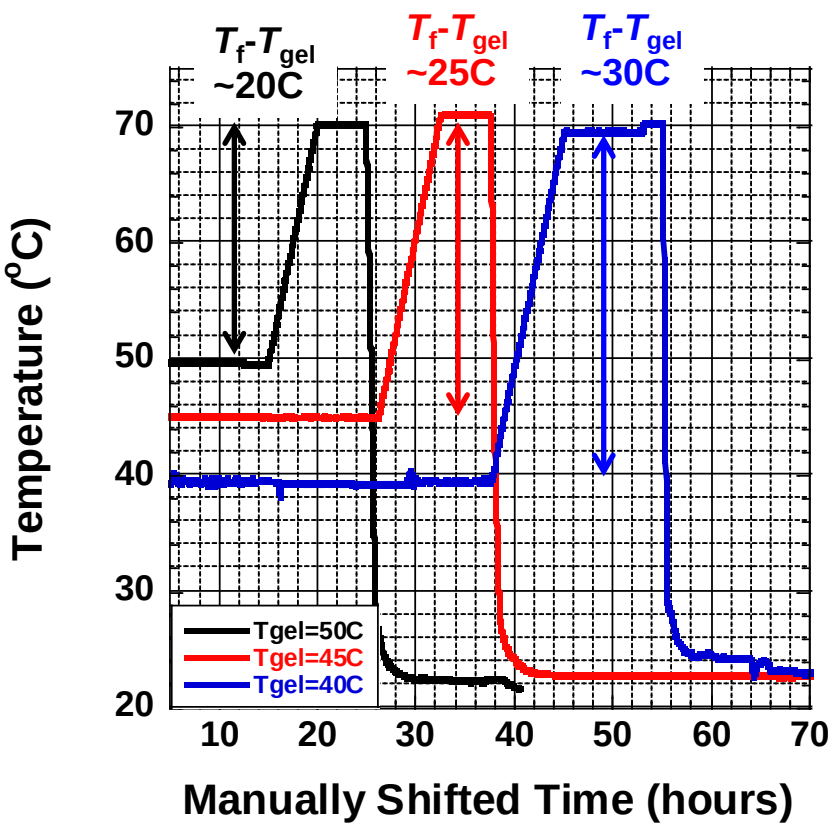


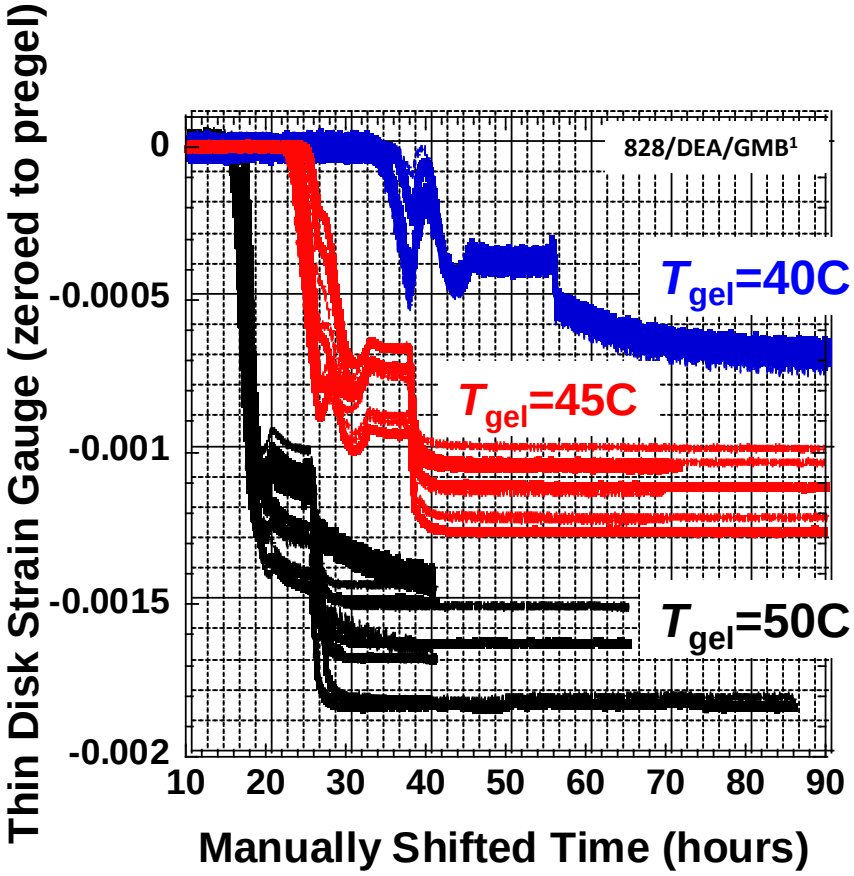
Kropka et al., SAND2016-5543

[1]http://www.sandia.gov/polymer-properties/828_DEA_GMB.html

No cracking/debonding observed and less disk deflection for larger post-gelation thermal ramp (thermal expansion offsetting cure shrinkage)

Dependence on Gel Temperature

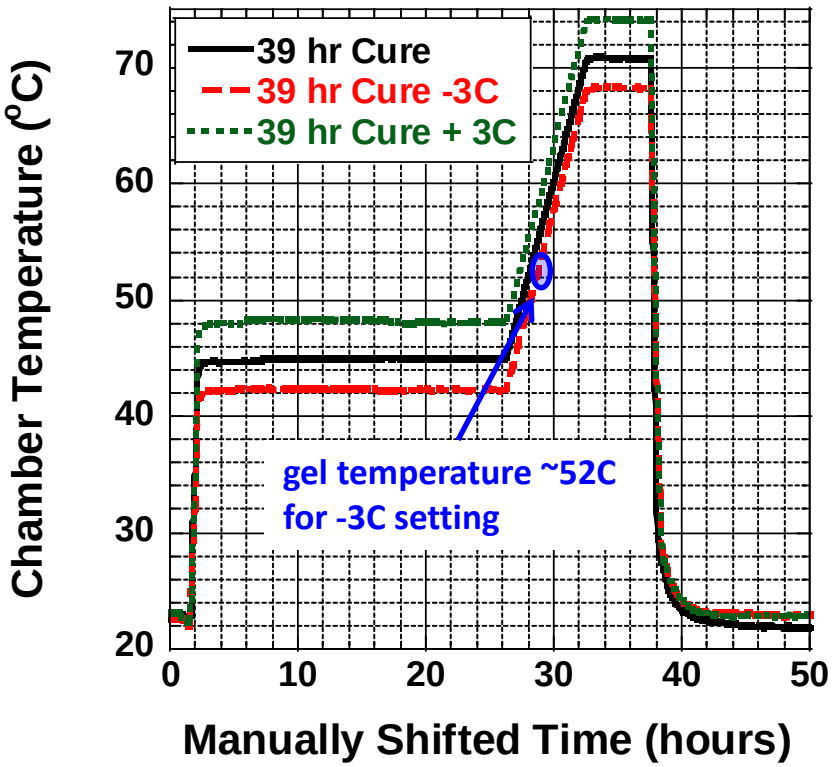


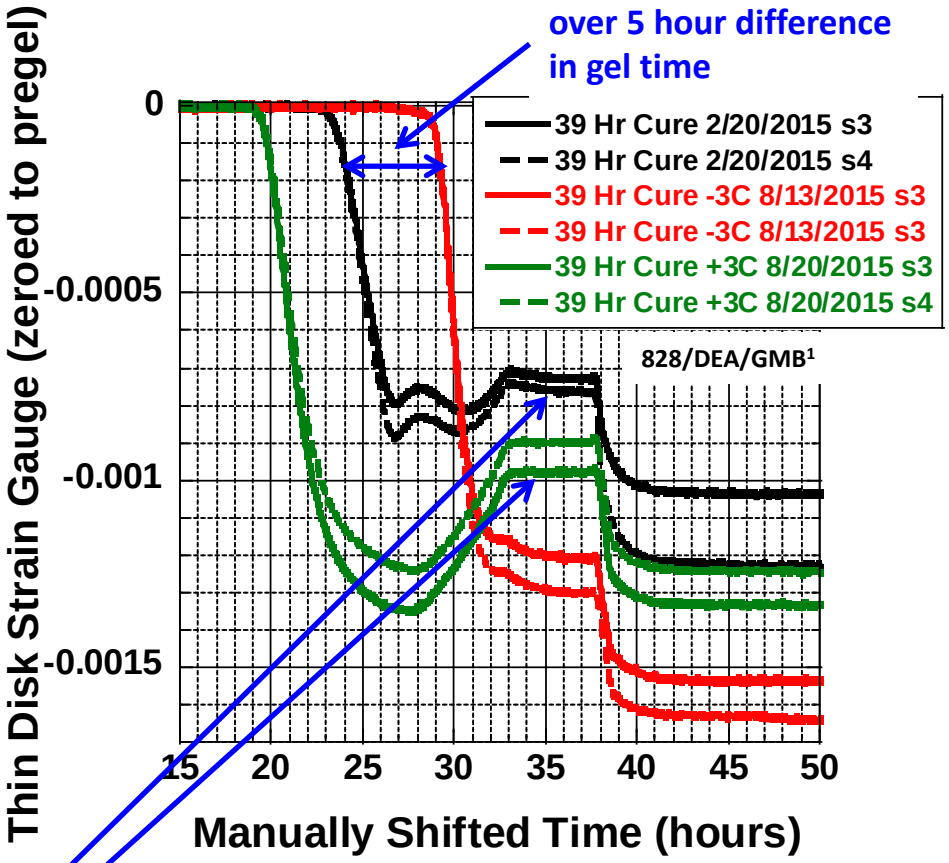


The difference between gel temperature and final cure temperature (T_f) appears to be a primary factor in determining residual stress developed

[1]http://www.sandia.gov/polymer-properties/828_DEA_GMB.html

Sensitivity to Temperature Variations





Can differences be accounted for solely by 3C higher gel temperature?

Findings:

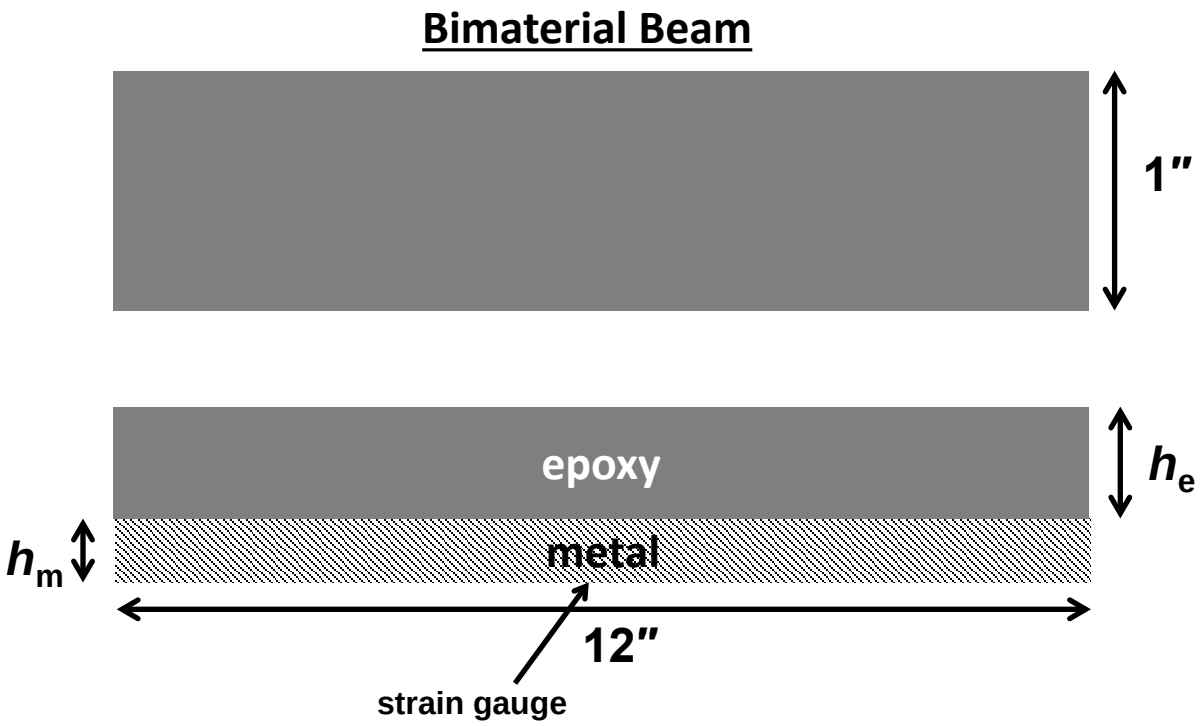
- A temperature 3C higher than designed results in a higher gelation temperature and resulting strains are consistent with the higher gel temperature
- A temperature 3C lower than designed also increases the gelation temperature (pushes gelation into the thermal ramp) and resulting strains are consistent with the higher gel temperature

[1]http://www.sandia.gov/polymer-properties/828_DEA_GMB.html

Summary

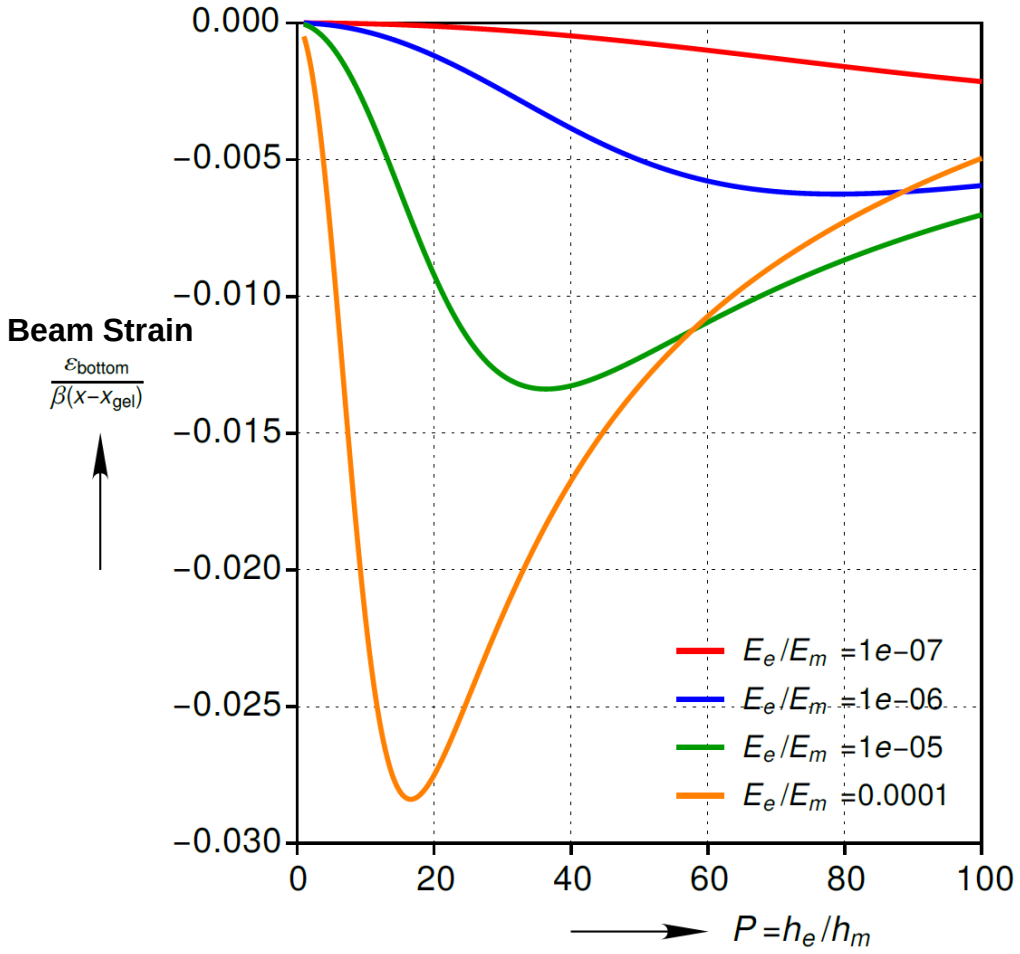
- **“Thin Disk on Cylinder” test geometry gives reproducible results with sensitivity to even small changes in temperature**
- **Methodologies to minimize stress associated with cure (e.g., balance cure shrinkage with thermal expansion) can be resolved**
- **The choice of an optimum cure schedule involves trade-offs amongst key parameters, for example:**
  - **Residual stress**
    - **At low extents of reaction when encapsulant material is “weakest”**
    - **At final state (e.g., room temperature storage)**
  - **Processing/Cure time**
- **Where application geometries vary from “Thin Disk on Cylinder” geometry, sensitivities of cure stress to test geometry should be evaluated**
- **Each encapsulant material will require a unique “optimum” cure schedule**

Free-surface Cure



h_e = thickness of epoxy
h_m = thickness of metal

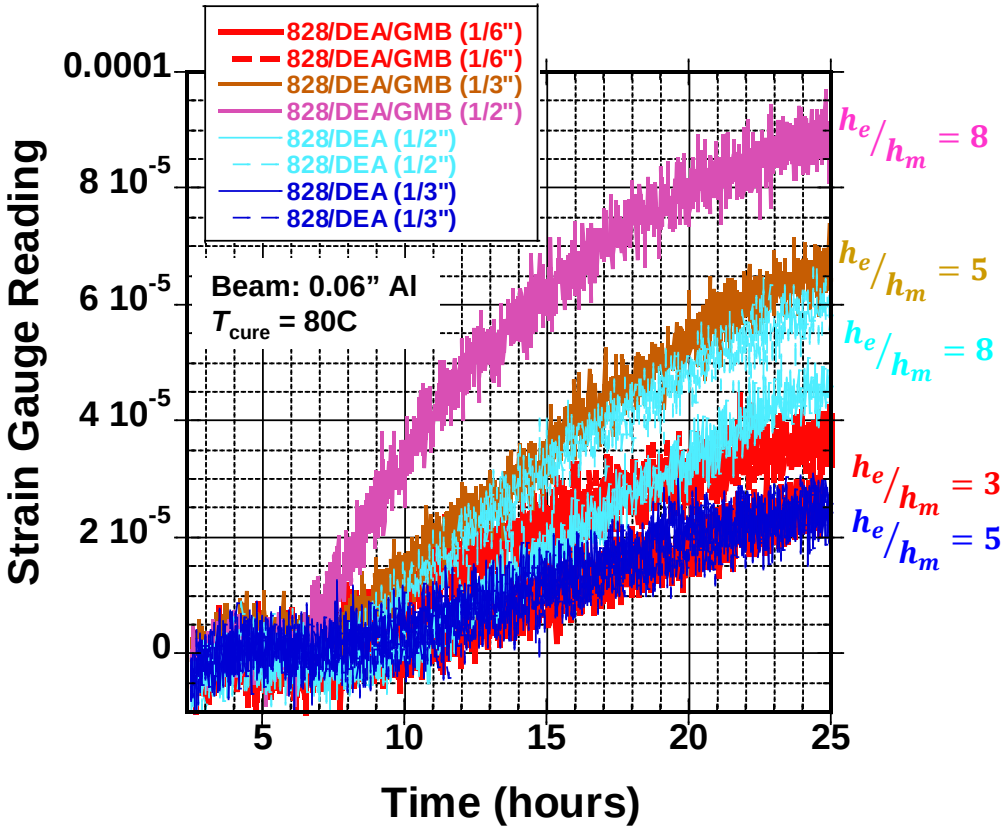
Geometry Considerations



Optimum h_e/h_m for maximum beam bending depends on modulus ratio of materials. For epoxy-aluminum beam during epoxy cure, the optimum ratio is > 17

E_e = Young's modulus of epoxy
E_m = Young's modulus of metal

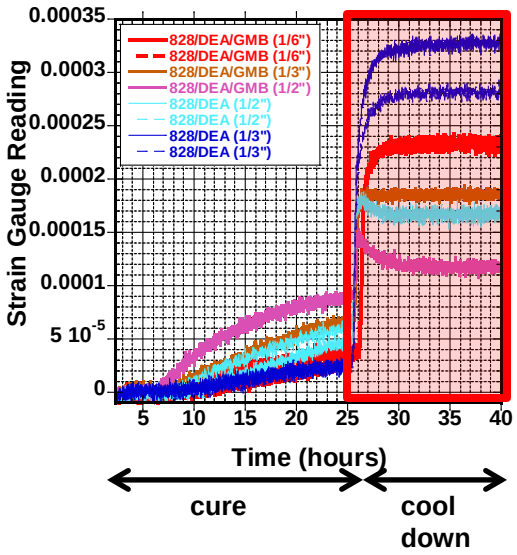
Epoxy Thickness Dependence of Cure Strain



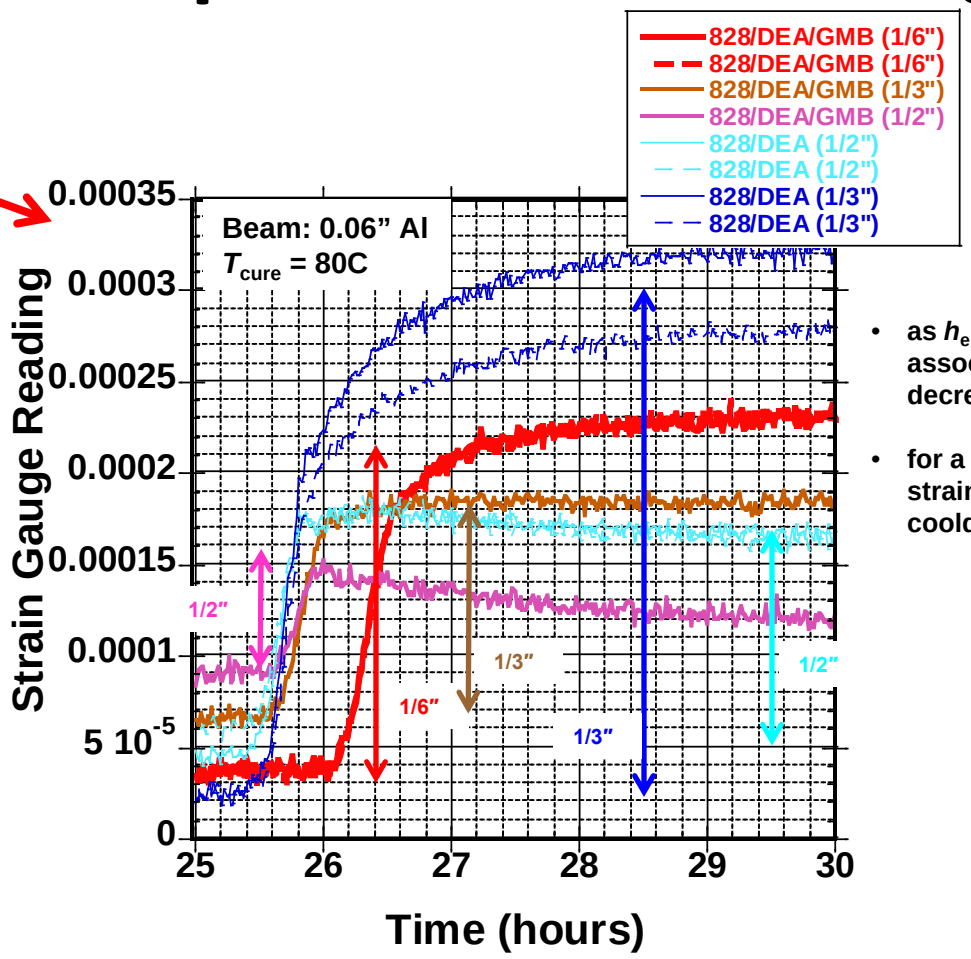
As anticipated, an increase in epoxy thickness (below $h_e/h_m = 17$) increases the beam strain during cure. The increase in equilibrium ($T>T_g$) modulus associated with GMB (~10x at full cure) addition outweighs the reduction in material shrinkage associated with cure (~2x) and increases the aluminum beam strain by ~ 2X

While GMB addition can help reduce stress associated with temperature changes below T_g in a fully cured, encapsulated part by reducing thermal expansion mismatches (between the encapsulant and encapsulate) without significant increase in encapsulant glassy modulus, the stress associated with free-surface cure (manufacturing) increases.

Epoxy Thickness Dependence of Cooling Strain



Note that cure in this less confined scenario (versus thin-disk-on-cylinder) is a much smaller fraction of the overall manufacturing stress (cure + cooldown)

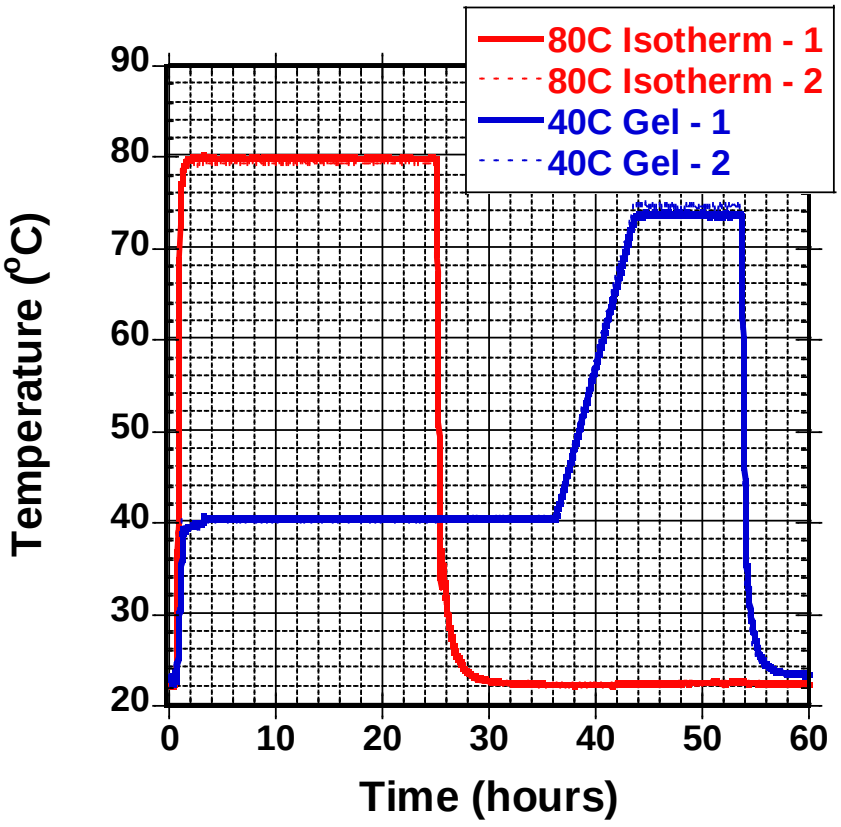


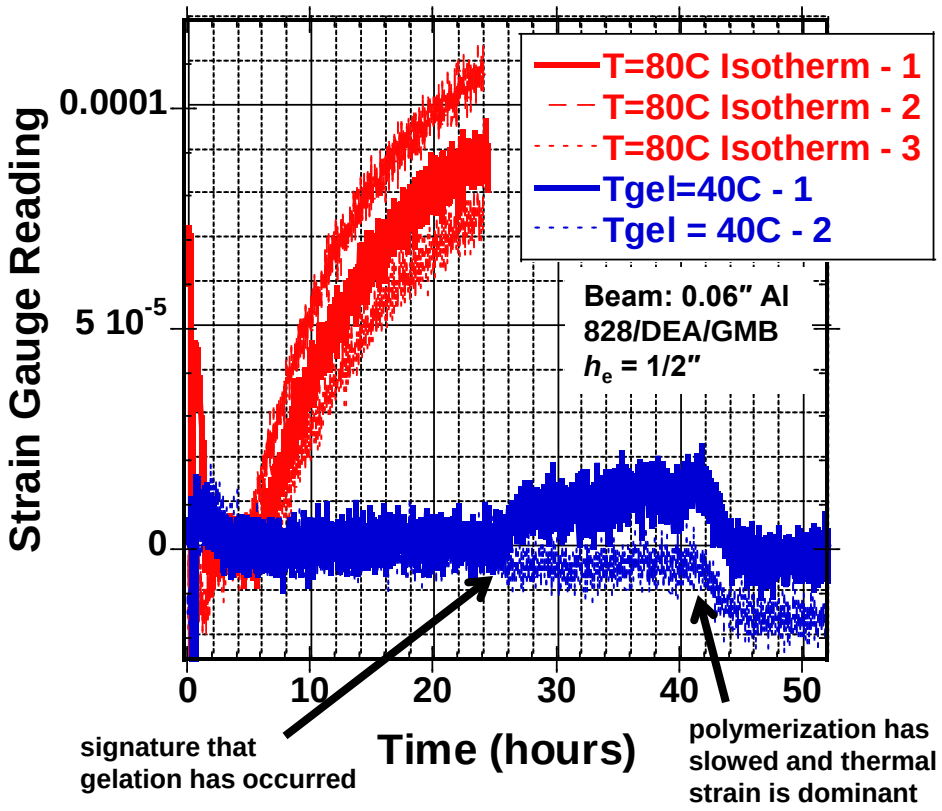
- as h_e increases, strain associated with cooldown decreases
- for a given h_e, GMB reduces strain associated with cooldown

Findings:

- Illustration of ability for GMB addition to reduce stress associated with temperature changes that go into the glass
- As h_e is increased, the stiffness of the epoxy layer is increased (particularly below Tg). The stiffer epoxy layer can contract the beam length-wise (during cooling) in addition to flexing the beam

Using Time-Temperature Profile to Reduce Cure Stress



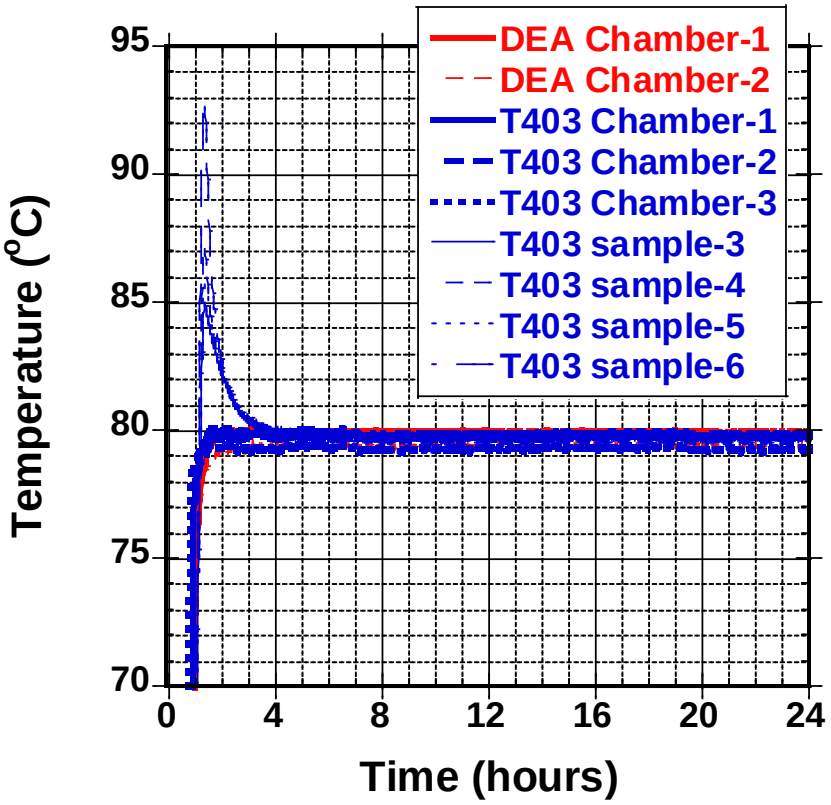


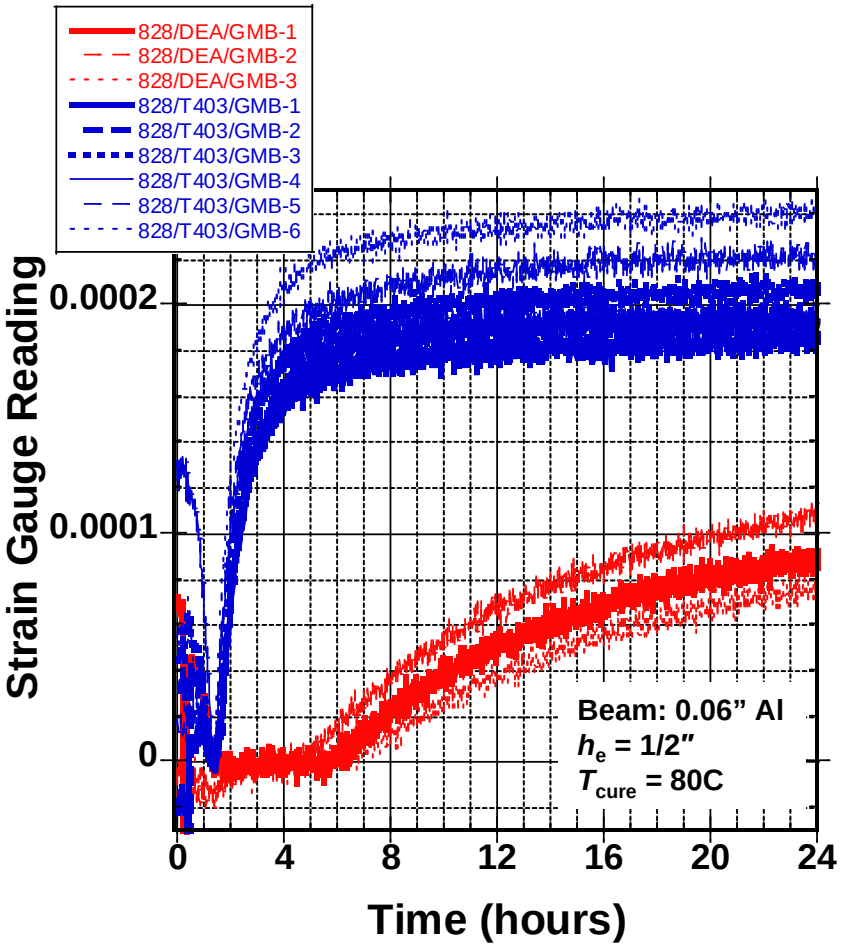
Finding:

Stress developed during free-surface cure can be reduced by implementing a post-gelation temperature ramp (as was also seen in confined cure)

Cure Stress Comparison Between Materials

-exothermic heating between 5-12C for ½" 828/T403/GMB samples on beam
-exothermic heating ~5C for 828/DEA/GMB sample in thin-disk on cylinder
-1/2" beam samples use 2X more encapsulant than thin-disk on cylinder
Need to check exothermic heating of 828/DEA/GMB in ½" bimaterial beam

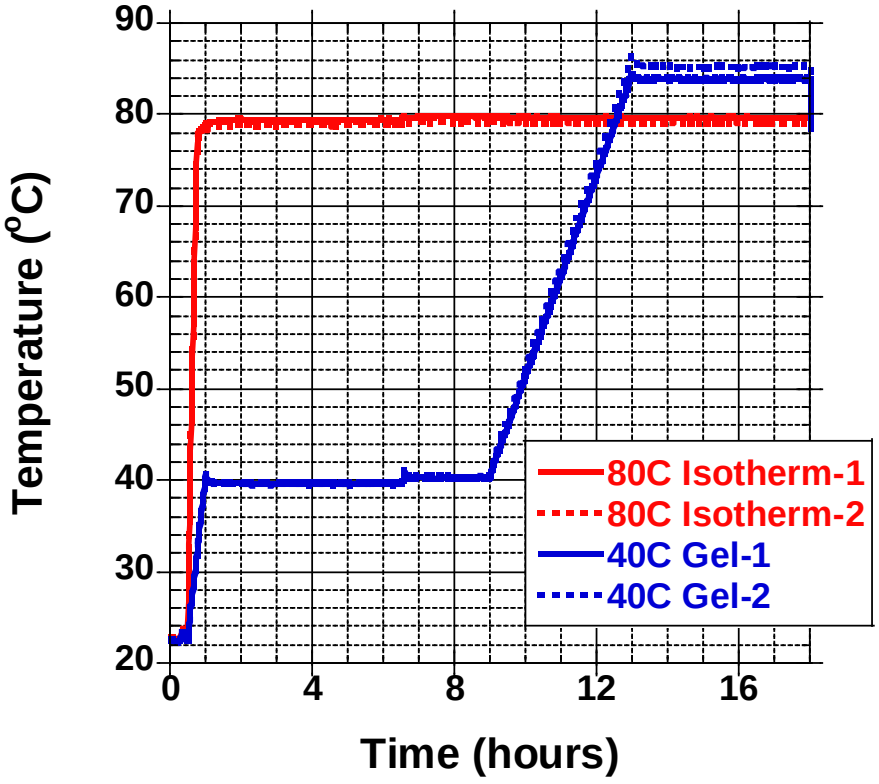


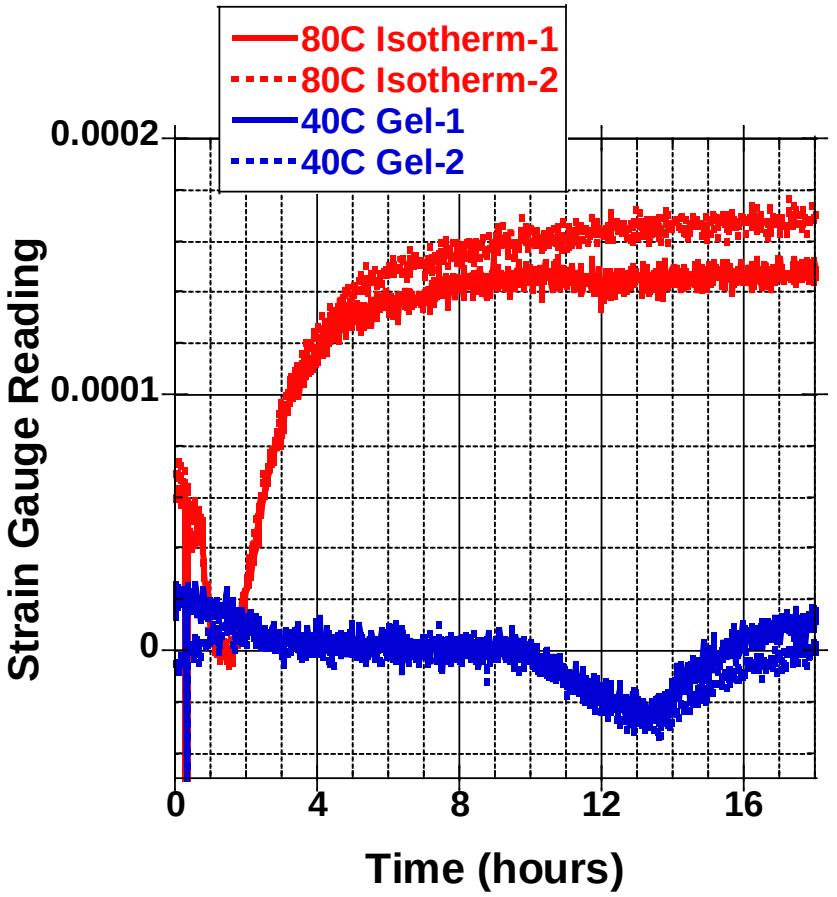


Finding:

Differences in beam strain between materials exist—need to verify whether differences are solely associated with material evolution during reaction (i.e., shrinkage and modulus development) or whether differences in exothermic heating between materials affect beam strain too

Cure Schedule Comparison for 828/T403/GMB





Finding:

Stress developed during free-surface cure can be reduced by implementing a post-gelation temperature ramp

Summary

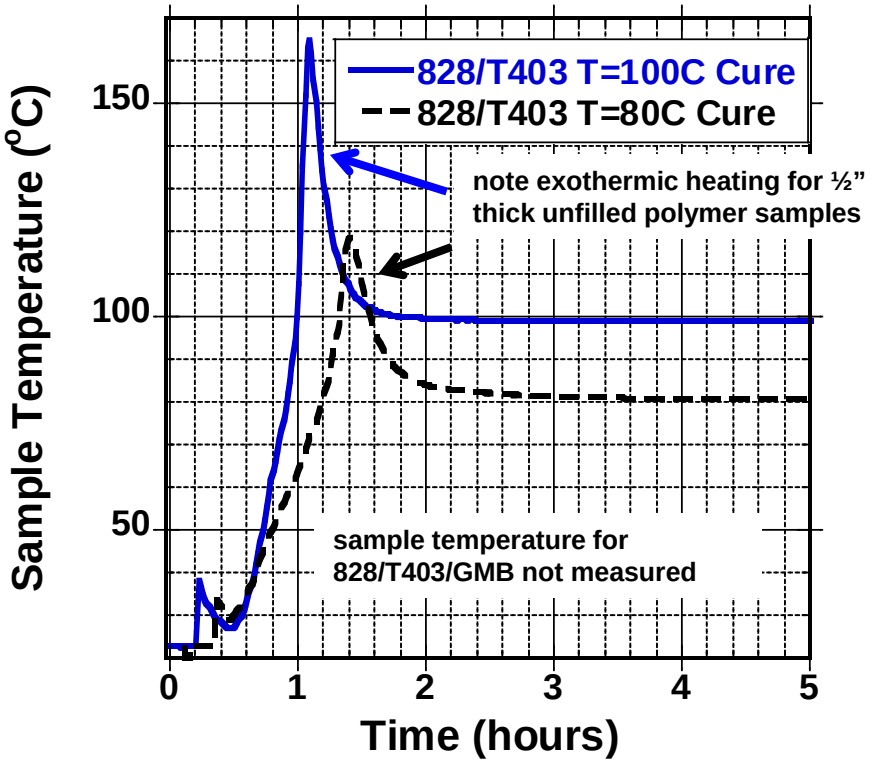
- **“Bimaterial Beam” test geometry gives reproducible results and geometry can be tuned to examine specific aspects (cure, cooldown, beam flexure, beam contraction)**
- **As was observed for confined cure, free-surface cure stress can be reduced by implementing a post-gelation temperature ramp to balance some of the material cure shrinkage with thermal expansion**
- **These two test geometries, Thin Disk on Cylinder and Bimaterial Beam, examine rather extreme cases of confinement. Most application geometries will fall somewhere in between these two extremes. Thus, time-temperature profile as a tool to reduce cure stress should be applicable to all encapsulation and adhesive applications.**

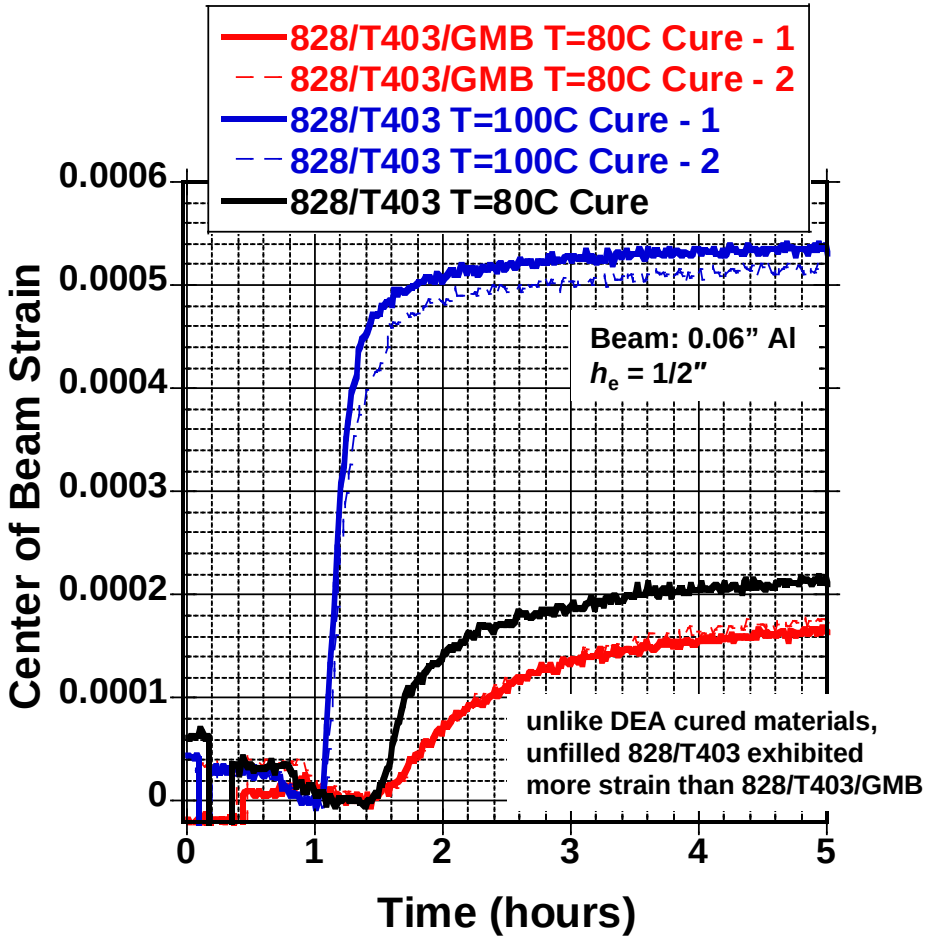
Final Remarks

- Stress developed during the manufacturing process of encapsulated components can be important
  - Methodologies to lower manufacturing stress exist
  - Test geometries to evaluate the specifics of a given material are available
- We have learned much about the reaction progress of 828/DEA and hope to be able to continue building our capabilities for this widely used material
- Promising results for predictive capabilities of the manufacturing process have been obtained, but more work is left to be done
  - Vitrification parameters need a closer look
  - Ability to predict behavior of more complicated materials (e.g., 828/DEA) is still TBD

Back-up Slides

828/T403: Fillers and Cure Temperature



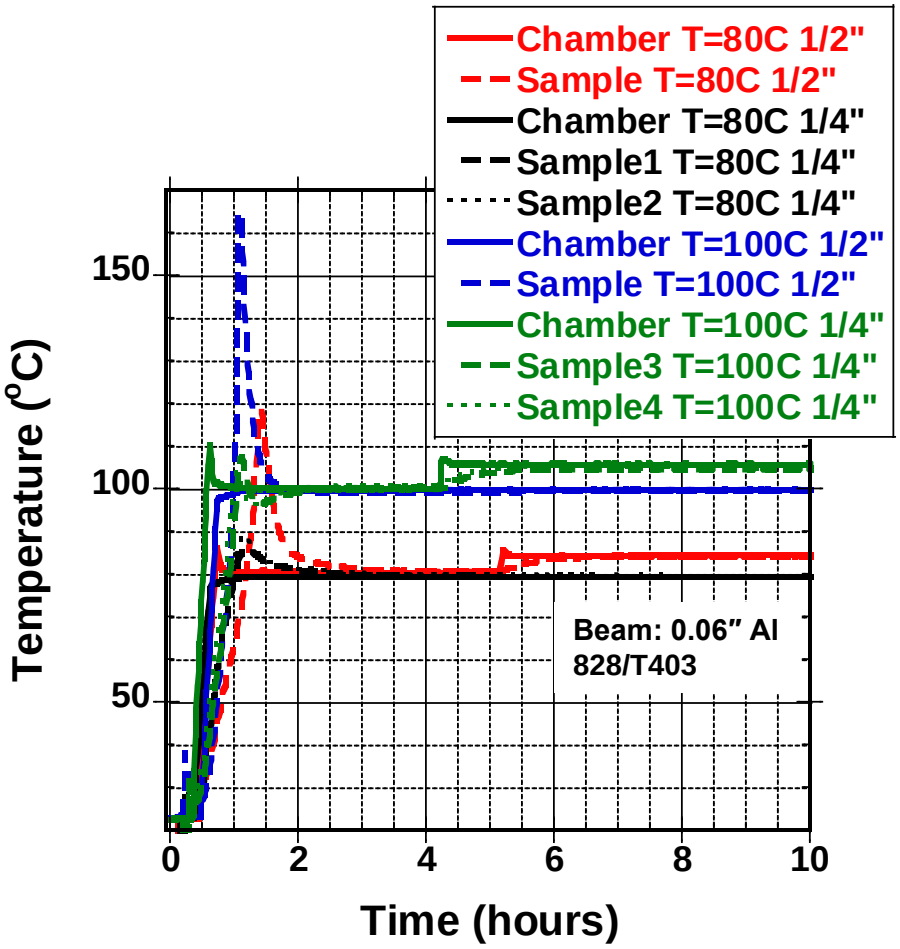


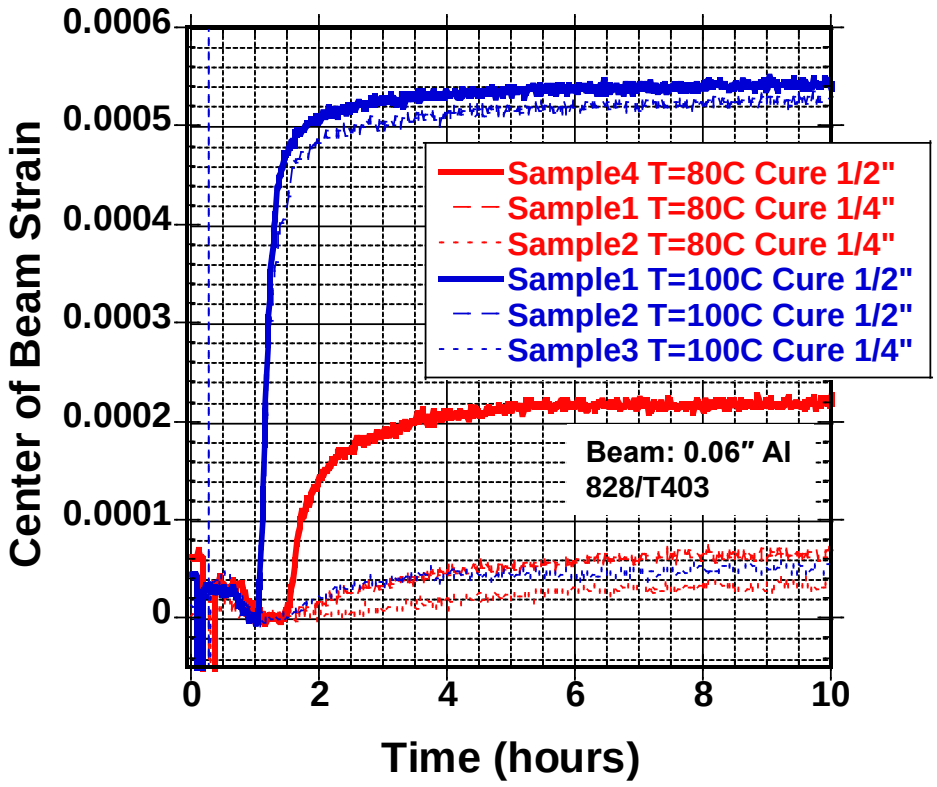
Finding:

Exothermic heating of unfilled 828/T403 ½" thick samples leads to a thermal contraction contribution to the beam strain, in addition to the cure shrinkage—this could account for more beam strain for T=100C vs. T=80C cure despite anticipated equivalent reaction extents AND for more beam strain for unfilled vs. GMB filled T=80C cure

Assumption: exothermic heating of GMB filled material would be less than for unfilled and this contributes to differences in beam strain between T=80C tests for materials

828/T403: Cure Temperature and Polymer Thickness



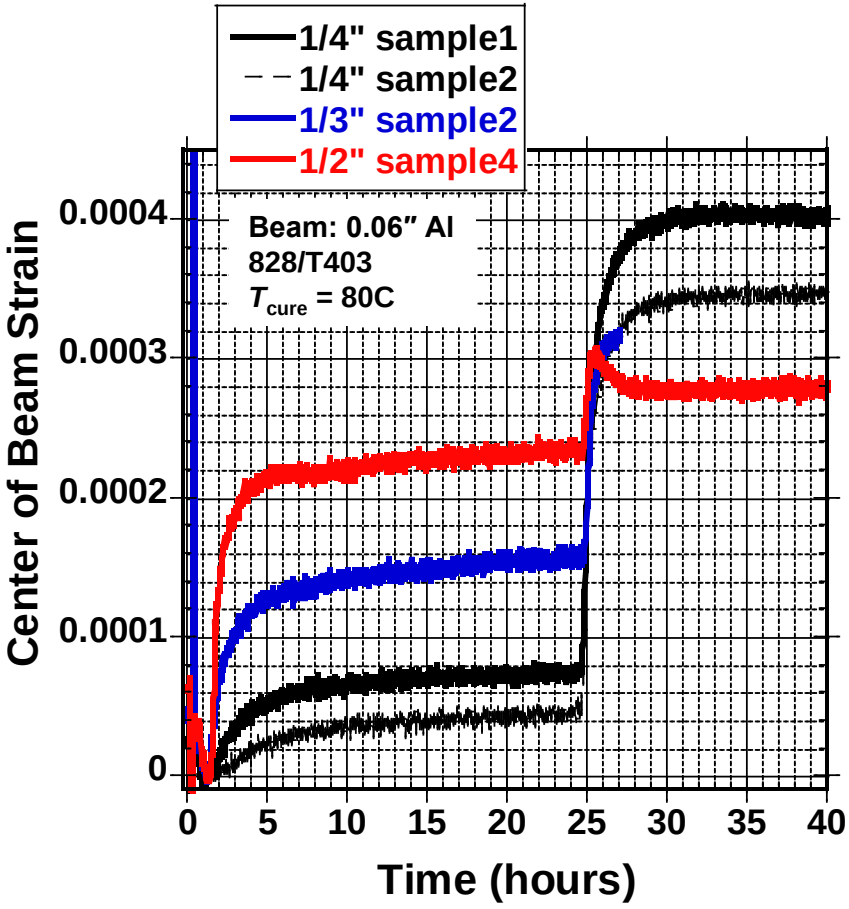


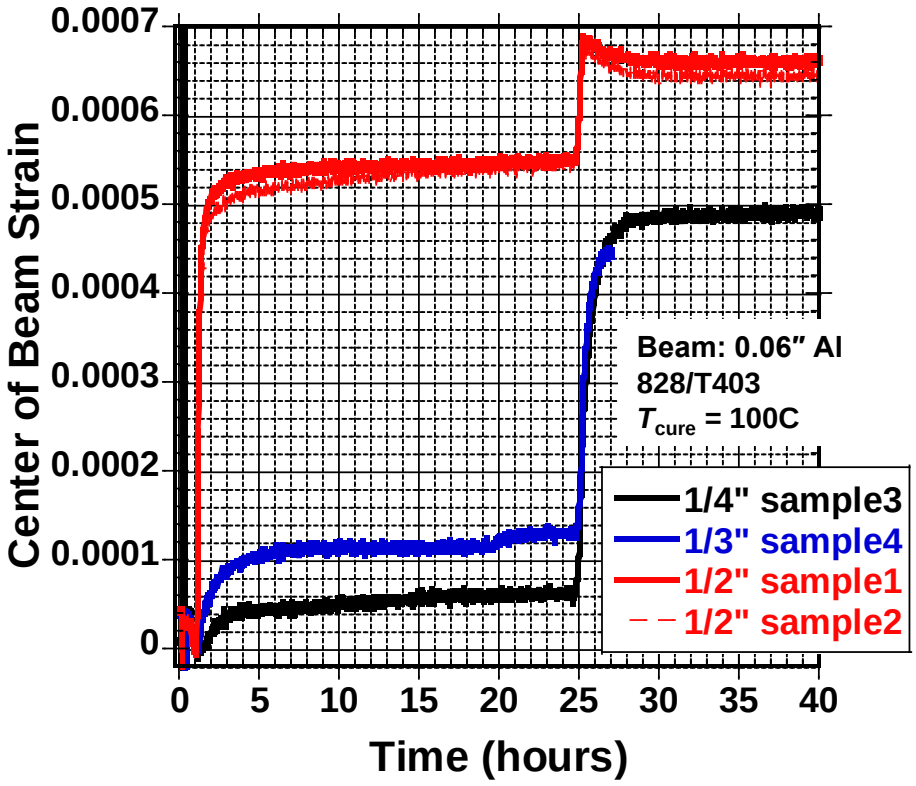
Findings:

- ¼" epoxy thickness significantly reduced exothermic heating
- ¼" epoxy thickness significantly reduced beam strain, which is a function both of epoxy thickness and cure temperature
- Within resolution of current measurements, when exothermic heating is minimized beam strain associated with cure is indistinguishable between T=80C and T=100C cure experiments

A lack of change in even the time of gelation signature between T=80C and T=100C cure for h_e=¼" casts doubt on the ability of the current test to resolve the effects of test variables at this h_e due to small beam strain signals (low signal-to-noise)

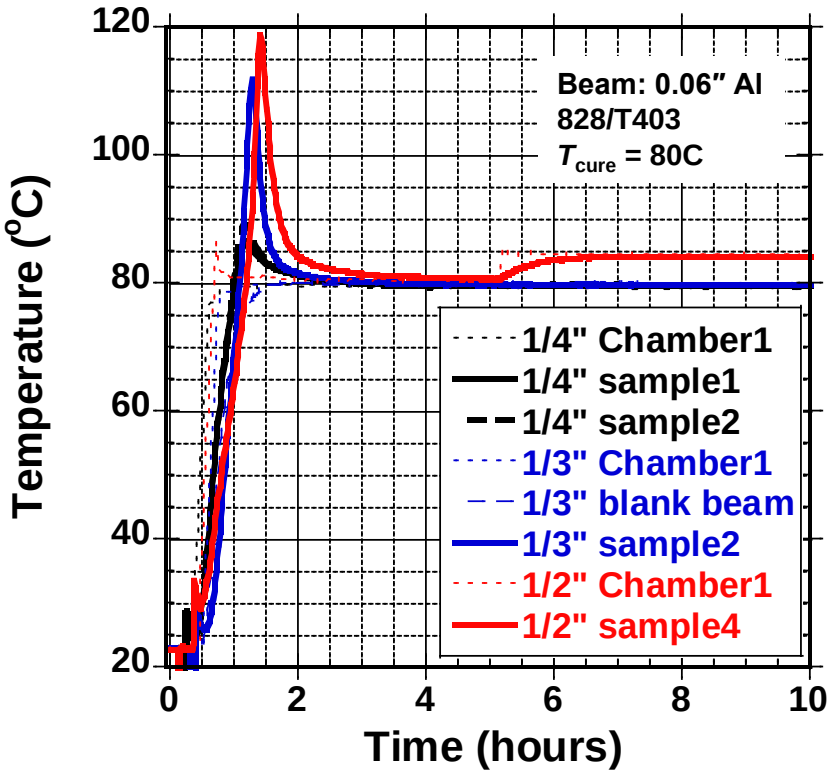
828/T403: Polymer Thickness Dependence

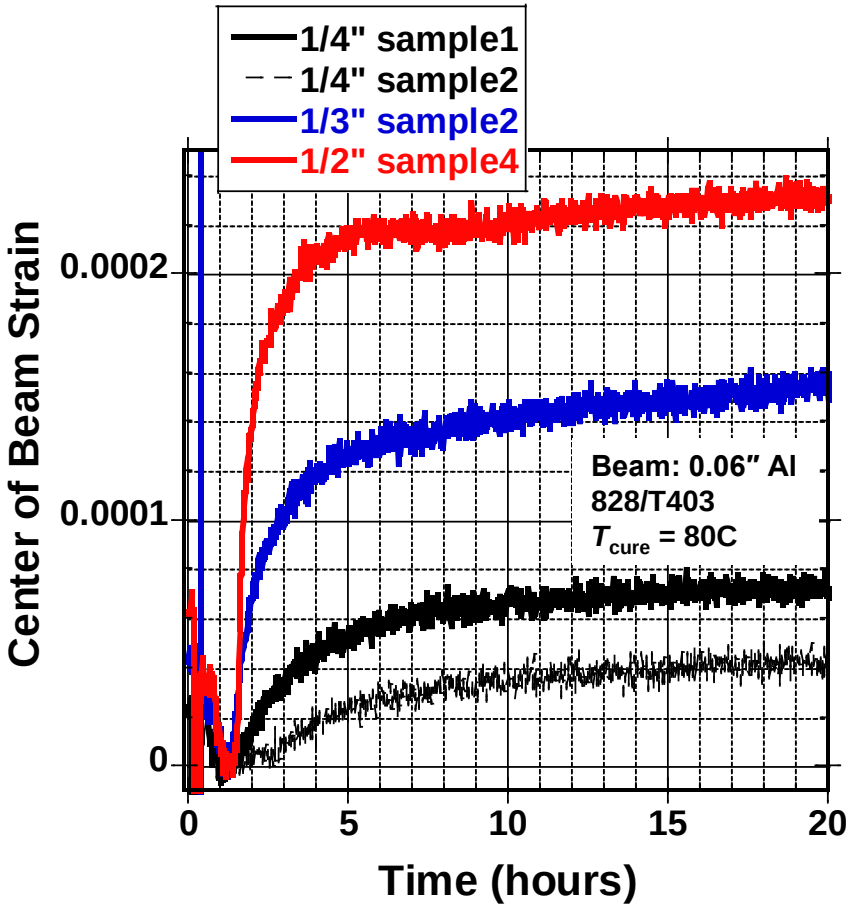




It would be interesting to see what fidelity the model needs in order to predict the thickness dependence of the cooldown response

828/T403: Polymer Thickness Dependence of T=80C Cure

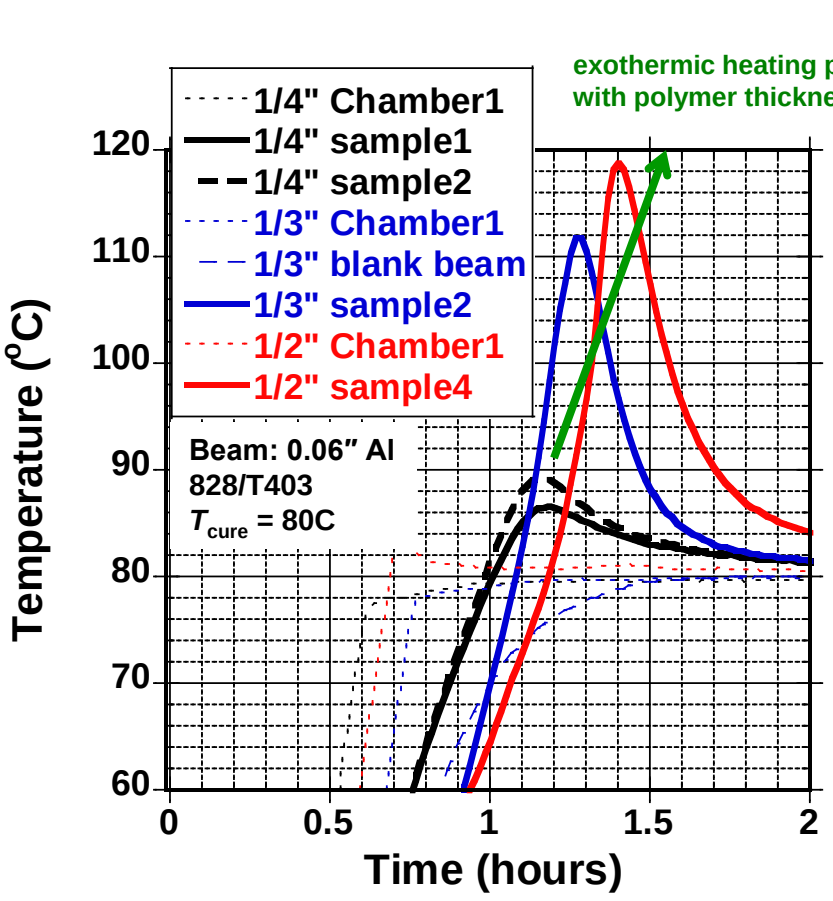


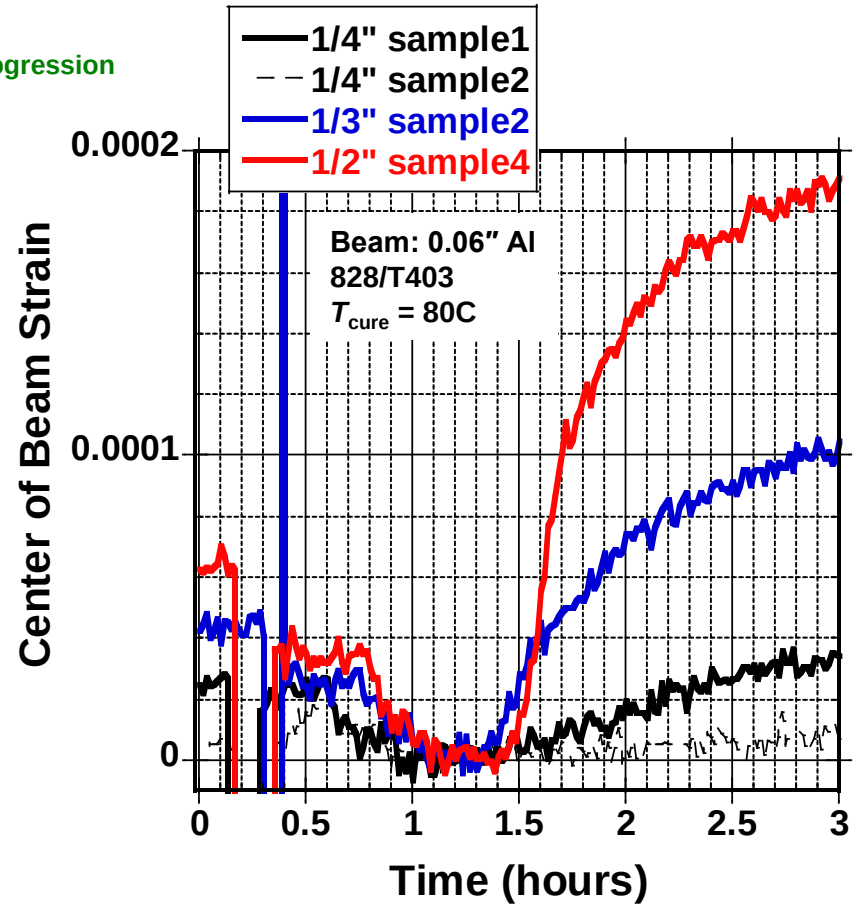


Findings:

- 1/3" exothermic heating much more similar to ½" than ¼"
- Despite similar exotherms, ½" beams experience more strain during cure than 1/3" beams. Thus, a polymer thickness dependence is likely resolved.

828/T403: Polymer Thickness Dependence of T=80C Cure

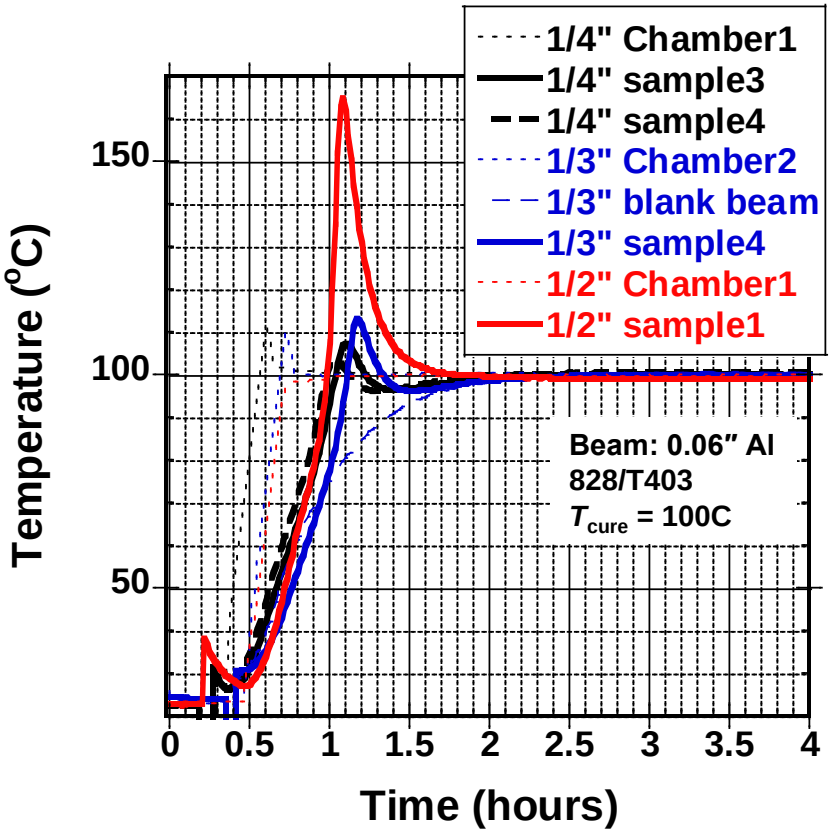


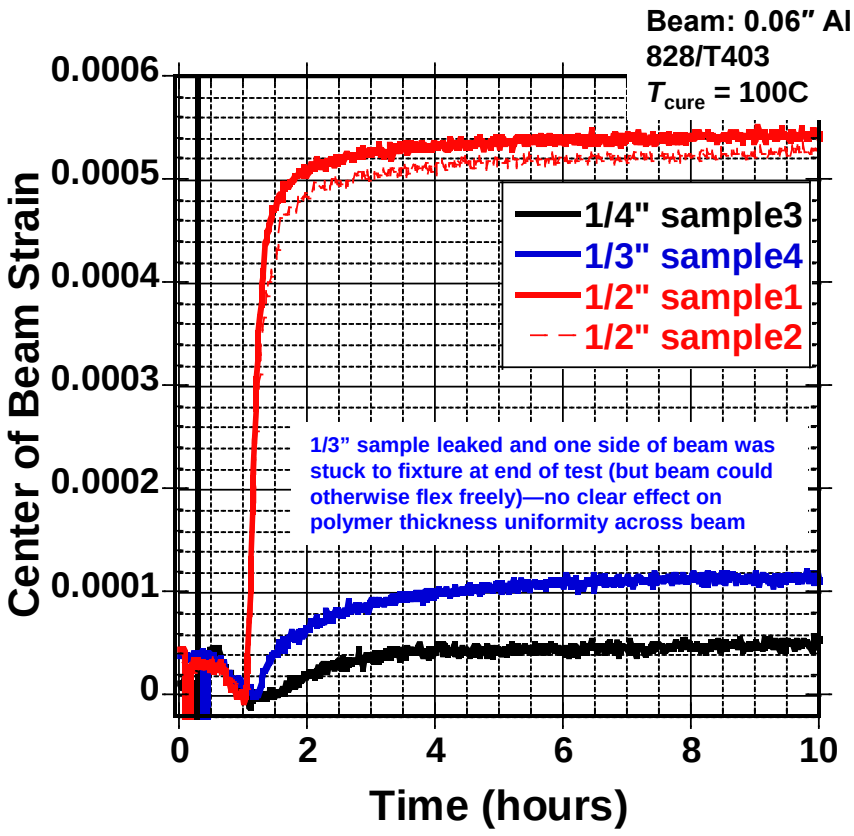


Findings:

- Independent of exothermic heating amount, initiation of beam deflection occurs at maximum sample temperature. This suggests the maximum reaction rate occurs at gelation for 828/T403 (see similar observations for 828/DEA in McCoy et al.)

828/T403: Polymer Thickness Dependence of T=100C Cure

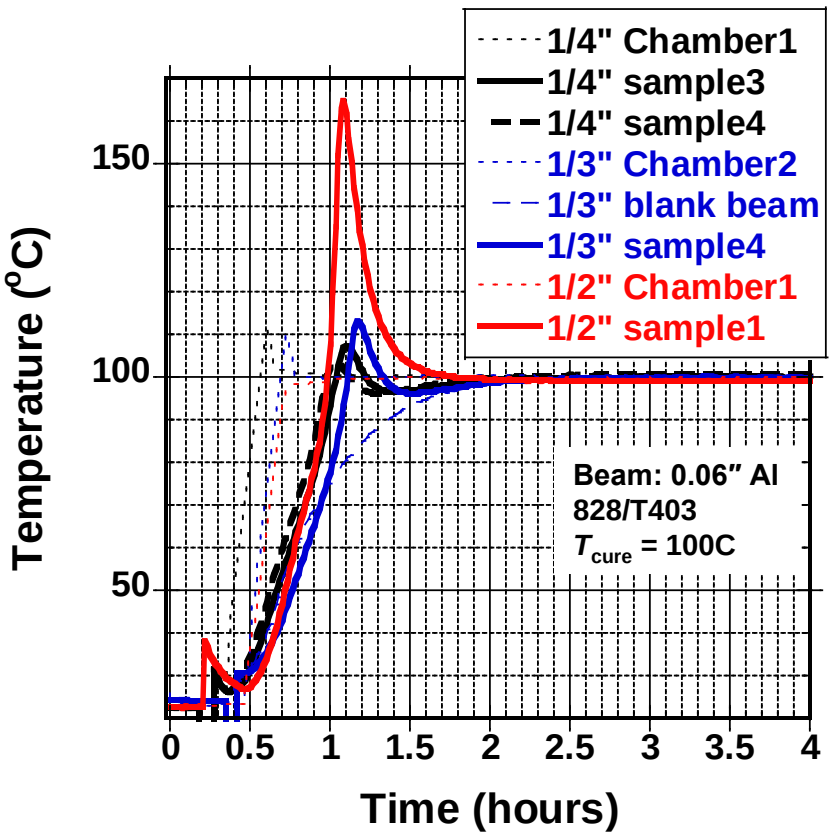


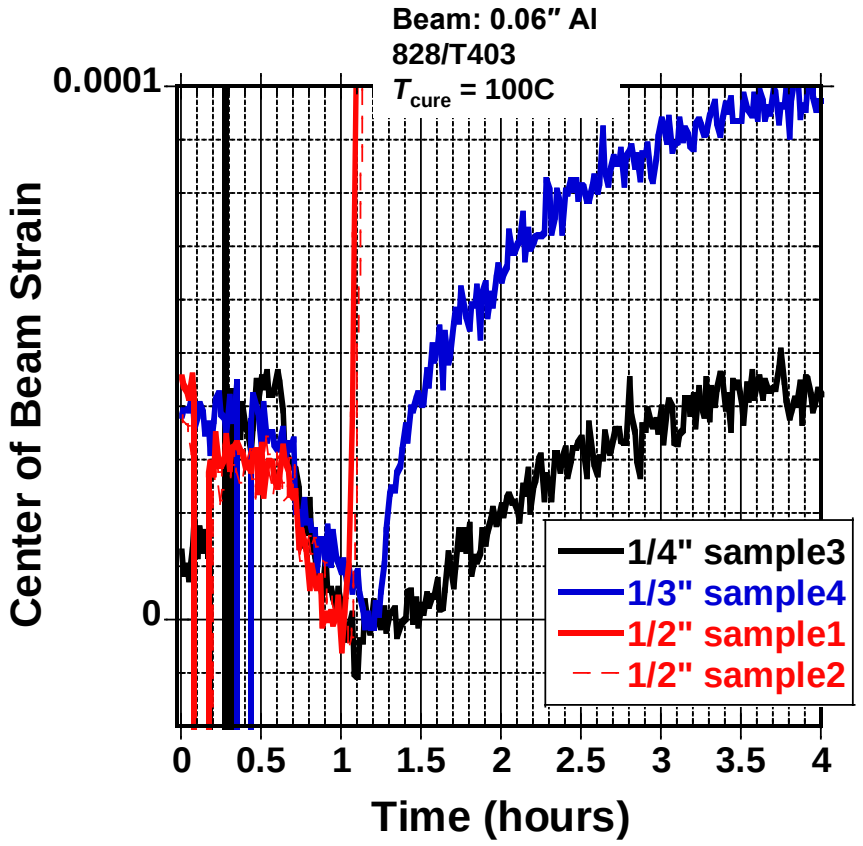


Findings:

- Unlike T=80C cure, 1/3" exothermic heating much more similar to ¼" than ½"
- Despite similar exotherms, 1/3" beams experience more strain during cure than ¼" beams. Thus, a polymer thickness dependence is likely resolved.

828/T403: Polymer Thickness Dependence of T=100C Cure





Findings:

- Independent of exothermic heating amount, initiation of beam deflection occurs at maximum sample temperature. This suggests the maximum reaction rate occurs at gelation for 828/T403 (see similar observations for 828/DEA in McCoy et al.)