SAND2015-2149C

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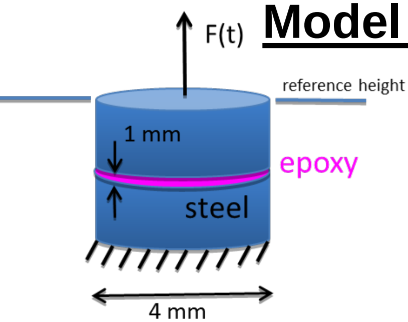
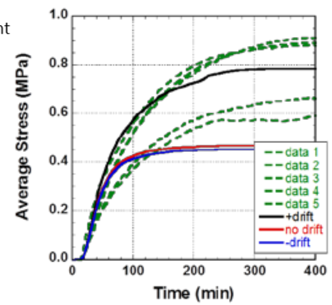
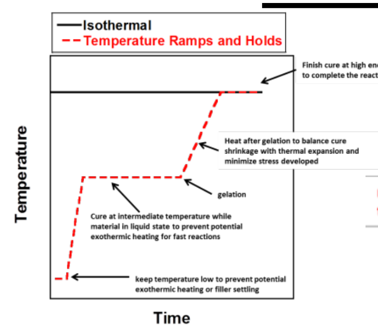
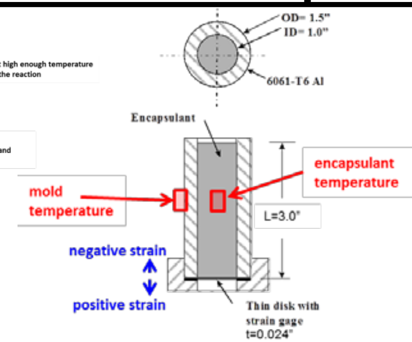
Model Validation

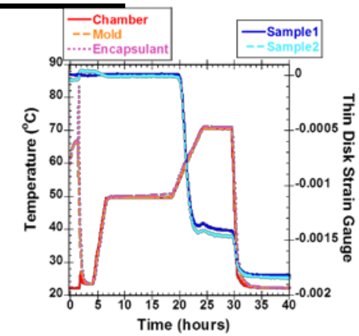




Cure Schedule Optimization







Residual Stress Developed During the Cure of Thermosetting Polymers

Jamie M. Kropka, Scott W. Spangler, Mark E. Stavig and Robert S. Chambers

Sandia National Laboratories, Albuquerque, NM

2015 Adhesives and Sealants Council Spring Conference

Nashville, Tennessee

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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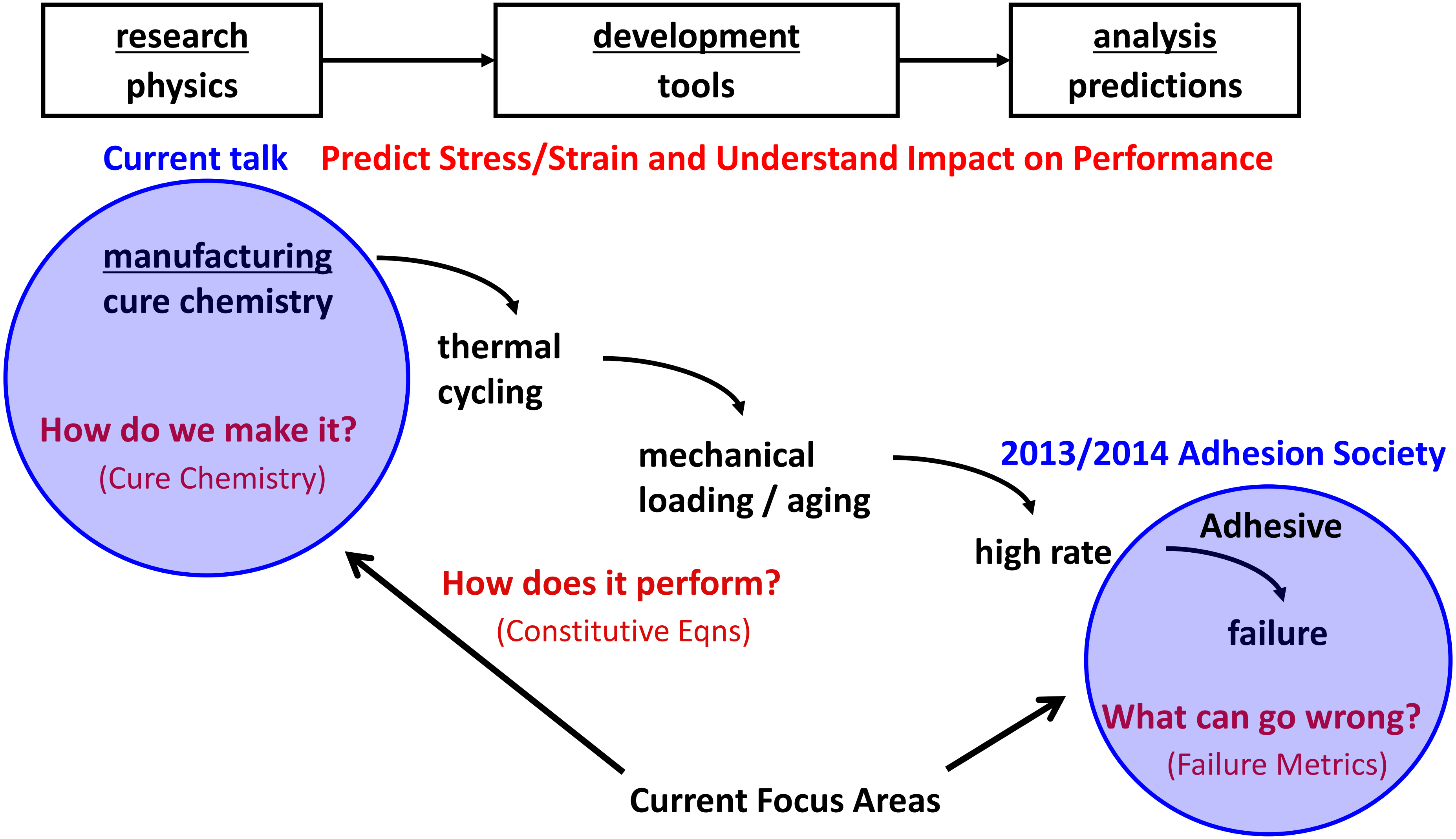
Our Vision: Validated Model-Based Lifecycle Engineering for Packaging Design

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



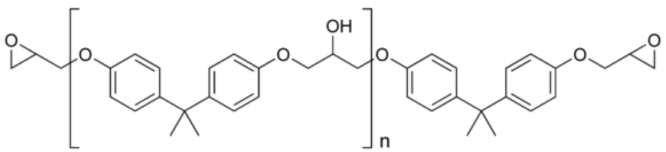
Polymer Thermoset Cure Stress Topics

1. Adhesive materials
2. Constitutive formalism for predicting cure stress: Simplified Potential Energy Clock (SPEC) Cure Model
3. Experimental characterization during cure and parameterizing the SPEC Cure Model
4. Validating SPEC stress predictions for a curing thermoset
5. Designing an optimum cure schedule

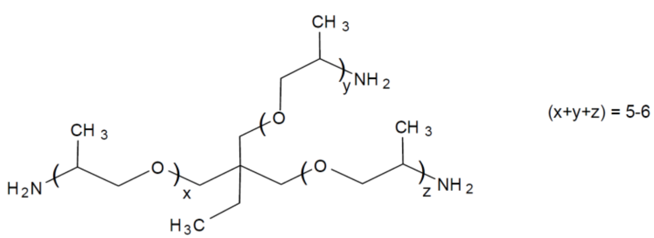
Adhesive Materials

828/T403[1]

EPON® Resin 828
Diglycidylether of Bisphenol-A



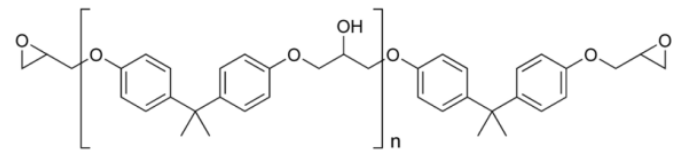
Jeffamine® T-403 Polyetheramine



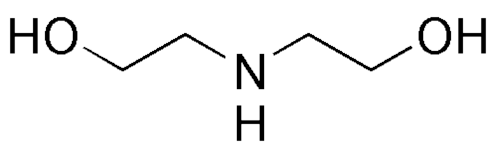
T_g ~ 80C

828/GMB/DEA[2]

EPON® Resin 828
Diglycidylether of Bisphenol-A



Diethanolamine



3M D32 glass microballoons

T_g ~ 70C

[1]Mix ratio (100:43 pbw 828:T403), cure, 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_GMB.html

Predicting Cure Stress: Parameterizing the Simplified Potential Energy Clock (SPEC) Cure Model

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

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

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

$$N = \left\{ \left[T(t) - T_{ref} \right] - \int_0^t ds\, f_v(t^* - s^*) \frac{dT}{ds}(s) \right\} + C_3 \left\{ I_1(t)_{ref} - \int_0^t ds\, f_v(t^* - s^*) \frac{dI_1}{ds}(s) \right\}$$

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

J.M. Caruthers, et al., *Polymer*, 2004, 45, 4577

D.B. Adolf, et al., *Polymer*, 2004, 45, 4599

D.B. Adolf, et al., *J. Rheol.*, 2007, 51, 517

D.B. Adolf, et al., *Polymer*, 2009, 50, 4257

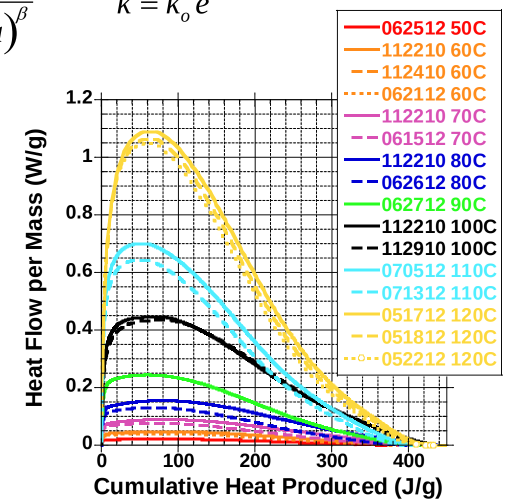
J.M. Kropka, et al., SAND2013-8681

Predicting Cure Stress: Parameterizing the SPEC Cure Model

Reaction Kinetics

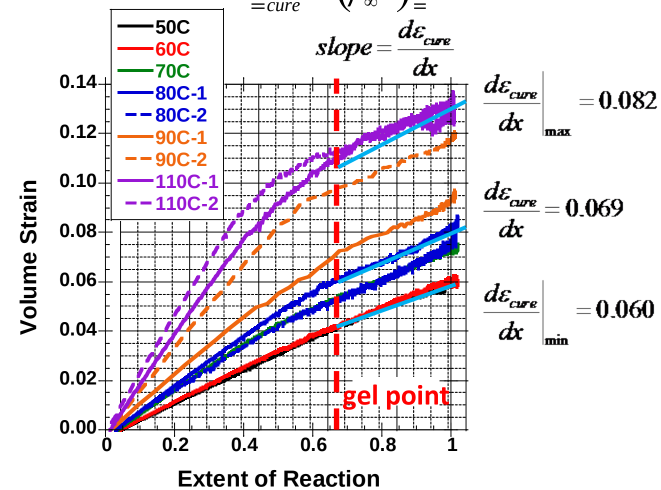
$$\frac{dx}{dt} = \hat{k}\left(b + x^m\right)\left(1 - x\right)^n \qquad \hat{k} \equiv \frac{k}{\left(1 + w\,a\right)^{\beta}} \qquad k = k_o e^{-\frac{E_a}{RT}}$$

828/T403 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
w	5x10^{-3}
β	1.3



Volumetric Cure Shrinkage

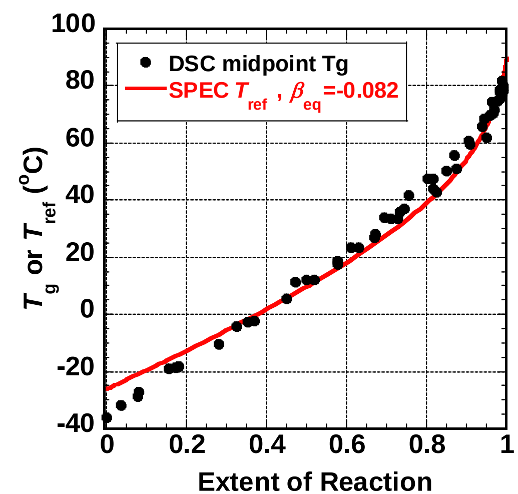
$$\underline{\underline{\varepsilon}}_{cure} = \left(\beta_\infty x\right)\underline{\underline{I}}$$



Evolution of Glass Transition Temperature During Cure

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

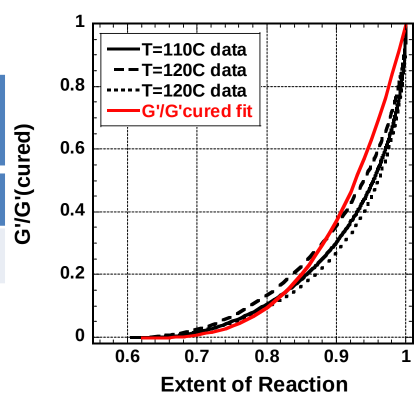
828/T403 T_{ref} Parameterization	
Parameter	**Value**
C_3	900 C
α_∞	500 ppm/C
C_{5a}	10 C
C_{5b}	0.97
C_{5c}	-105 C
C_{5d}	1.0088
C_{5e}	0.73



Evolution of Equilibrium Shear Modulus During Cure

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

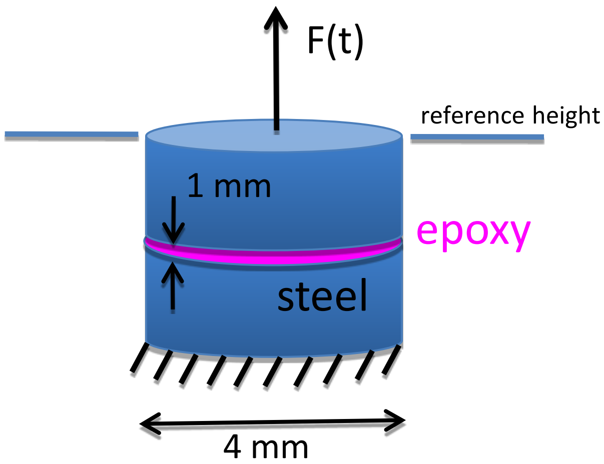
828/T403 $G_\infty(x)$ Parameterization	
Parameter	**Value**
x_{gel}	0.62



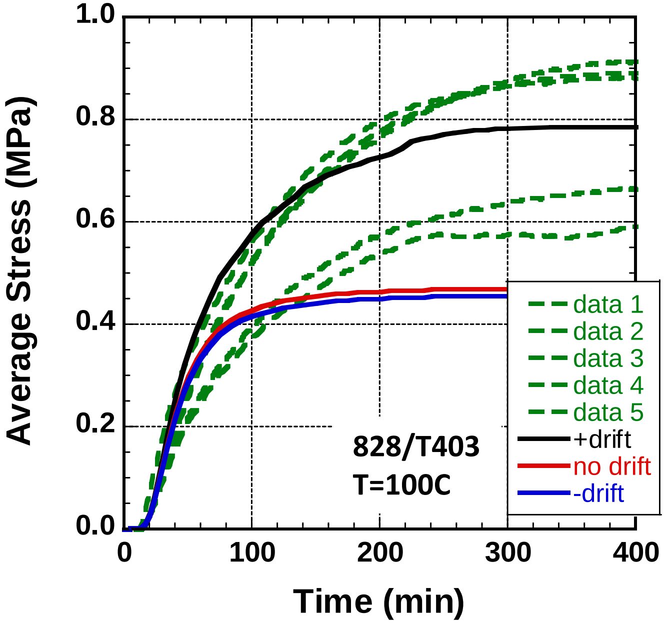
J.M. Kropka, et al., SAND2013-8681

Predicting Cure Stress: Validation Tests

The Simple Test



Rubbery Cure Results



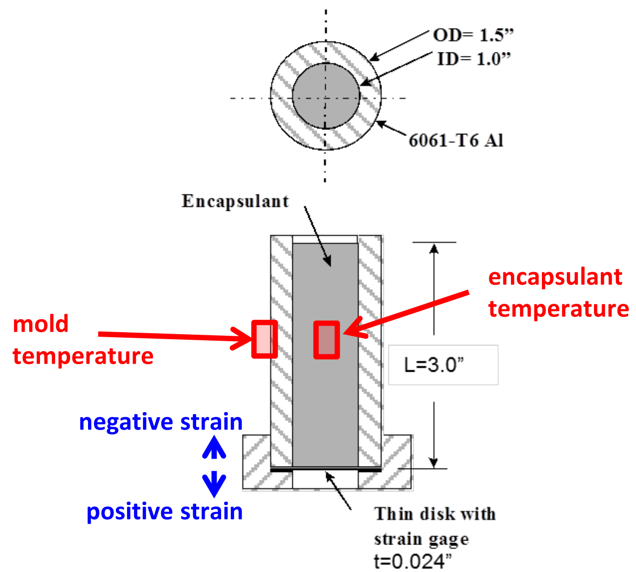
Good agreement between predictions and data, with known variations in boundary conditions during the test accounting for the spread in the data

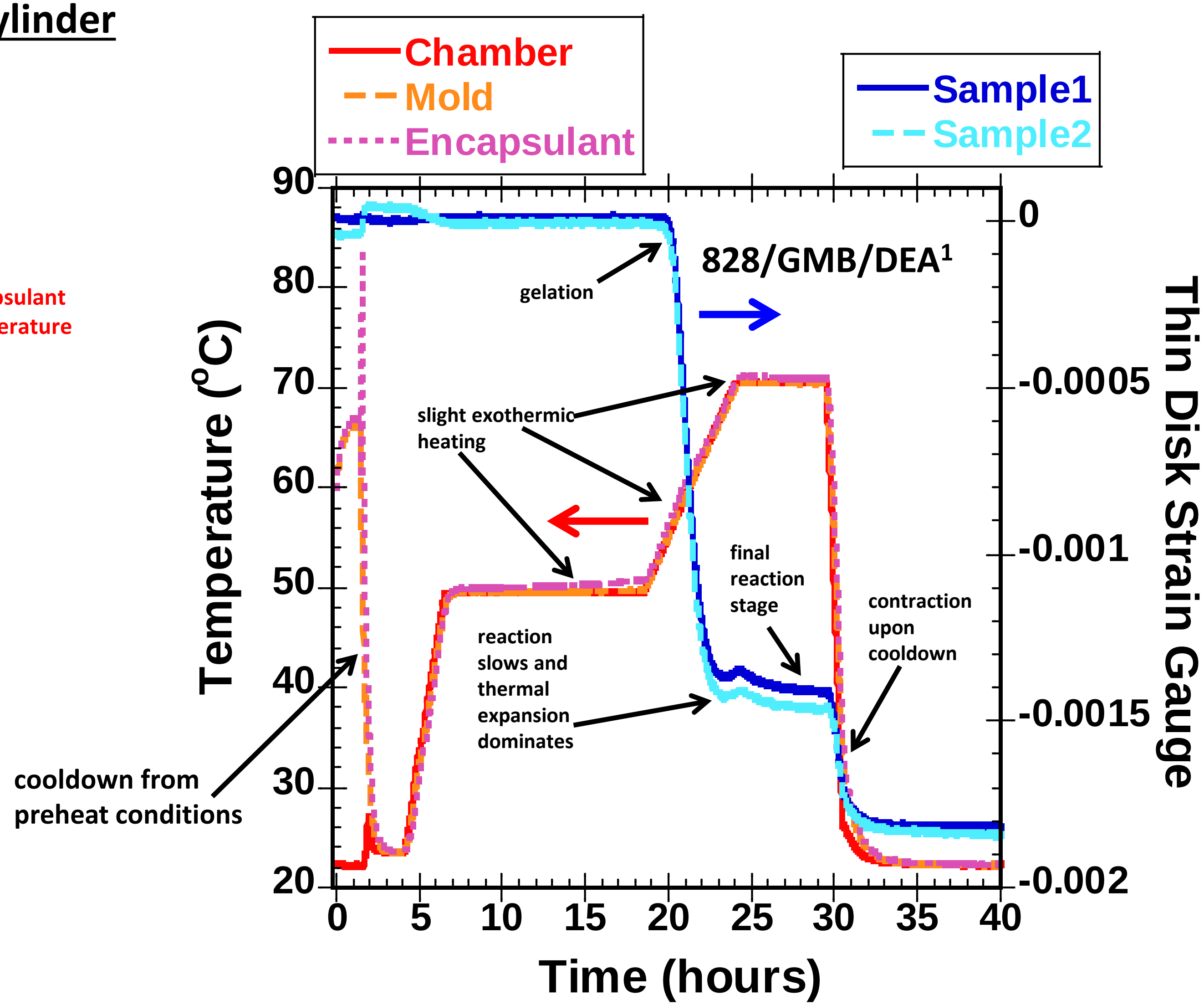
This capability will enable the design of cure schedules to minimize stress

J.M. Kropka, et al., SAND2013-8681

Predicting Cure Stress: Validation Tests

Geometry: Thin Disk on Cylinder



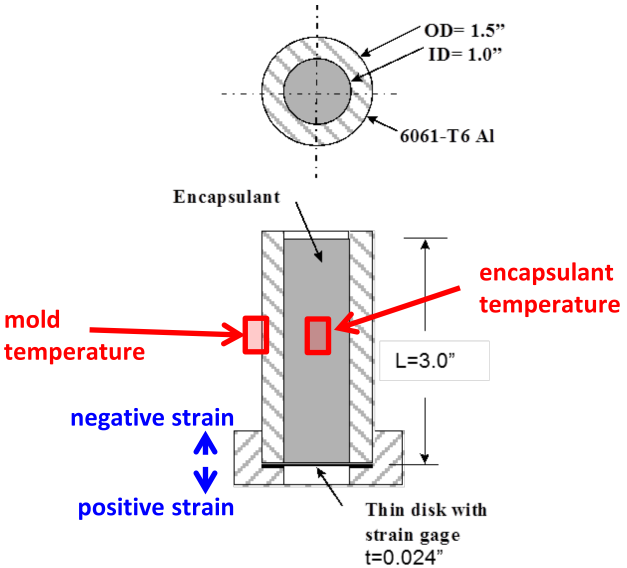


Thin disk deflection gives structural response during cure

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

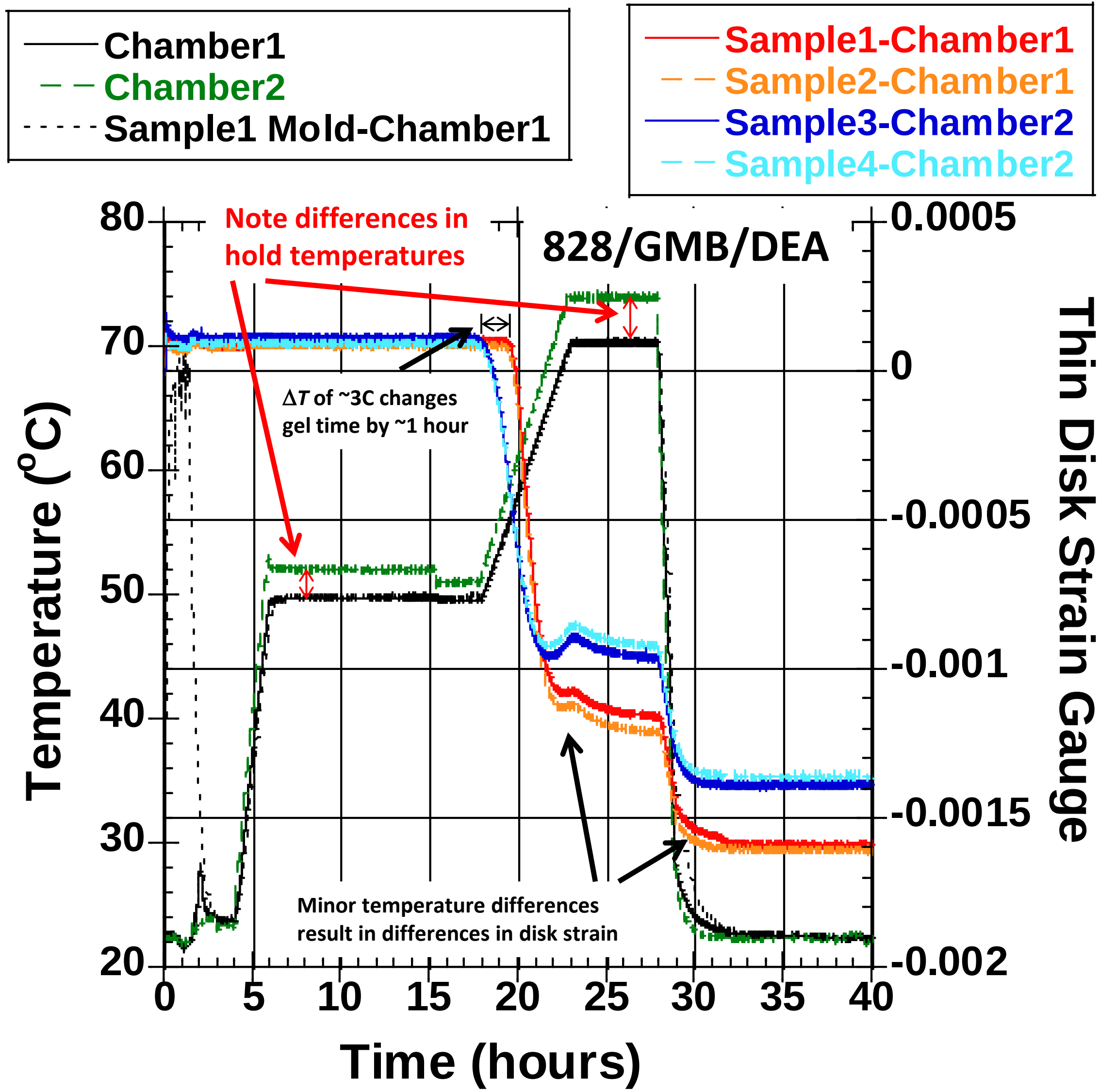
Simplified Geometry Test: Indication of Temperature Profile Sensitivity

Geometry: Thin Disk on Cylinder



Cure Cycle:

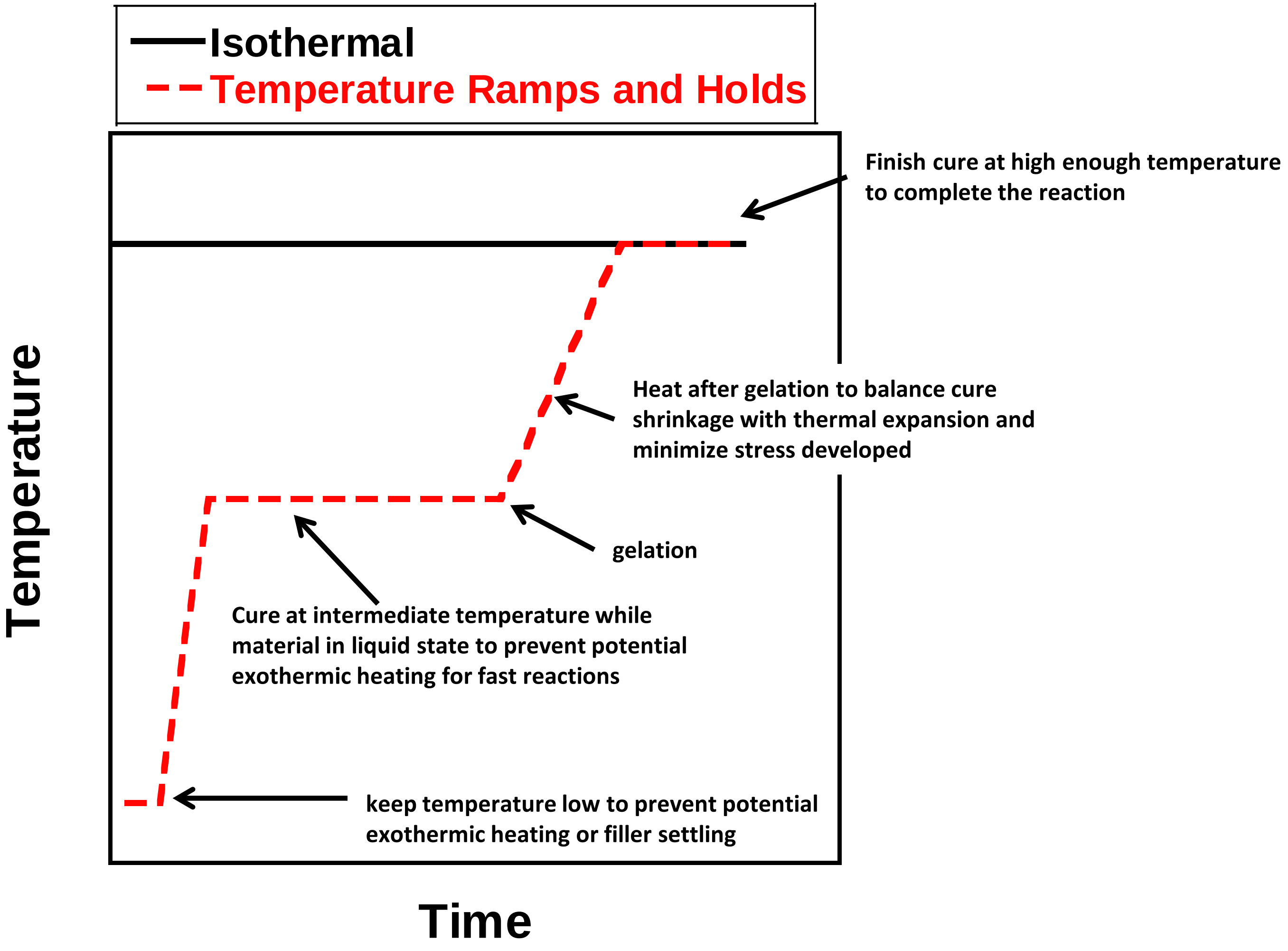
1. 2 hours at T=25C
2. 2 hour ramp to T=50C
3. 12 hours at T=50C
4. 5 hour ramp to T=71C
5. 5 hours at T=71C



Some Important Findings:

- Small changes in temperature (potentially within batch-to-batch variability) affect strain developed during cure and resulting strain after cooldown to room temperature—**there are sensitivities!**
- “Thin Disk on Cylinder” test enables resolution of these sensitivities and provides a rich dataset to test model predictions

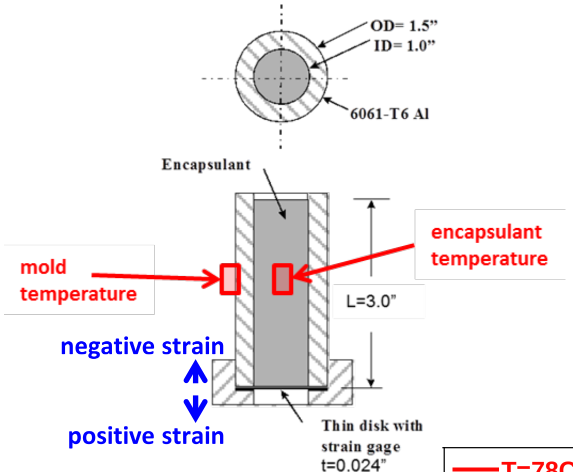
Designing an Optimum Cure Schedule



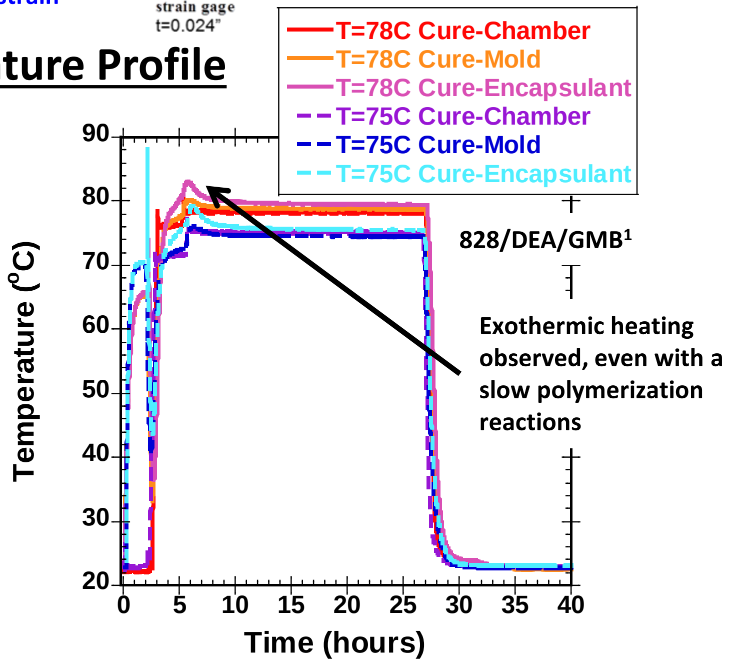
Isothermal reaction at a high temperature may be the fastest method to achieve complete cure, but other factors may drive the time-temperature profile in a different direction

Isothermal Cure

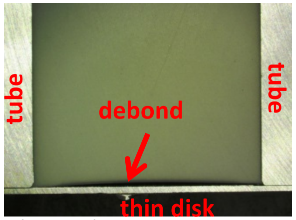
Geometry: Thin Disk on Cylinder

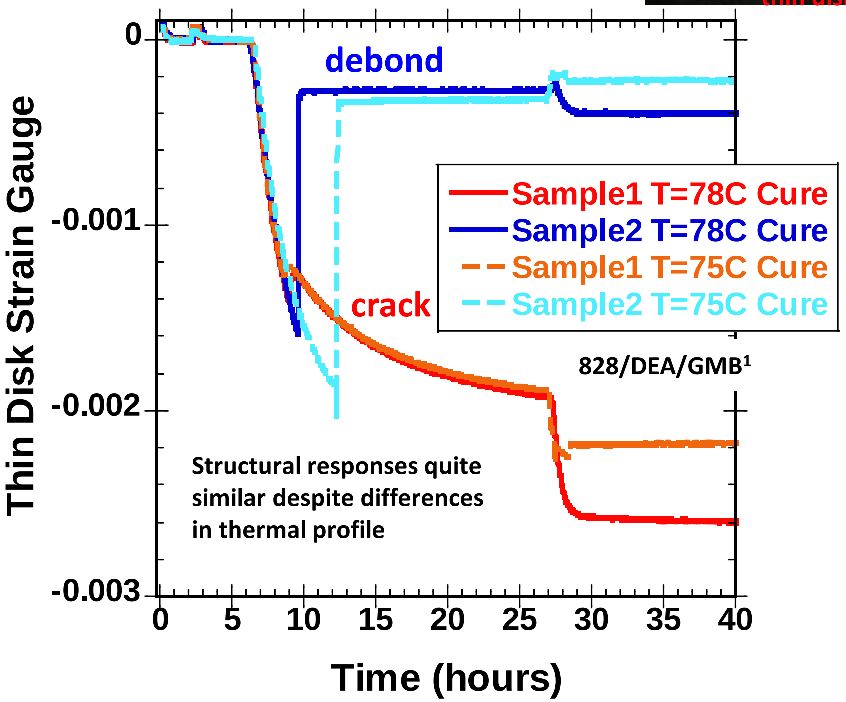


Temperature Profile

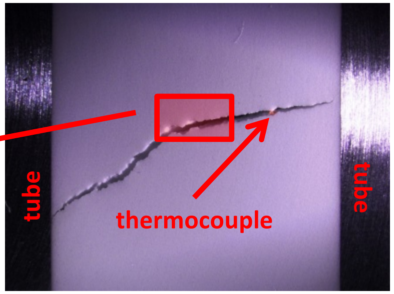


Structural Response





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

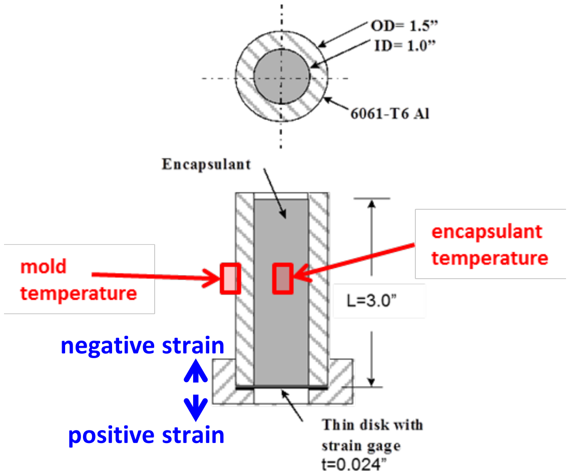


Failure can occur during cure…can it be avoided by minimizing stress?

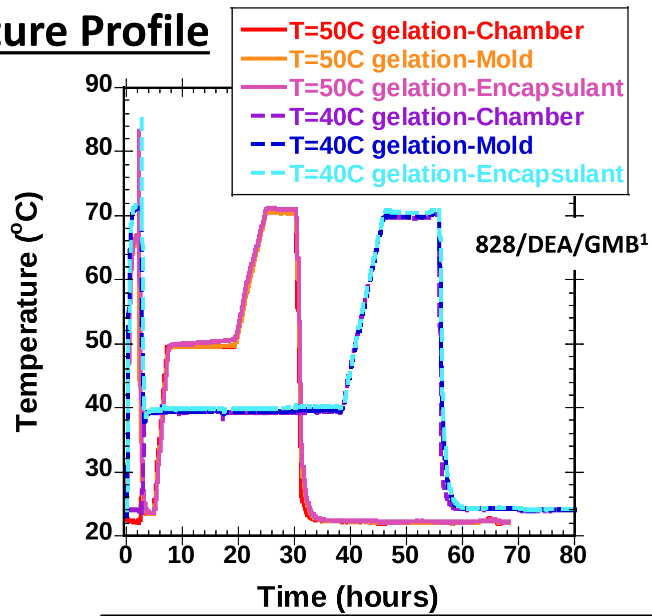
[1]http://www.sandia.gov/polymer-properties/828_DEA_GMB.html

Cure with Temperature Ramps and Holds

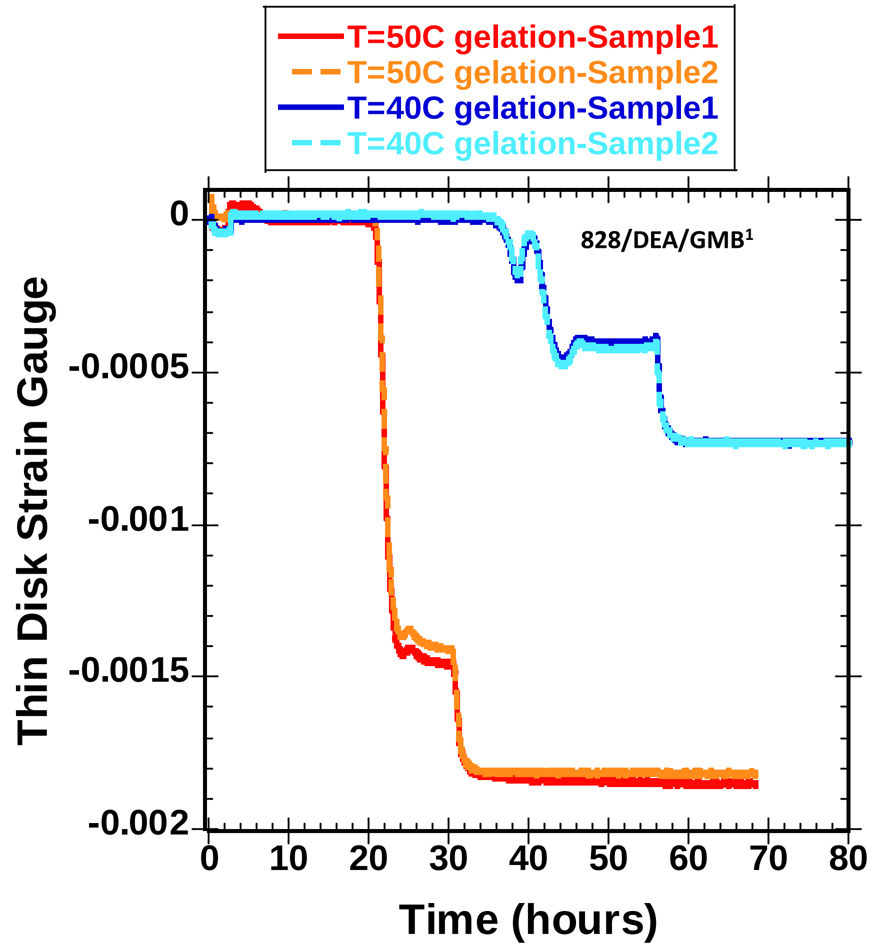
Geometry: Thin Disk on Cylinder



Temperature Profile



Structural Response

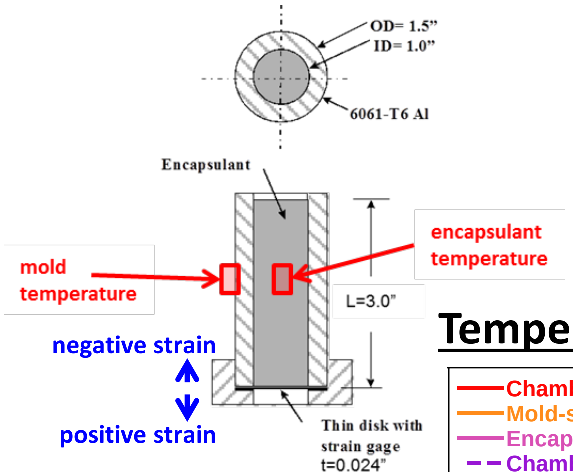


[1]http://www.sandia.gov/polymer-properties/828_DEA_GMB.html

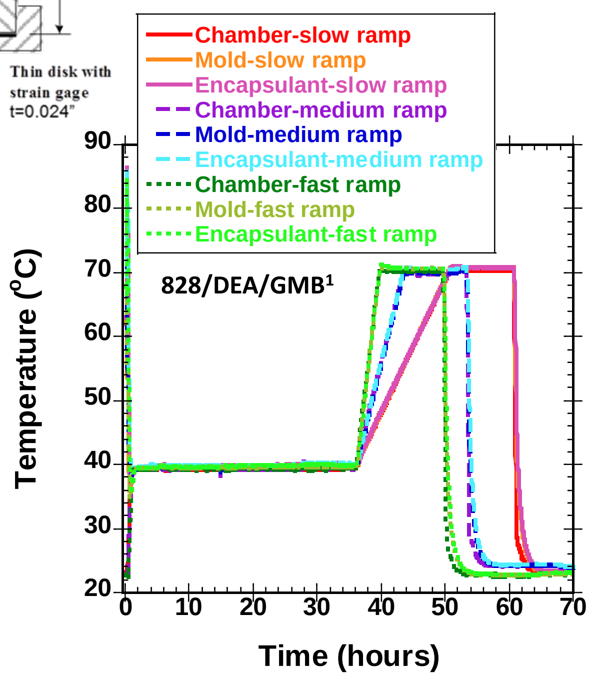
No cracking/debonding observed and less disk deflection for larger post-gelation thermal ramp (thermal expansion offsetting cure shrinkage)

Role of Temperature Ramp Rate

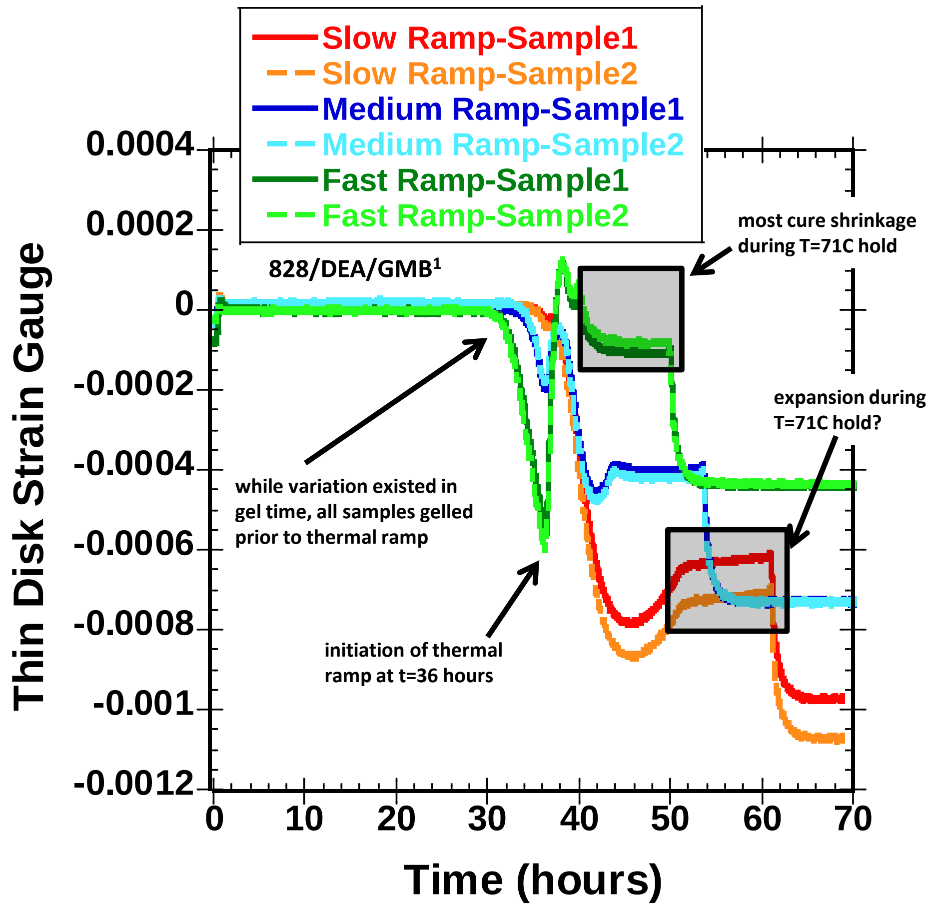
Geometry: Thin Disk on Cylinder



Temperature Profile



Structural Response



Faster temperature ramps result in less lid deflection at end of cure and cooldown

Is this due to a larger CTE for the partially-cured material? A history dependence due to the evolving reference state?

Summary

- Constitutive formalism to predict stress evolution during polymer thermoset cure developed and validated for "rubbery" cure
- Simplified geometry structural tests ("Thin Disk on Cylinder"), in addition to serving as a model validation tool, prove useful to examine cure stress dependence on cure schedule parameters even when a validated cure model may not be available

Looking Forward

- Parameterizing/modifying the constitutive formalism for "more complicated" materials like the 828/DEA/GMB shown in experiments here is under way
- Further validation of the constitutive formalism to predict stress evolution when vitrification occurs during cure is needed