



SAND2014-19769C

Residual Stress Developed During Cure of Thermosetting Polymers

TCG-XIV – Munitions Reliability and Lifecycle Technology

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All-TCG Technology Review: Rodeo 2014

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

Polymer Nonlinear Viscoelastic (NLVE) Model

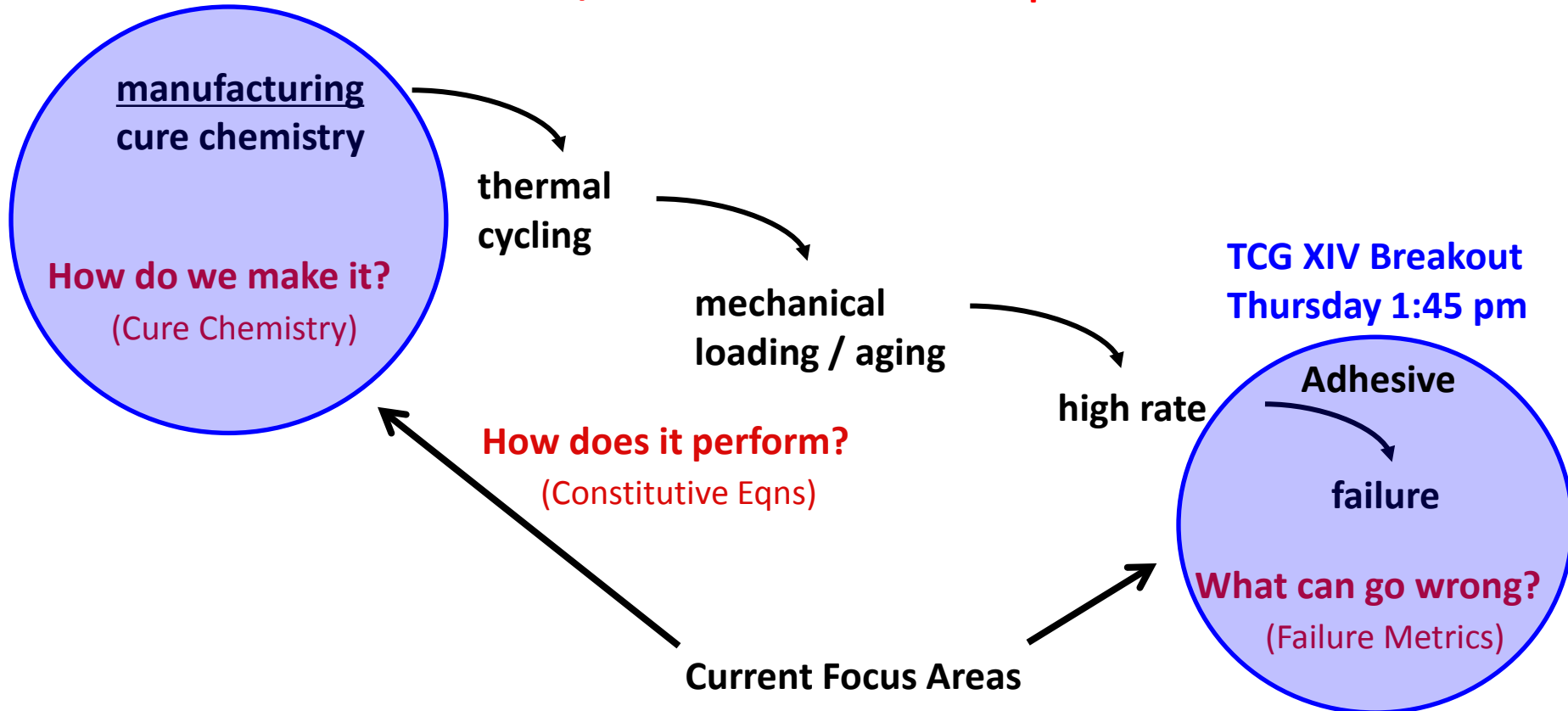
J.M. Caruthers, et al., *Polymer*, 2004, 45, 4577

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

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



Current talk Predict Stress/Strain and Understand Impact on Performance



Polymer Thermoset Cure Stress Topics

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

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

$$\underline{\sigma} = \left[\Delta K \int_0^t ds f_v(t^* - s^*) \frac{dI_\varepsilon}{ds}(s) - \Delta(K\alpha) \int_0^t ds f_v(t^* - s^*) \frac{dT}{ds}(s) - \Delta(K\beta) \int_0^t ds f_v(t^* - s^*) \frac{dx}{ds}(s) \right] \underline{I} \\ + 2\Delta G \int_0^t ds f_s(t^* - s^*) \frac{d\varepsilon_{dev}}{ds}(s) + [K_\infty I_\varepsilon - K_\infty \alpha_\infty \Delta T - K_\infty \beta_\infty \Delta x] \underline{I} + 2 \int_0^t ds G_\infty(s) \frac{d\varepsilon_{dev}}{ds}(s)$$

cure shrinkage terms

changing reference state term

Material time is computed by using a shift factor, a

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

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

$$N = \left\{ [T(t) - T_{ref}] - \int_0^t ds f_1(t^* - s^*) \frac{dT}{ds}(s) \right\} + C_3 \left\{ I_1(t)_{ref} - \int_0^t ds f_1(t^* - s^*) \frac{dI_1}{ds}(s) \right\} \\ + C_4 \left\{ \int_0^t \int_0^t ds du f(t^* - s^*, t^* - u^*) \frac{d\varepsilon_{dev}(s)}{ds} : \frac{d\varepsilon_{dev}(u)}{du} \right\} + C_5(x(t)) \left\{ [x(t) - x_{ref}] - \int_0^t ds f_1(t^* - s^*) \frac{dx}{ds}(s) \right\}$$

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

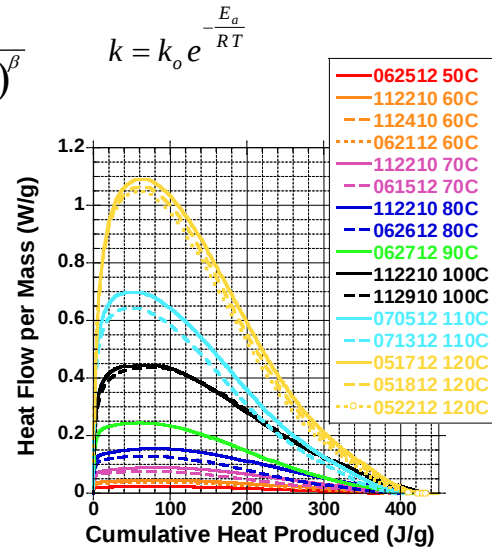
J.M. Kropka, et al., SAND2013-8681

Predicting Cure Stress: Parameterizing the SPEC Cure Model

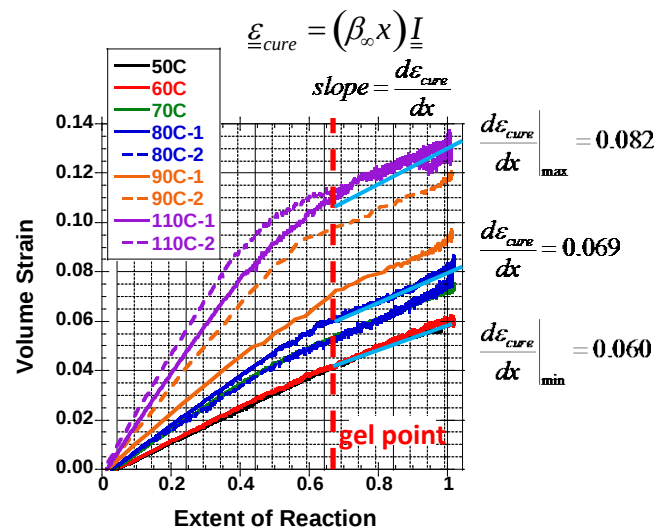
Reaction Kinetics

$$\frac{dx}{dt} = \hat{k}(b + x^m)(1-x)^n \quad \hat{k} \equiv \frac{k}{(1+wa)^\beta}$$

828/T403 Reaction Parameters	
Parameter	Value
E_a	13.8 kcal/mole
k_o	$2.17 \times 10^5 \text{ s}^{-1}$
b	0.17
m	0.33
n	1.37
w	5×10^{-3}
β	1.3



Volumetric Cure Shrinkage

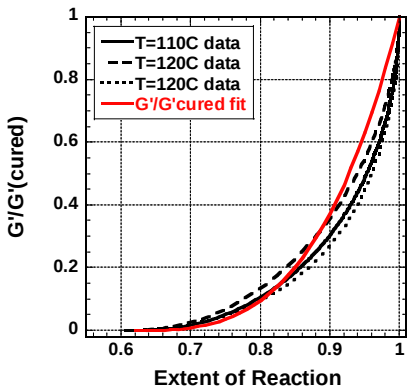


Evolution of Glass Transition Temperature During Cure

Evolution of Equilibrium Shear Modulus During Cure

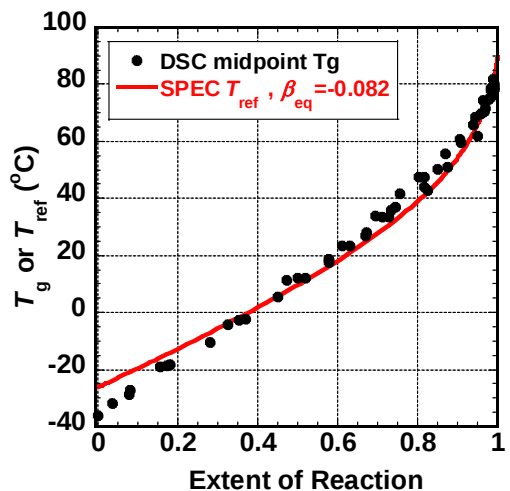
$$\frac{G_{\infty}(x)}{G_{\infty}(1)} = \left[\frac{x^2 - x_{gel}^2}{1 - x_{gel}^2} \right]^{8/3}$$

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



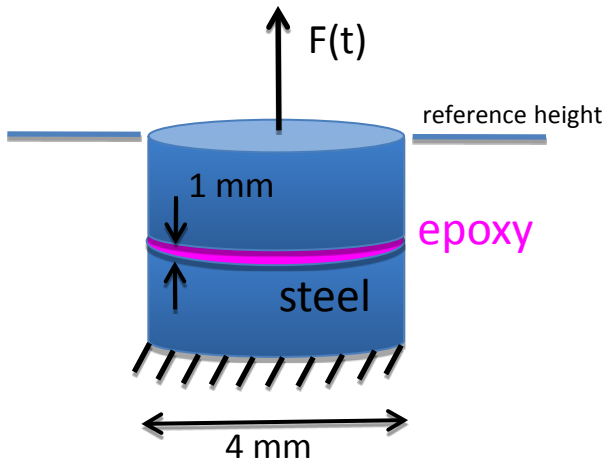
$$T_{ref}(x) = T_{ref} - \frac{[C_3\beta_{\infty} + C_5(x(t))](x(t) - x_{ref})}{(1 - C_3\alpha_{\infty})} \quad C_5(x(t)) = C_{5a} + \frac{C_{5c}}{(C_{5d} - C_{5b}x)^{C_{5e}}}$$

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

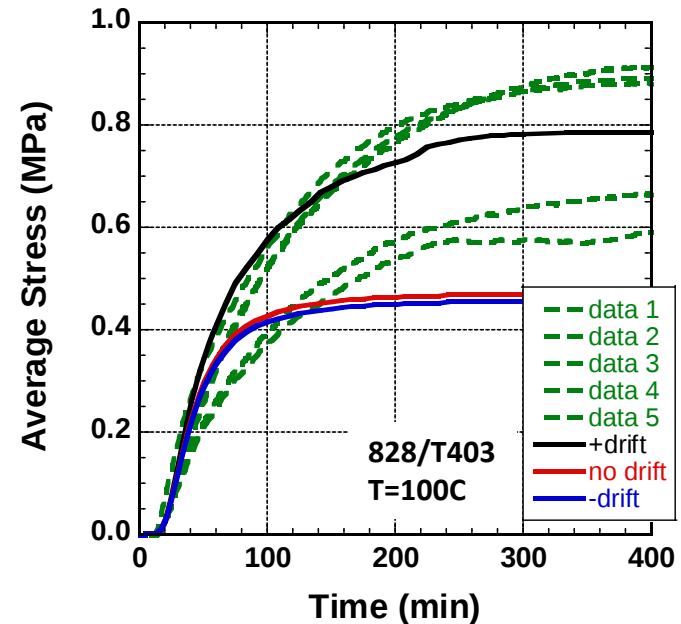


Predicting Cure Stress: Validation Tests

The Simple Test



Rubbery Cure Results

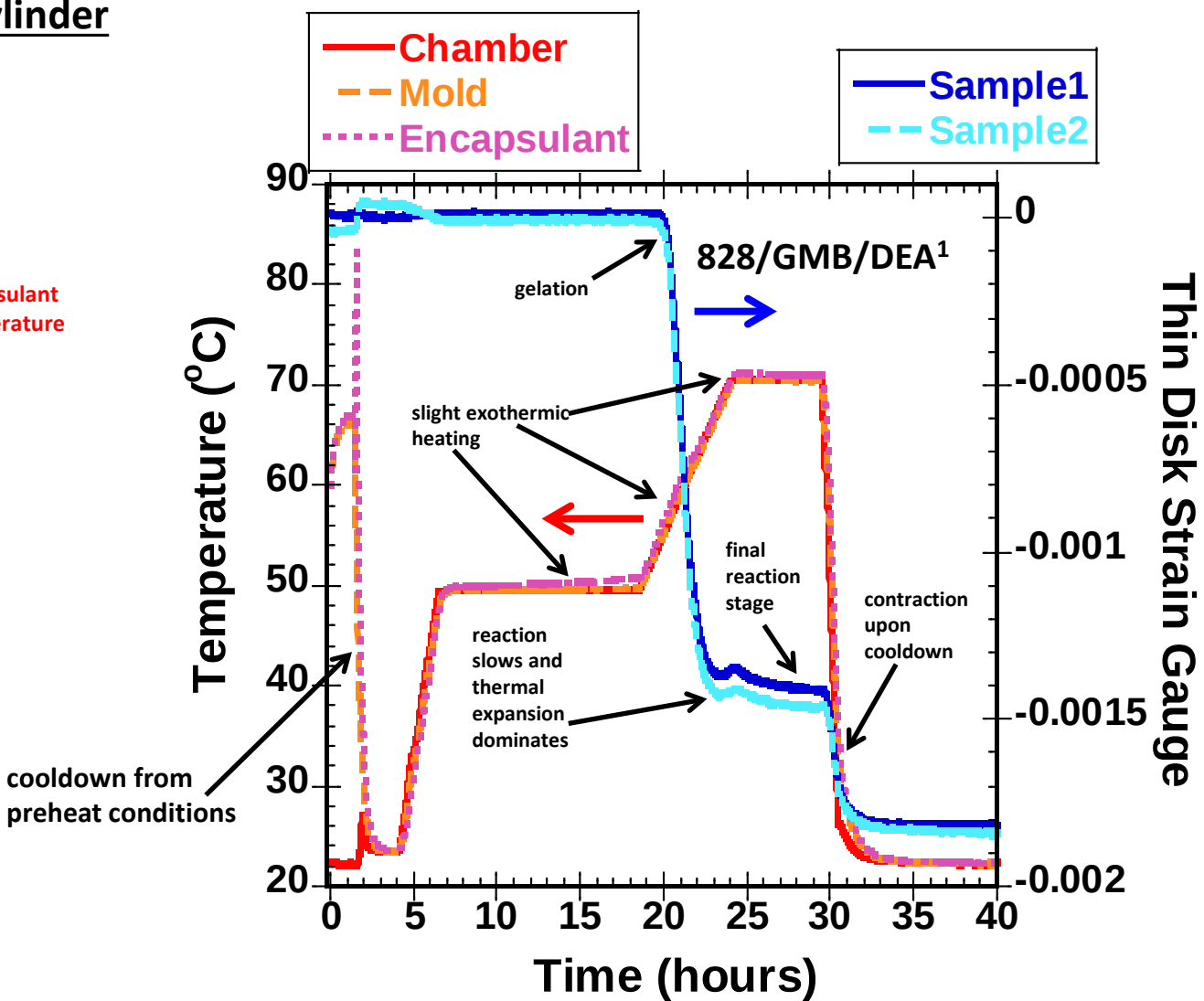
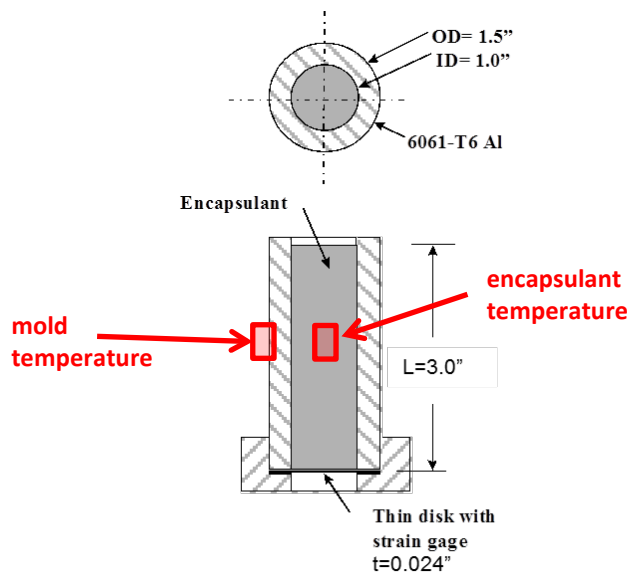


Good agreement between predictions and data, with known variations in boundary conditions during the test accounting for the spread in the data

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

Predicting Cure Stress: Validation Tests

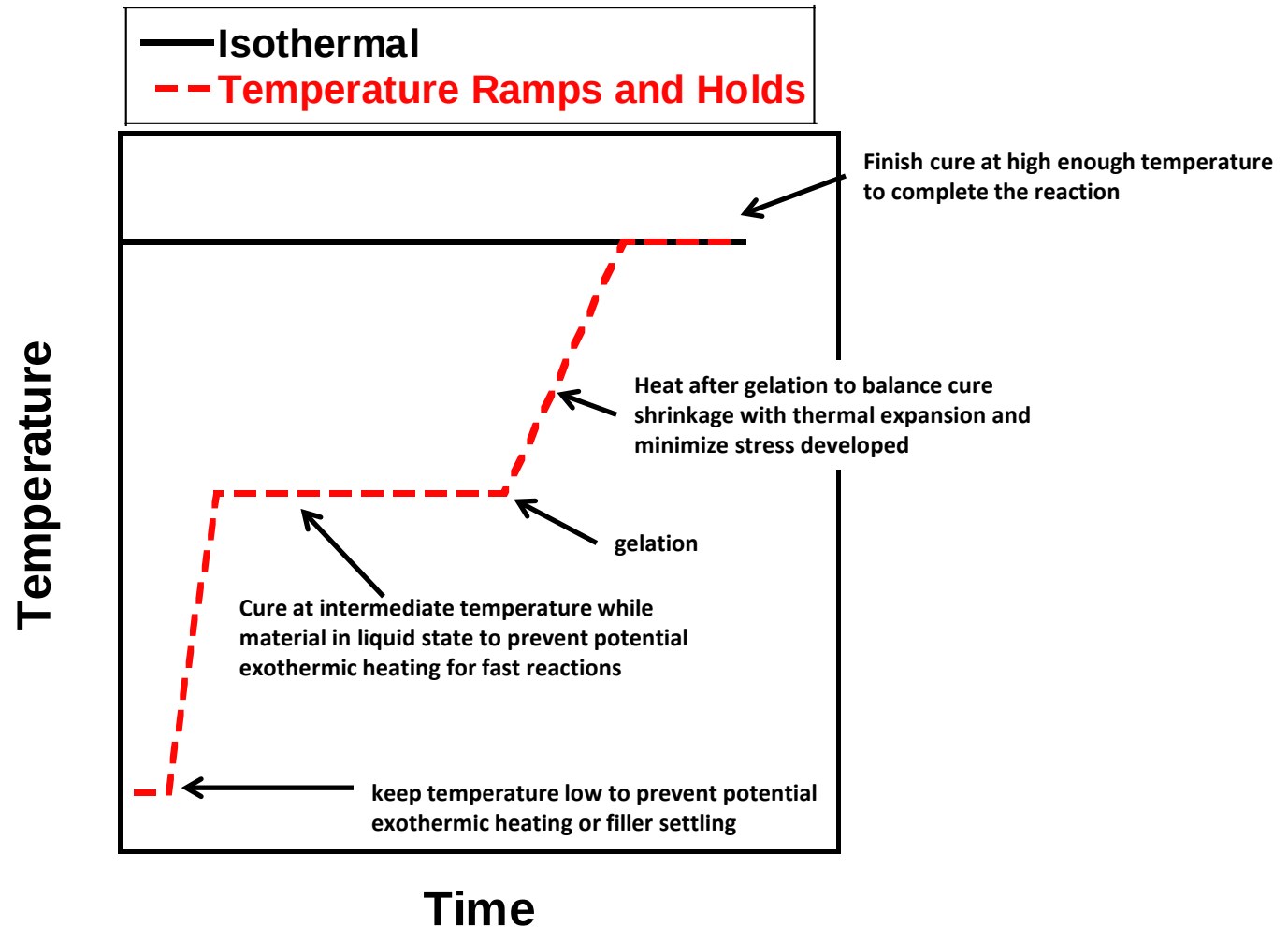
Geometry: Thin Disk on Cylinder



Thin disk deflection gives structural response during cure

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

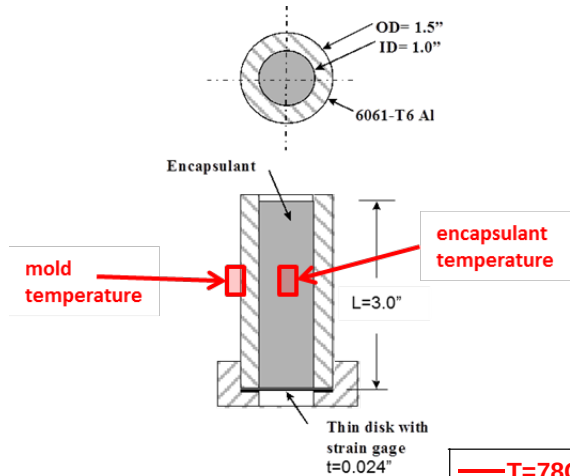
Designing an Optimum Cure Schedule



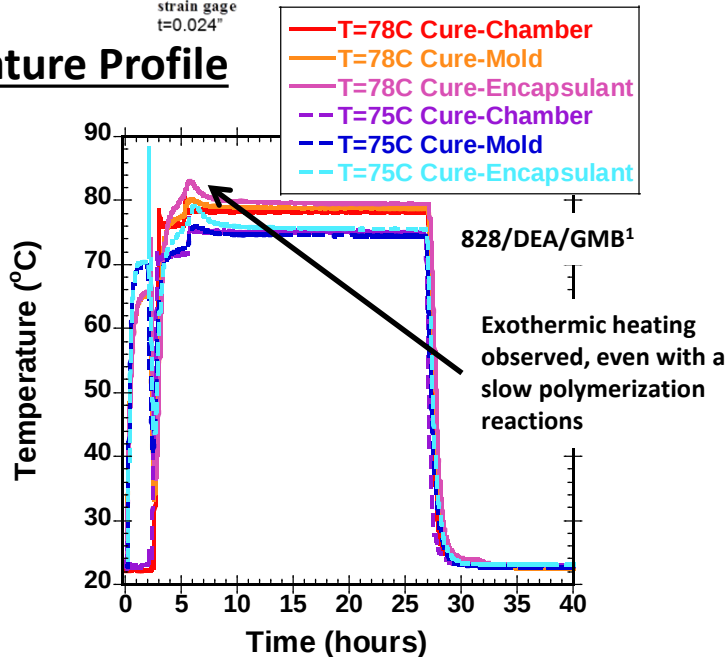
Isothermal reaction at a high temperature may be the fastest method to achieve complete cure, but other factors may drive the time-temperature profile in a different direction

Isothermal Cure

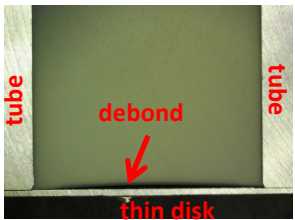
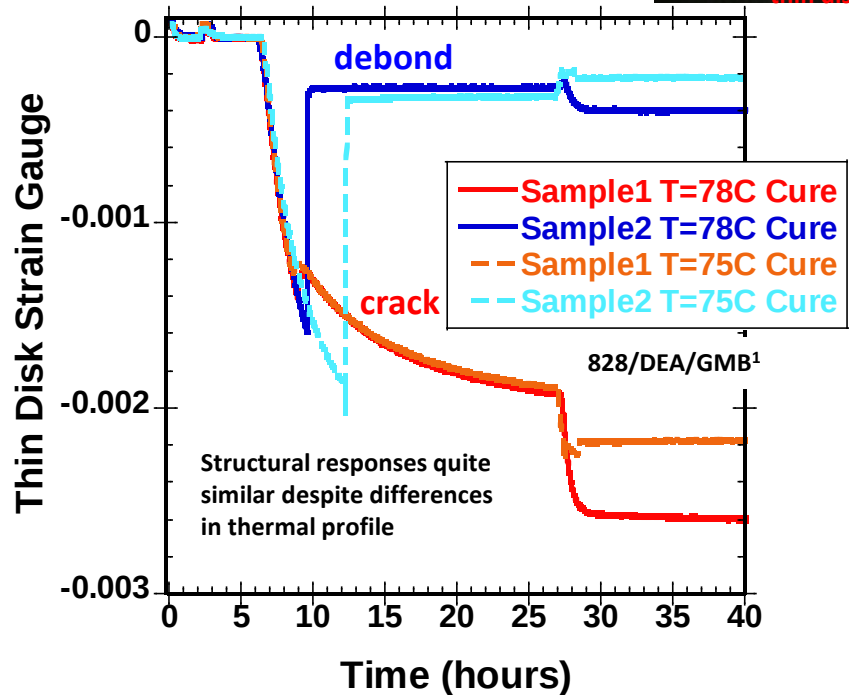
Geometry: Thin Disk on Cylinder



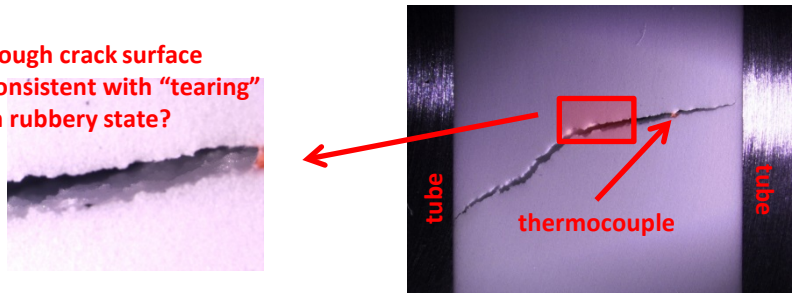
Temperature Profile



Structural Response



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

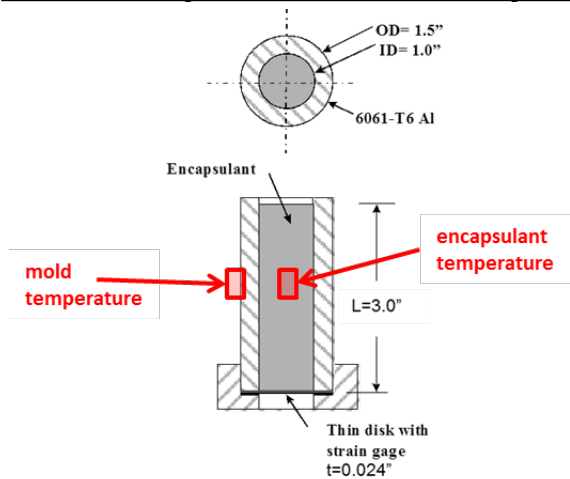


Failure can occur during cure...can it be avoided by minimizing stress?

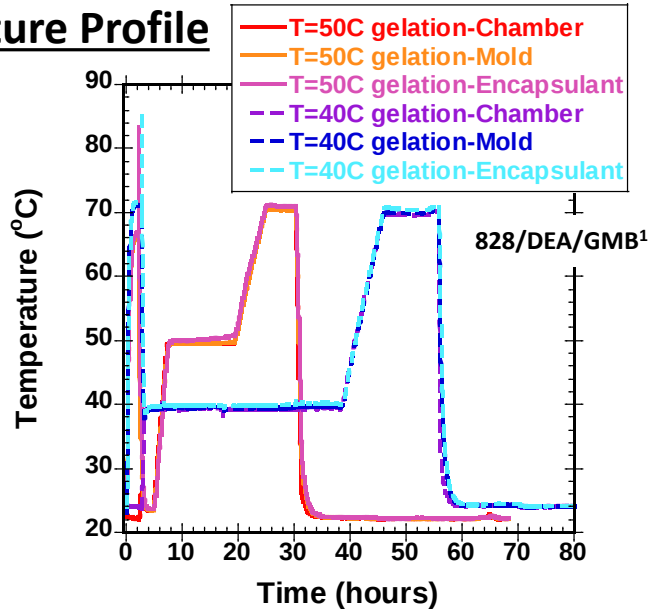
¹http://www.sandia.gov/polymer-properties/828_DEA_GMB.html

Cure with Temperature Ramps and Holds

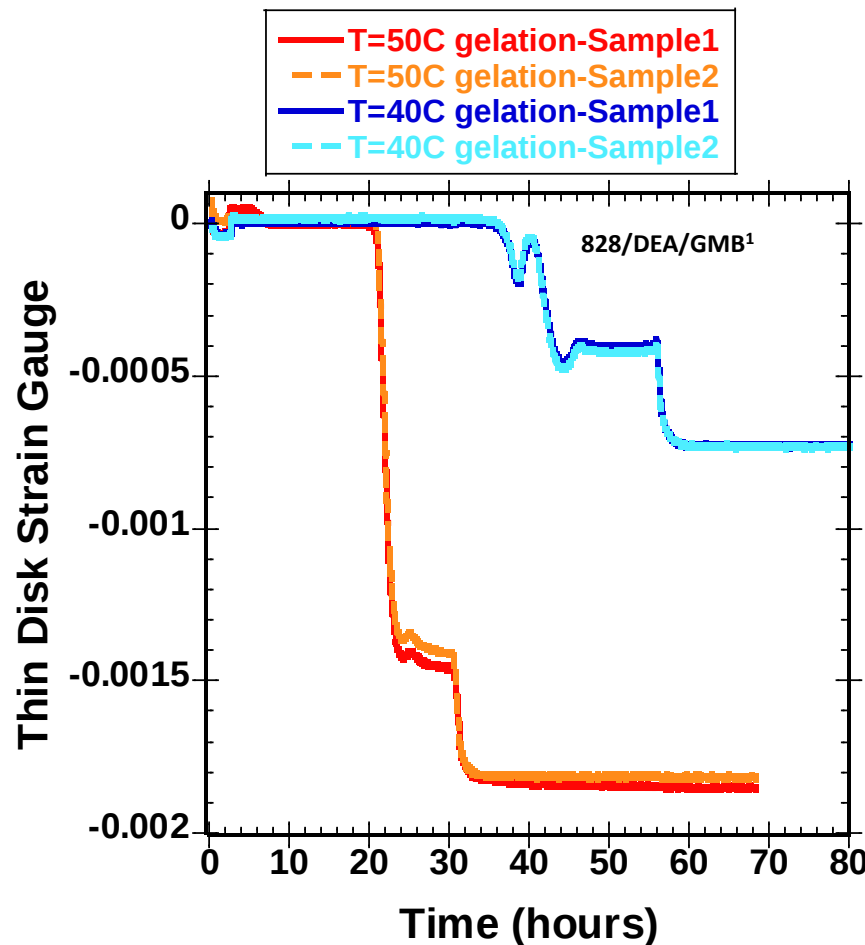
Geometry: Thin Disk on Cylinder



Temperature Profile



Structural Response

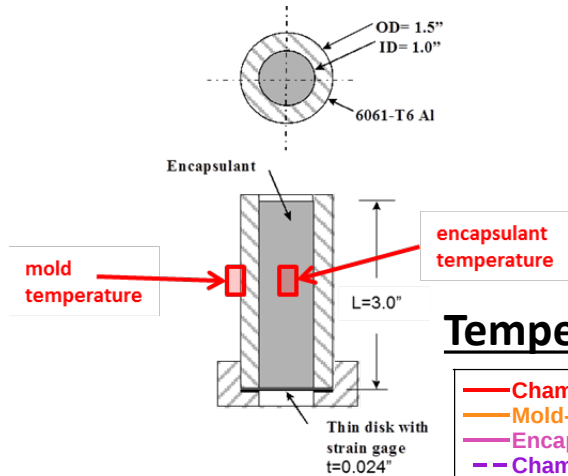


¹http://www.sandia.gov/polymer-properties/828_DEA_GMB.html

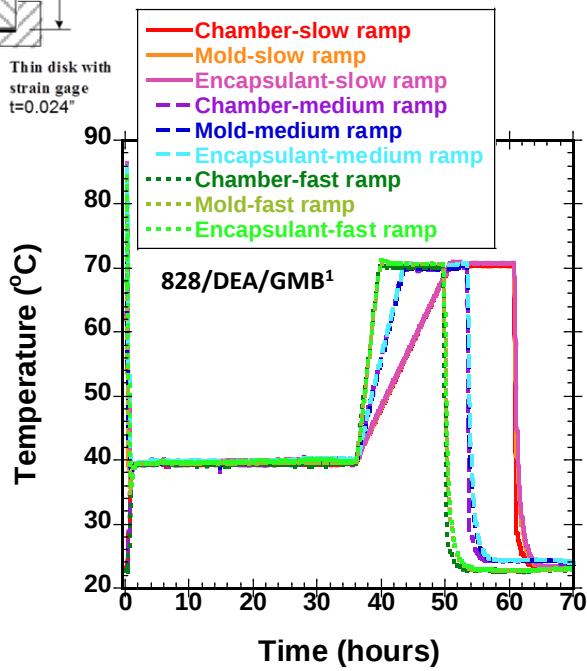
No cracking/debonding observed and less disk deflection for larger post-gelation thermal ramp (thermal expansion offsetting cure shrinkage)

Role of Temperature Ramp Rate

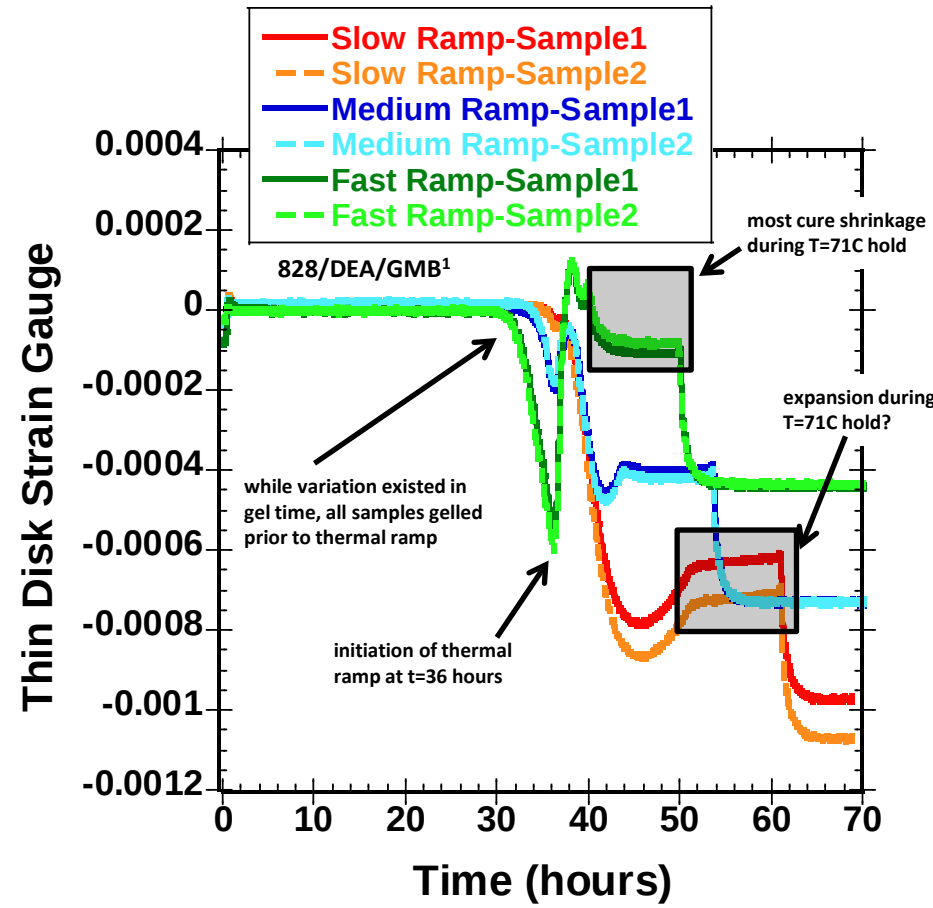
Geometry: Thin Disk on Cylinder



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