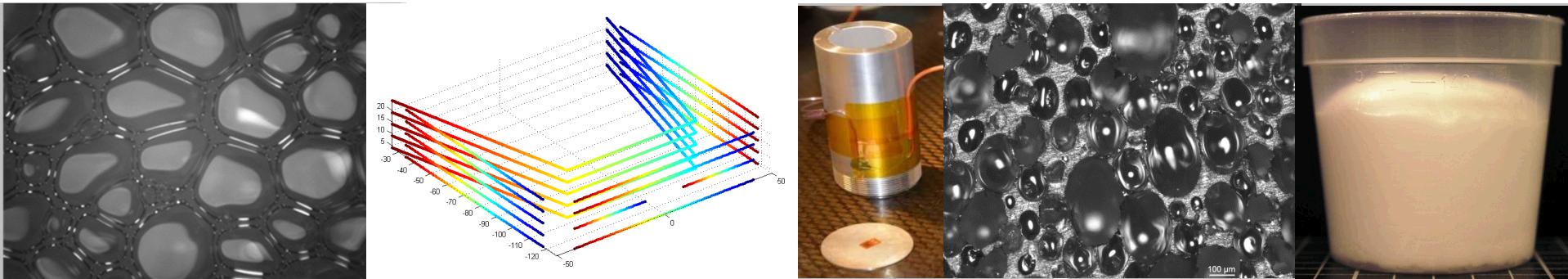


*Exceptional service in the national interest*



# Measuring and Modeling the Dimensional Stability of High Density Polyurethane Foams

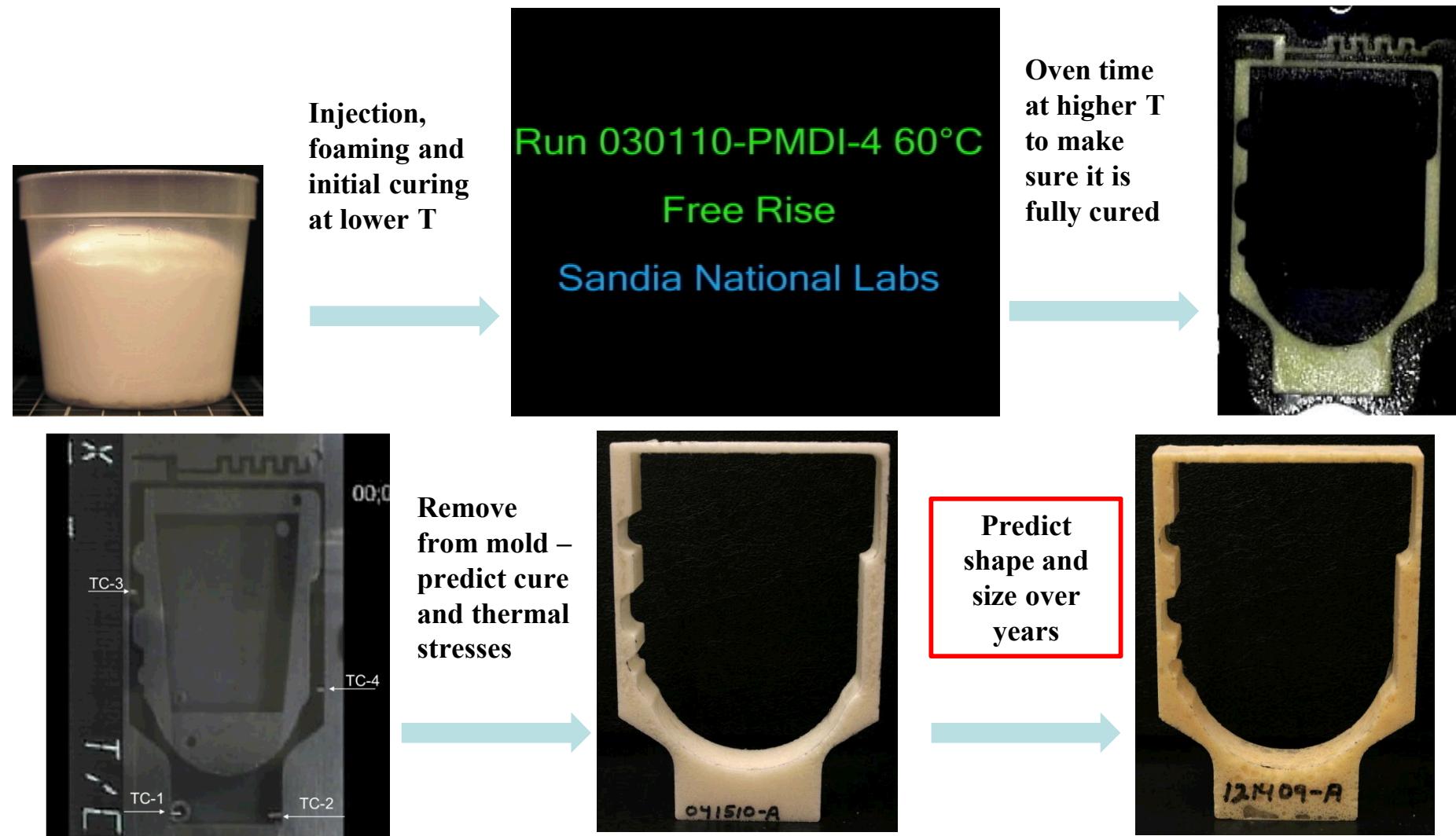
Kevin N. Long, Lisa A. Mondy, Christine C. Roberts, Haoran Deng,  
Mark Stavig, Mathias C. Celina, Melissa Soehnel, Rekha R. Rao

31<sup>rst</sup> Polymer Processing Society, Seoul, South Korea  
Session G9, June 11, 2015



# The Challenge: Predicting How Manufacturing Conditions Impact Component Dimensional Stability

## A Typical Process



# Polyurethane (PMDI) Foams

## Application Space

- PMDI is used as an **encapsulant** and as a **structural material** to mitigate against shock and vibration



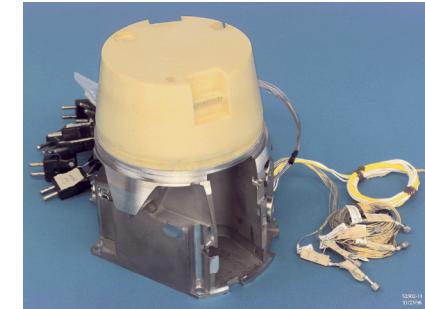
## The Problems

- Voids, Density Variations, **Residual Stress**
- **Short Term**: Meet Tight Geometric Specifications
- **Long Term**: Long term shape change/loss of component function

PU has a short pot-life: models can help reduce defects and improve filling process

## Objective

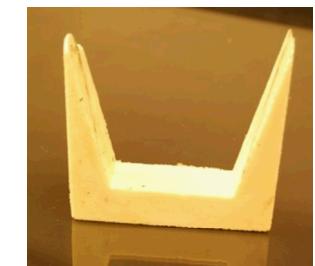
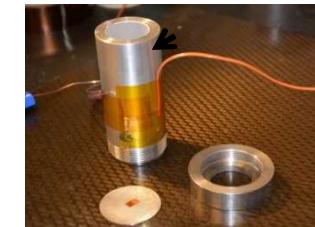
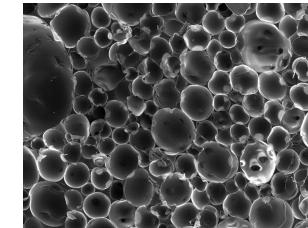
- Describe **mold filling, density, cure variations, and residual stresses** due to manufacturing result in residual stresses and associated component warpage over time.



Mock component encapsulated with PMDI from “KCP Encapsulation Design Guide” (Mike Gerdin, UUR)

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# Three Stages of Material Response



## Stage I

Fluid

### Pre-Gel (0- $10^3$ seconds)

Chemistry results in both gas production (foaming) and matrix polymerization (curing)

Foaming liquid rises to fill the mold until polymer matrix gelation

Heat, pressure generated

Gelation

## Stage II

Soft-Solid

### Post-Gel Cure ( $10^3$ – $10^4$ seconds)

Variations in temperature cause variations in density and extent of cure

Solid polymer matrix locks in density gradients

Further gas production causes bubble pressurization with minimal volume increase

Vitrification

## Stage III

Solid

### Vitrified and Released ( $10^4$ + seconds)

Residual stresses, density, and properties vary spatially

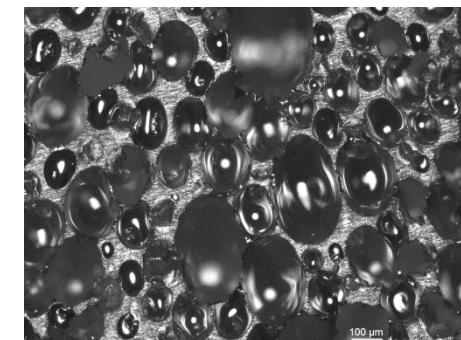
Both long and short term shape change is possible as different parts of the foam relax at different rates

Boundary conditions strongly influence residual stresses

Processing parameters at earlier stages will affect quality of part at later stages

# Warpage Occurs in Stage III

- **Shape stability** over weeks, months, years matters
  - Tight tolerances (microns) lead to low part yields
  - Expensive molds currently designed based on average shrinkage amounts, institutional knowledge, trial-and-error.
- A sample's dimensional **changes are nonuniform** -- >  
Physical property gradients from previous manufacturing steps
  - Confirmed players: Density, extent-of-cure, residual stress gradients
- **Many possible sources** for dimensional changes
  - Stress Relaxation
  - Continued cure of material
  - Bubble pressure, loss of CO<sub>2</sub>
  - Hydration/Dehydration (Swelling)



**Hypothesis:** Spatial variations in density and extent of cure from manufacturing couple with cure shrinkage, thermal expansion, and confining conditions during cure to produce a complex residual stress state that relaxes over time.

# Non-Linear Curing Viscoelastic Solid (II and III)

## Balance Laws and Solution Fields:

- Mass + Momentum (*Displacements*)
- Species Balance (*Chemical Reaction Extent*)
- Energy (*Temperature*)

## Solid State Non-Linear Viscoelastic (NLVE) Model Initial Conditions

- Initialize *temperature, foam density, and reaction extent* from simulation stage 1
- Directly initialize the stress-free reaction and temperature (expansion free)
- Assume the NLVE viscous stresses are initially zero

## Stress prediction based on the universal curing model developed at SNL

DB Adolf and RS Chambers, "A thermodynamically consistent, nonlinear viscoelastic approach for modelling thermosets during cure," *J. Rheology*, 2007.

### Cauchy Stress:

SNL Non-linear Viscoelastic Curing Model (Adolf & Chambers 2007)

$$\underline{\underline{\sigma}} = \underline{\underline{\sigma}}[\log \underline{\underline{U}}, T, x, \text{histories}]$$

Logarithmic Strain

Temperature

Extent of matrix cure

### Material and Laboratory Time Relation

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

### Density Scaling

$$\psi[\rho_0] = \left( \frac{\rho_0}{\rho_{ref0}} \right)^p \psi[\rho_{ref0}] \quad \text{Free Energy}$$

$$\underline{\underline{\sigma}}[\rho_0] = \left( \frac{\rho_0}{\rho_{ref0}} \right)^p \underline{\underline{\sigma}}[\rho_{ref0}] \quad \text{Cauchy Stress}$$

# Curing NLVE Model Continued

- Relaxation behavior and mechanical properties depend on the *temperature, extent of cure, and histories of deformation*

## Material Time Dependencies

### Thermal

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

### Shear Deformation

### Pressure

### Matrix Cure

## Glass Transition Evolution

$$T_{ref}(x) = T_{ref} - \frac{\left[ C_3 \beta_\infty + C_5(x(t)) \right] (x(t) - x_{ref})}{(1 + C_3 \alpha_\infty)}$$

$$C_5(x(t)) \equiv C_{5a} + C_{5b} x$$

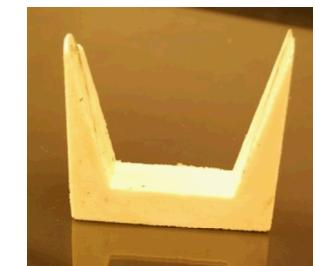
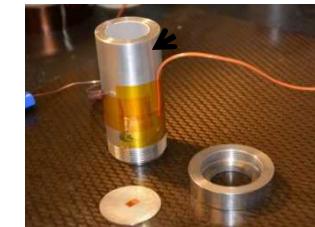
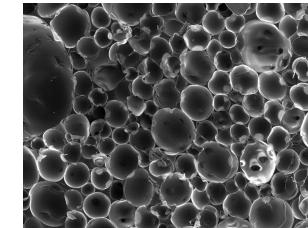
## Shear Modulus

$$G_g(T) = G_{gef} + \frac{\partial G_g}{\partial T}(T - T_{ref}) + \frac{\partial G_g}{\partial x}(x - x_{ref})$$

$$G_\infty(T) = \left\{ G_{ref} + \frac{\partial G_\infty}{\partial T}(T - T_{ref}) \right\} \left[ \frac{x^m - x_g^m}{x_{ref}^m - x_g^m} \right]^n$$

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# Curing Non-Linear Viscoelastic Model Calibration

## 1) Oscillatory Shear

- Isofrequency
- Temperature Sweep of a “Fully Cured” Foam Torsion Bar
- Shear moduli
- Shear Relaxation Function
- TTS above Tg

## 2) Thermal Mechanical Analysis

- Isofrequency
- Temperature Sweep of a “Fully Cured” Foam Bar
- Coefficients of Thermal Expansion
- Bulk/Thermal Relaxation Function

## 4) DSC

- Isothermal and Cyclic Temperature Sweeps of “Dry Foam”
- Isothermal Reaction Kinetics
- Glass Transition Evolution

## 5) Uniaxial Compression

- Isothermal and Cyclic Temperature Sweeps of “Dry Foam”
- Yield phenomena (Deformation Induced Mobility)

## 3) ATR Infrared Spectroscopy

- Various Isothermal Spectral Measurements of the “Dry Foam”
- Matrix Cross-linking Reaction Kinetics

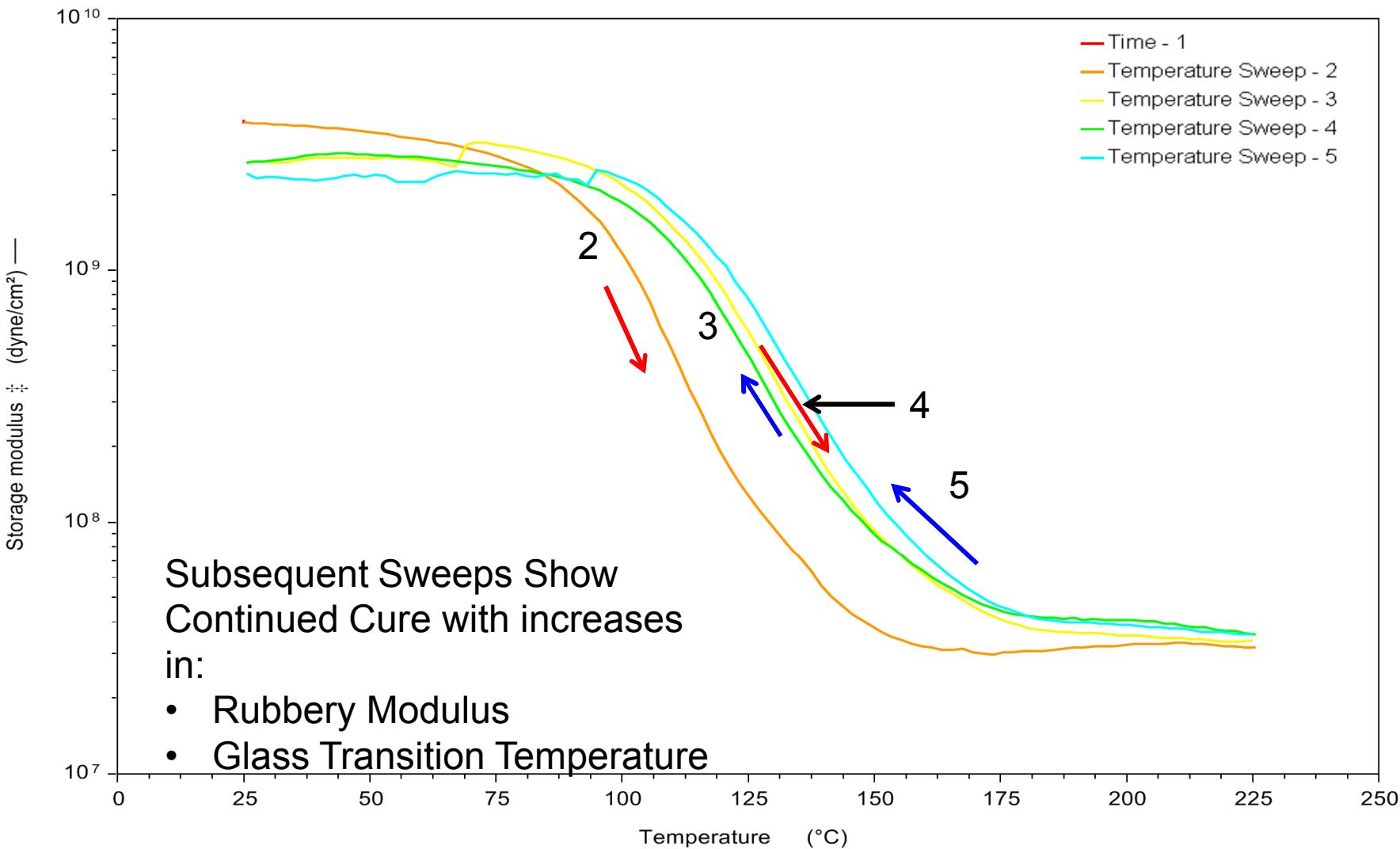
## 6) Cure Shrinkage and Rubbery Shear Modulus Evolution during Cure

- “Dry Foam” Dimensional change measurements during cure

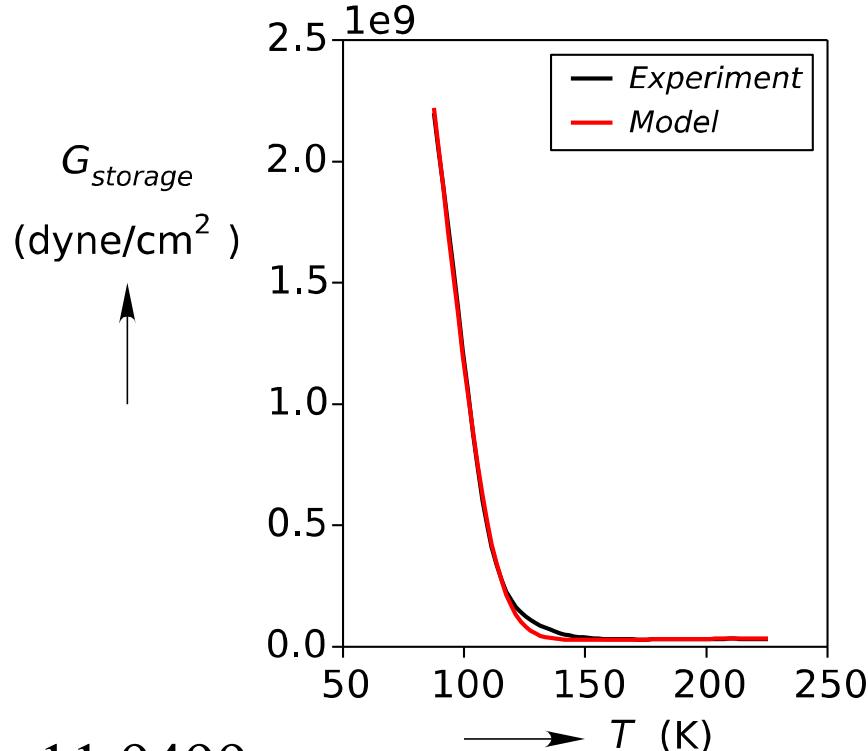
# 1) Oscillatory Shear. KCP Cure Schedule—Cool to RT—Cut

Torsion Bars—Isofrequency Sweep Up—Sweep Down—Sweep Up—Sweep Down

Structural 10 lbs. Foam bar (1)



# 1) Oscillatory Shear Fitting



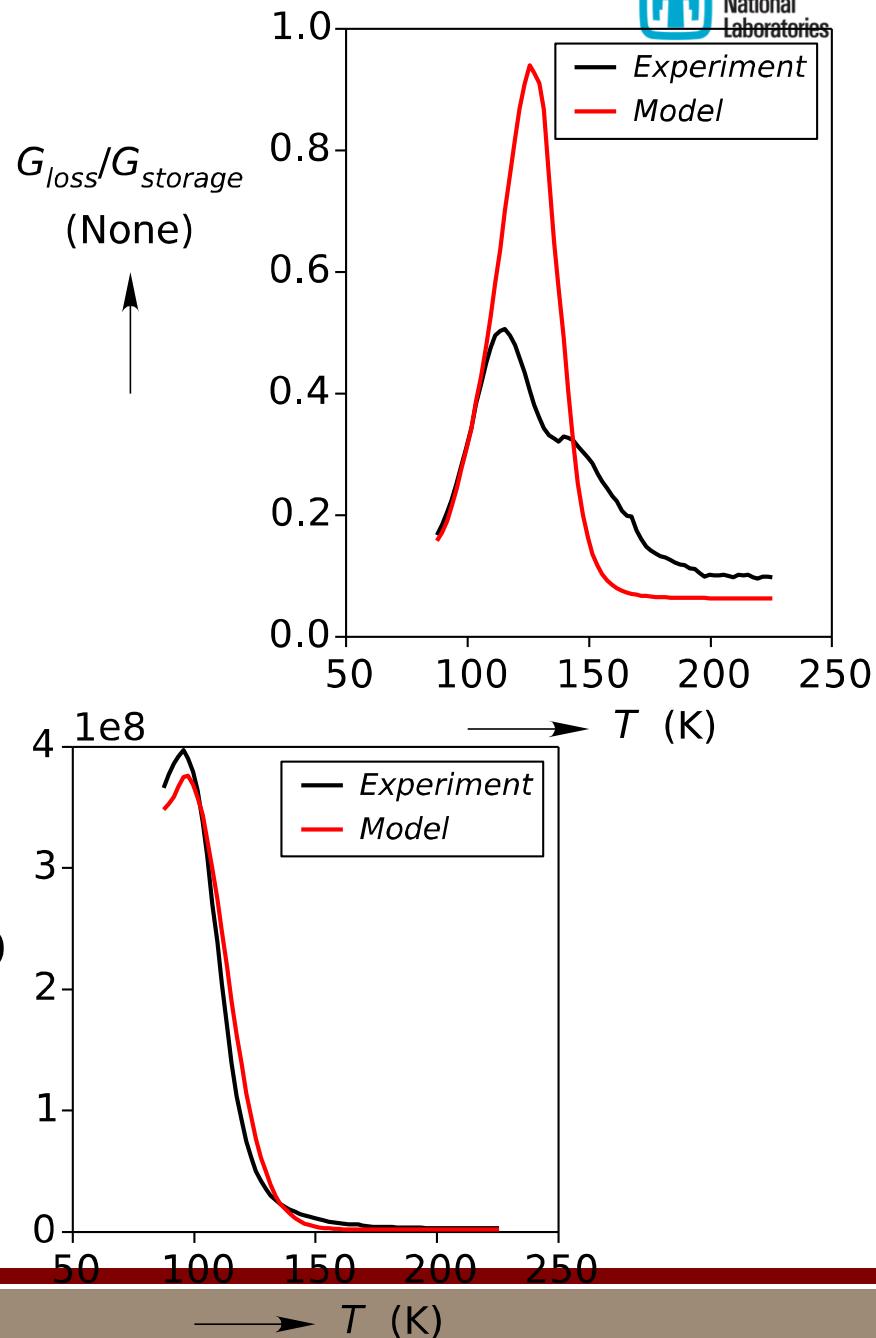
$$C_1 = 11.9499$$

$$C_2 = 98.591 \text{ } C$$

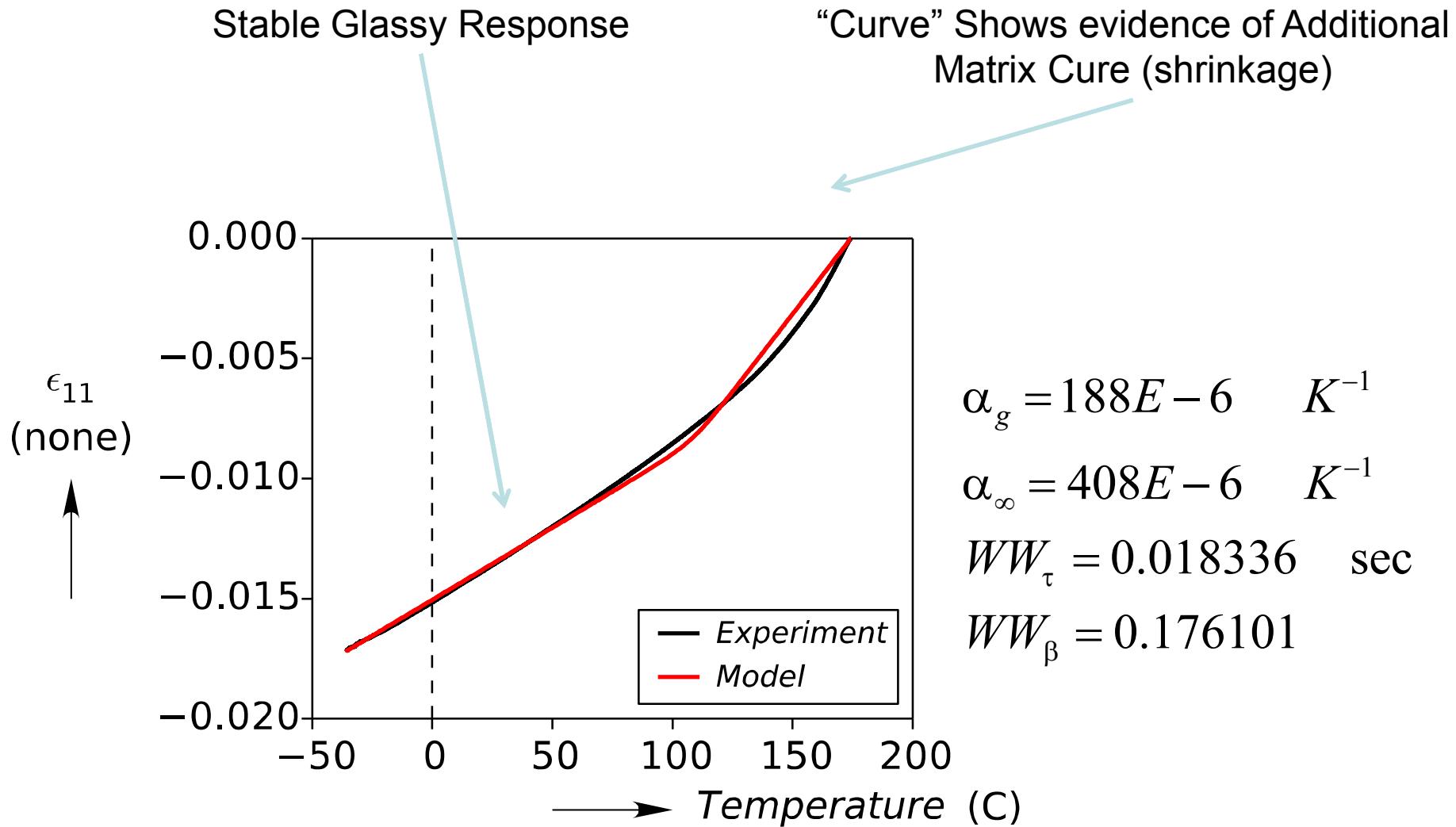
$$T_{ref0} = 115.47 \text{ } C$$

$$WW_{\tau} = 0.9216E-3 \text{ } s$$

$$WW_{\beta} = 0.181$$



## 2) Brute Force TMA Fitting



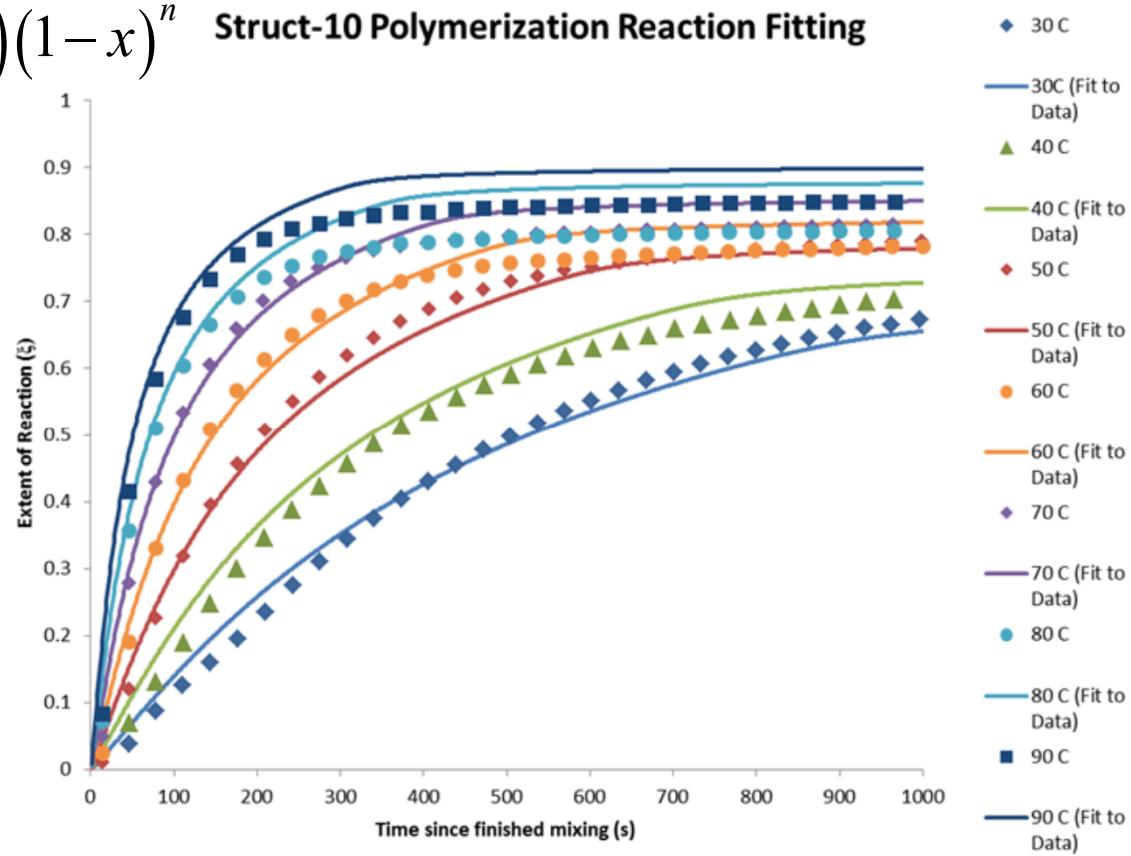
### 3) Single Extent of Reaction Calibration from ATR IR Spectroscopy

Reaction Kinetics Follow a Modified Kamal 1974 Single Reaction Extent Description.  
Vitrification arresting of the cure kinetics is assumed to follow the simple Debenidetto Form

$$\frac{\partial x}{\partial t} = \frac{k_0 \exp\left(-\frac{E_a}{RT}\right)}{(1+wa)^\beta} (b+x^m)(1-x)^n \quad \text{Struct-10 Polymerization Reaction Fitting}$$

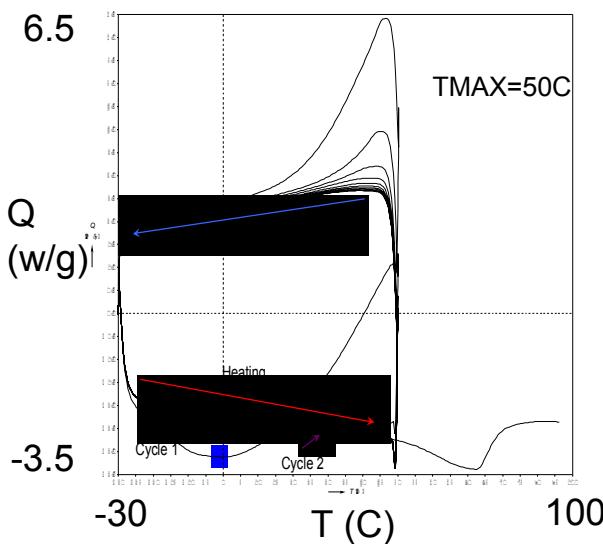
$$\log_{10} a = \frac{-C_1(T - Tg[x])}{C_2 + T - Tg[x]}$$

$$Tg[x] = \frac{Tg_0(1-x) + x\Delta Tg_\infty}{1-x+\Delta x}$$

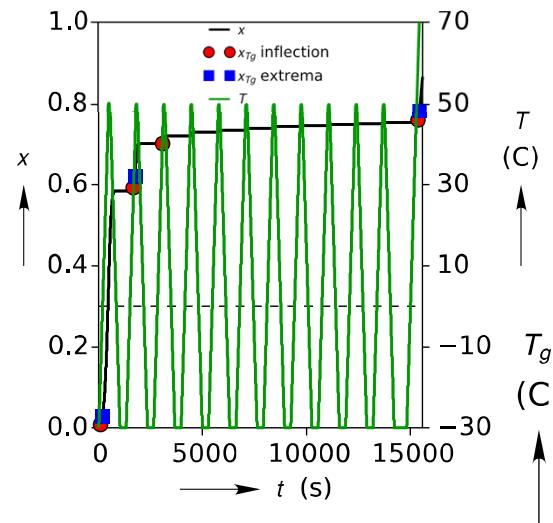


## 4) Differential Scanning Calorimetry to Estimate $x$ $T_g$ vs. $x$

- Differential Scanning Calorimetry (DSC) to examine the **time-temperature (t-T) history** of the curing (dry) foam
- **Integrate the (IR) calibrated reaction kinetics** subject to the t-T histories from the traditional cycling DSC scanning thermograms to estimate an extent of cure
- Interpret the glass **transition onset** at the t-T point where the upward T ramp endotherm experiences an **inflection point**

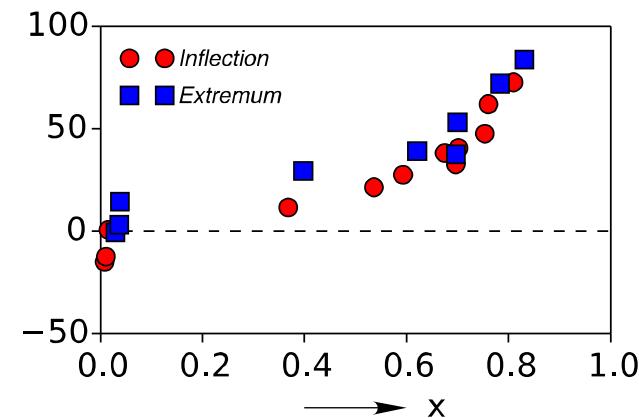


- 10 mg sample
- Cycle the temperature between -30 C and TMAX
- Ramp up to 100+C at end of test (10 cycles)



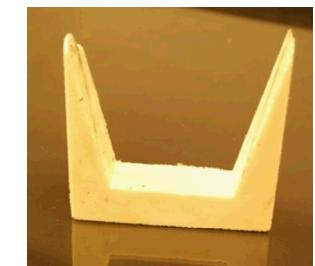
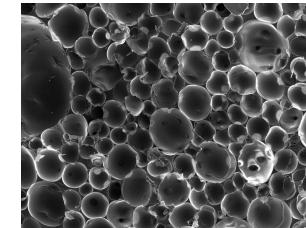
- Each test (TMAX varies) gives several point for  $T_g$  as  $f(t)$
- Integrate the t-T history with assumed kinetic reaction fit to translate  $t$  to extent of cure  $x$ .

Collection of Data from 3 Tests with different TMAX cycle temperatures



# Outline

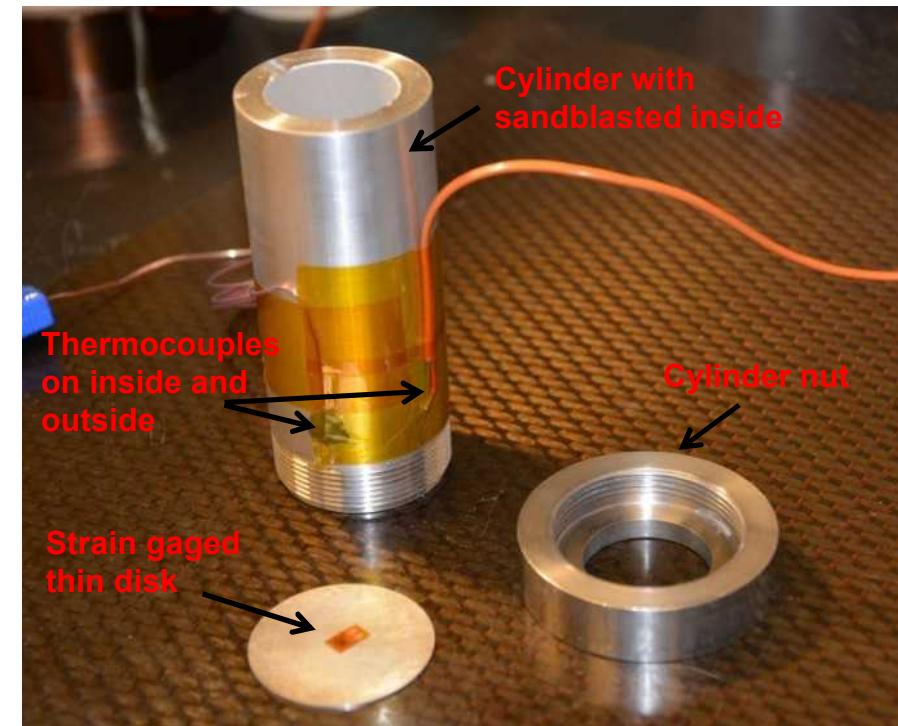
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# We Tried for a Simple Experiment

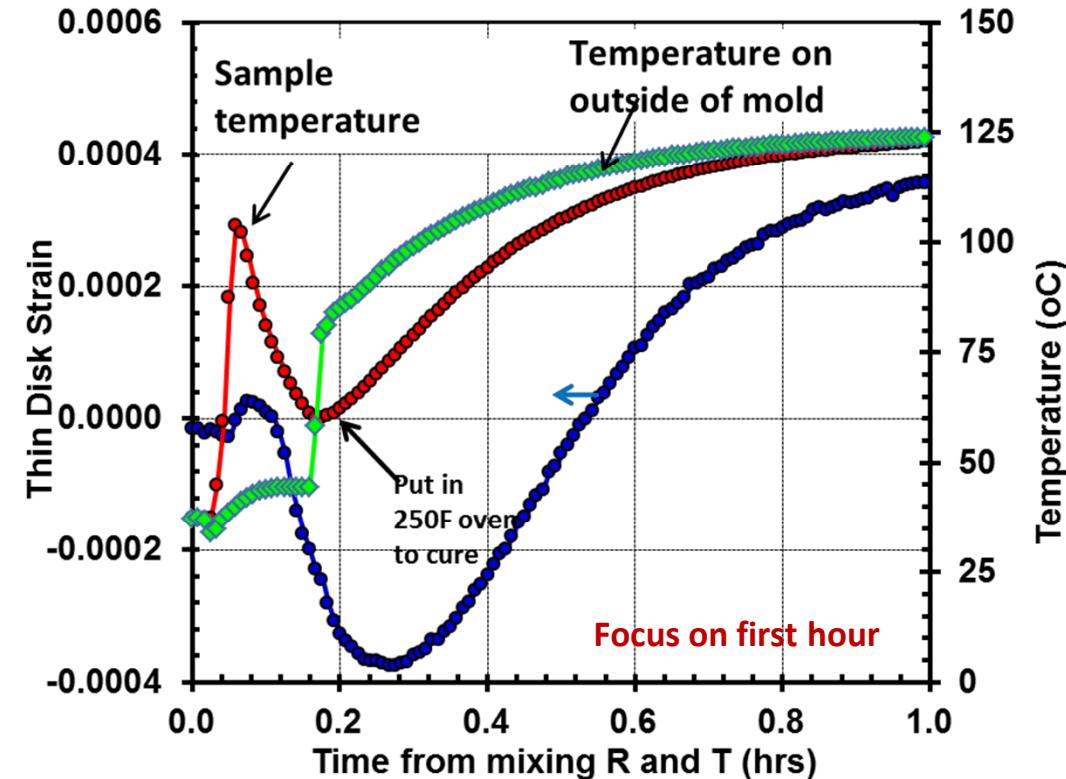
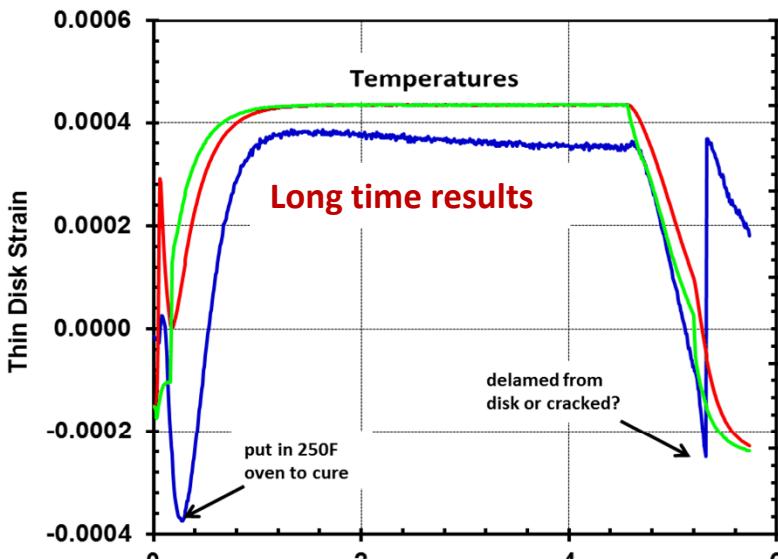
- Previously used at Sandia to look at stresses from curing epoxies.
- Dry Foam. Foam precursors removed of water – No foaming reaction
  - Shrinkage of polyurethane only, no effects of gas diffusion
  - Assume matrix shrinkage is the same for the “dry” and “wet” foams
- Cure schedule (Approximated from our in-house schedule)
  - Precursors preheated 30 °C
  - Mold preheated 40 °C
  - After 10 mins, cure at 120 °C
- Observe temperature, strain of metal disk

**Goal:** Fitting only the cure shrinkage parameter, how closely can we model this relatively simple experiment?

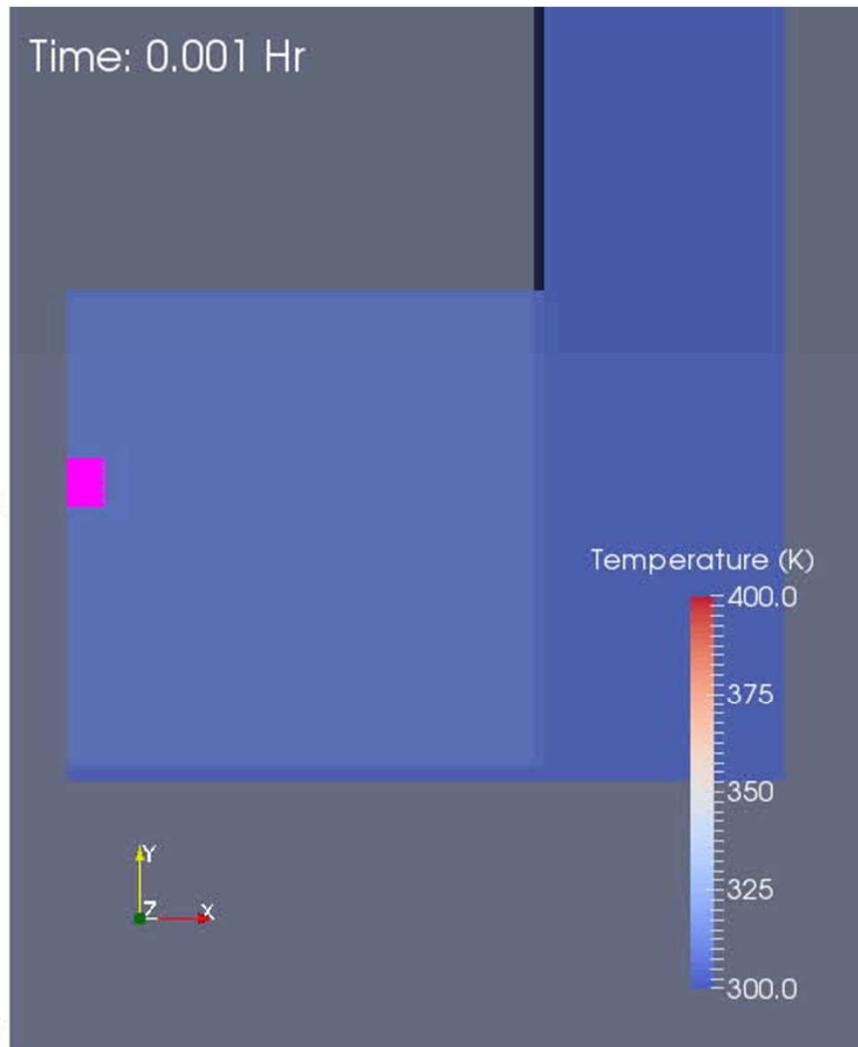
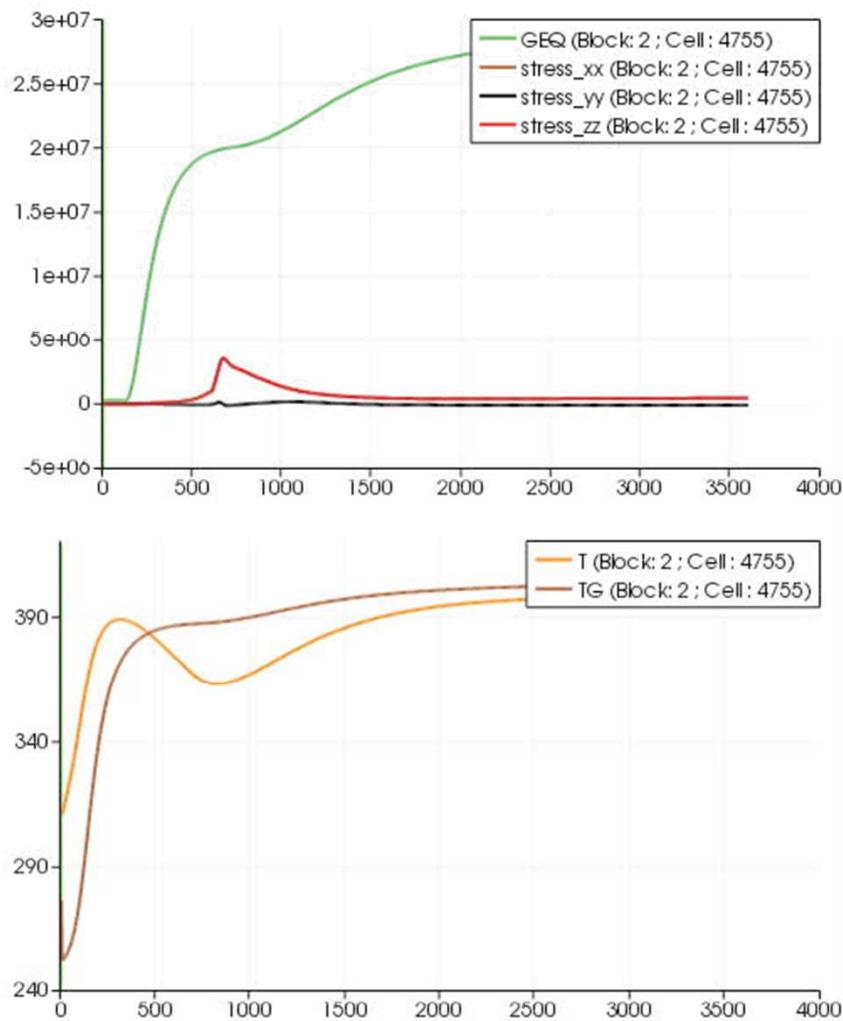


# Pop-Off Test Results

- Large initial exotherm
- Both thermal and curing strains observed
- Delamination upon cooling
- Some foaming still observed in “dry” foam
- Uncertainty in thermocouple placement



# Pop-Off Test Simulation

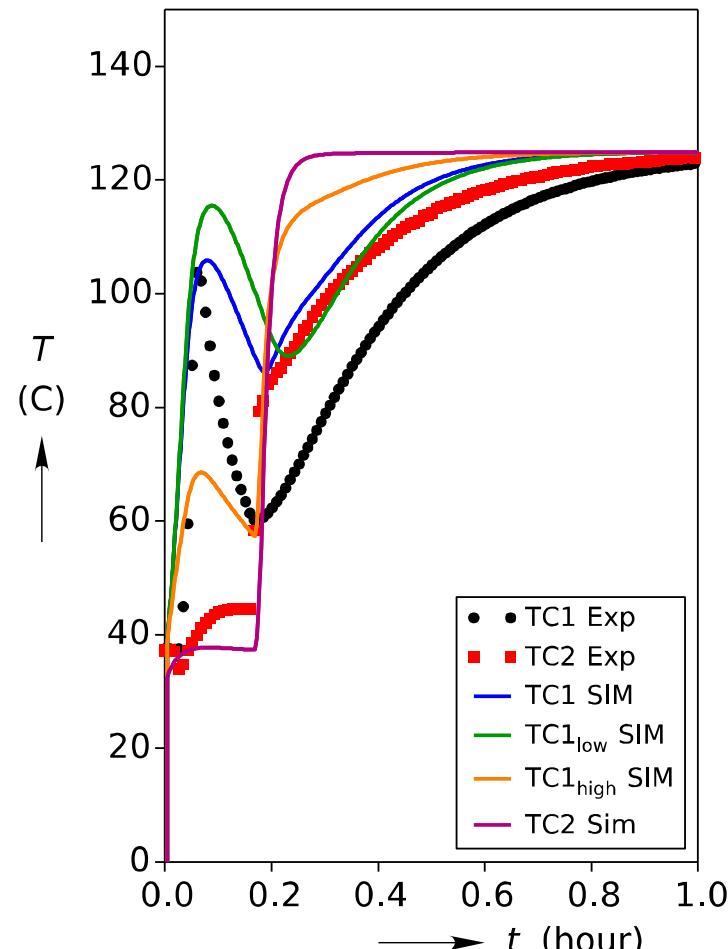
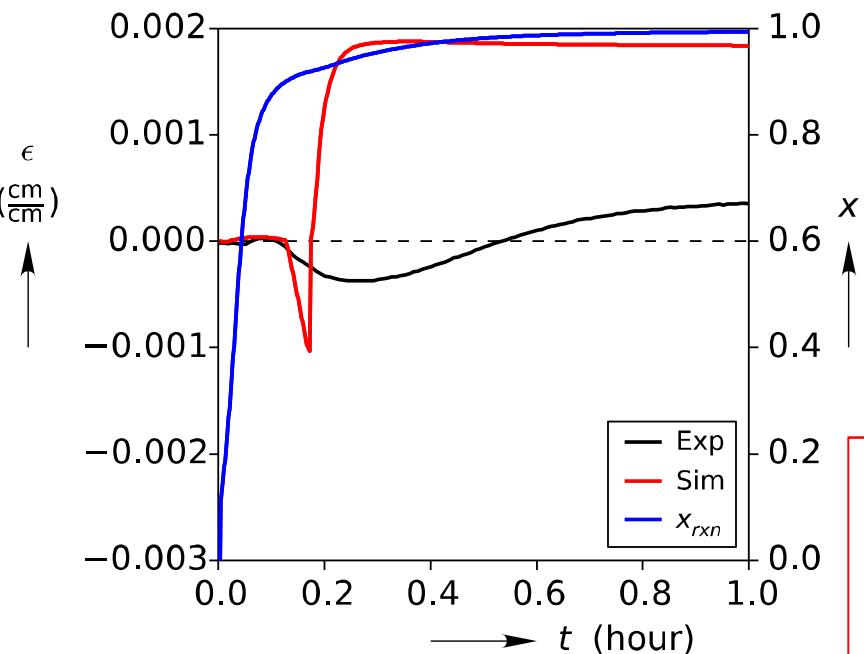


# Pop-Off Test: Comparison to Experiment

Qualitative thermal behavior predicted

Uncertainty in thermocouple location creates  
large uncertainty in model fidelity

Experimental cooling rates faster than predicted

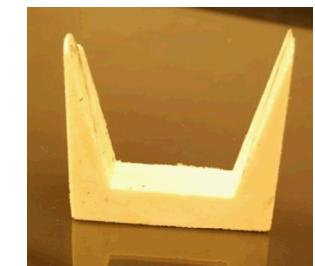
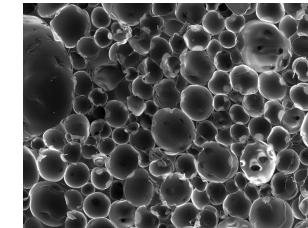


Qualitative strain behavior captured. Quantitative predictions require thermal, curing, and modulus evolutions to be accurate

Question equivalence between dry foam  
and true foam material parameters

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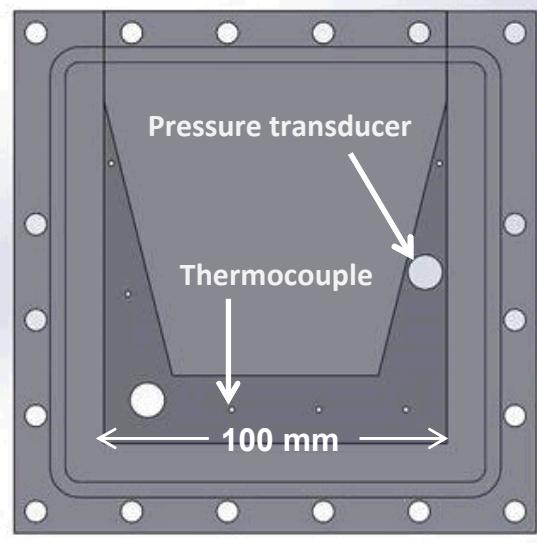
# Cure Shrinkage Monitoring

**Goal:** Observe cure shrinkage and warping over months to provide model validation data

- Geometry involves both thin and bulky regions
- Initially, filling conditions approximate in-house cure schedule
  - PMDI S10 foam injected at 40 °C, overpacked to 12.5 lb/ft<sup>3</sup>
  - After 15 mins, cured in oven at 120 °C for 4 hrs
  - Two separate filling orientations “C” and “U”
- Coordinate Measurement Machine (CMM by Xzyce)
  - Calibrated to measure 100 mm length to +/- 3 µm accuracy
  - Parts stored in dry desiccator when not being measured

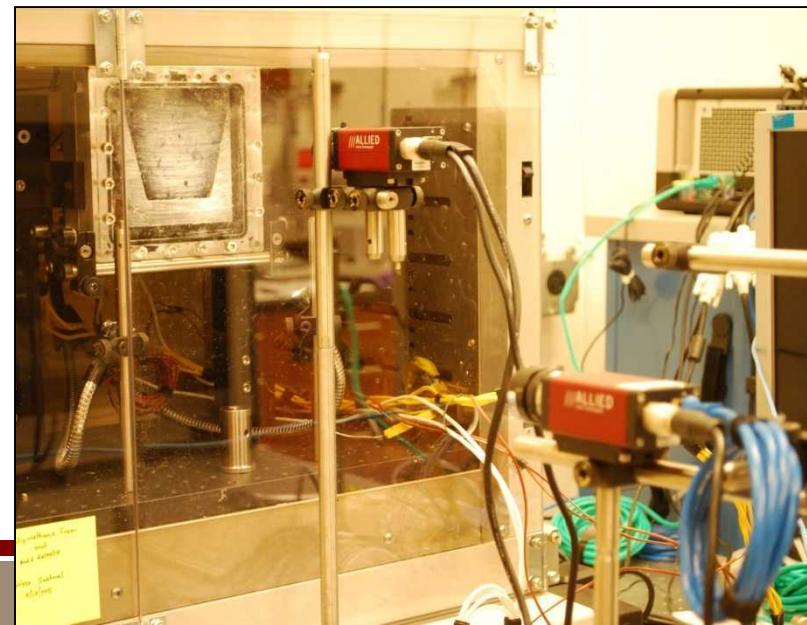


CMM measures dimensional changes



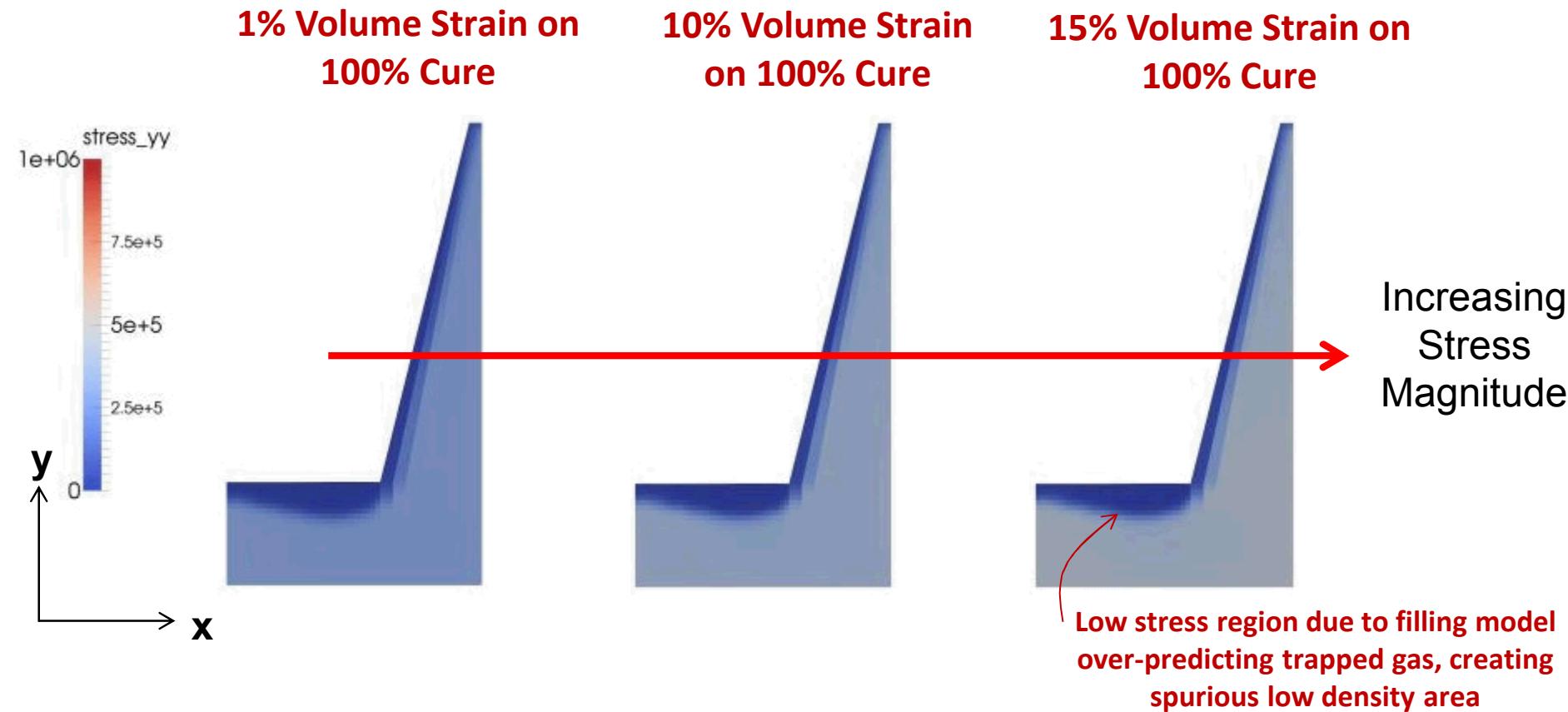
Ports for thermocouples and pressure transducers to record parameters during foaming.

Fill filmed using cameras, transparent oven door



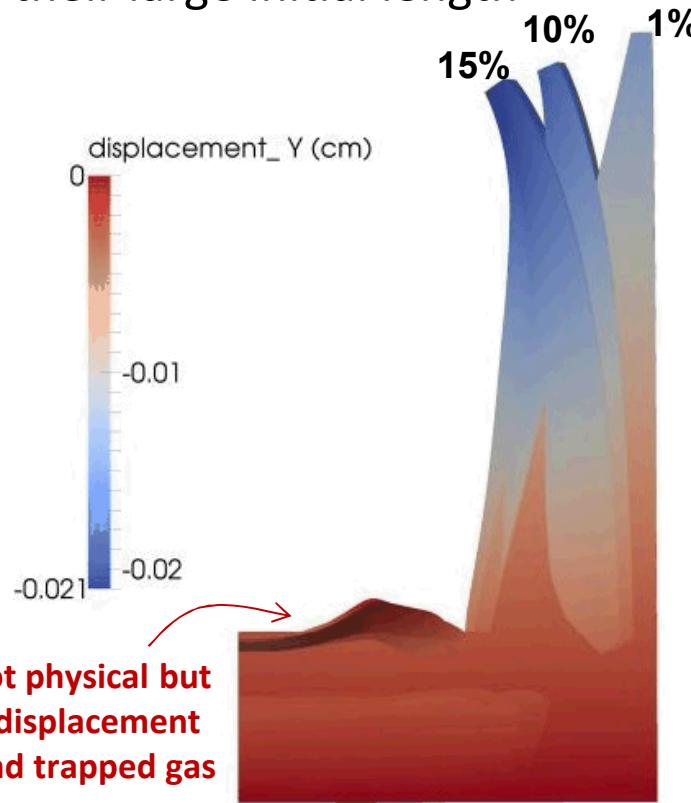
# Staple Mold Predictions: Stress in mold

- Currently, magnitude of cure shrinkage is an input parameter to the nonlinear viscoelastic model
- Cure shrinkage exacerbates the residual stress state prior to release from mold

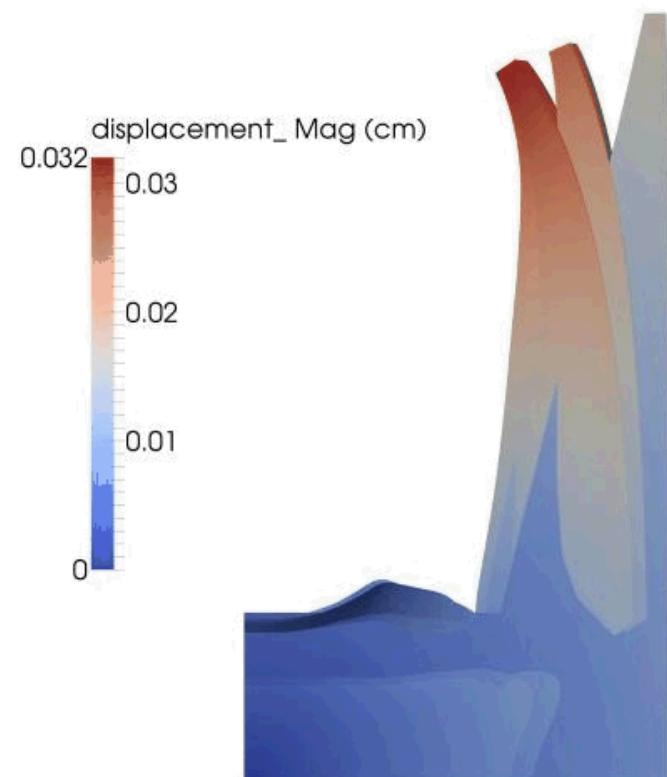


# Staple Mold Predictions: Dimensional Stability

- Vary cure shrinkage in simulations to see the effect on warpage
- Cure shrinkage exacerbates the loss of dimensional stability
- Long, slender regions deform most because of spatial variations in stress and their large initial length



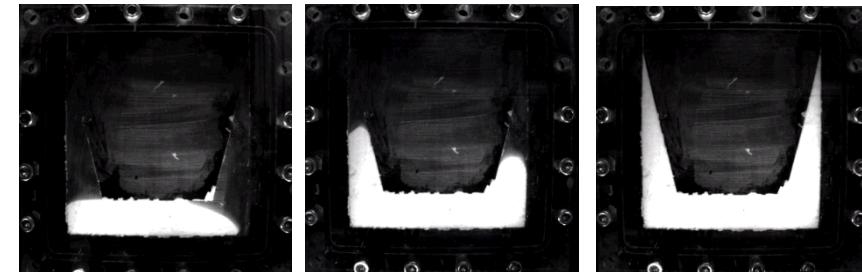
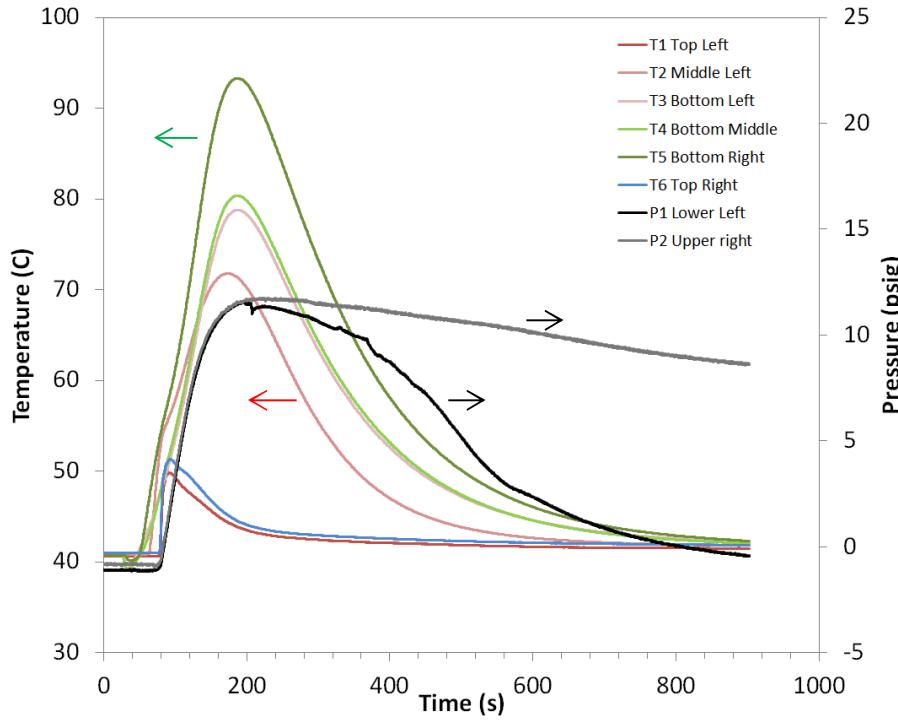
Displacements (cm) amplified by 100



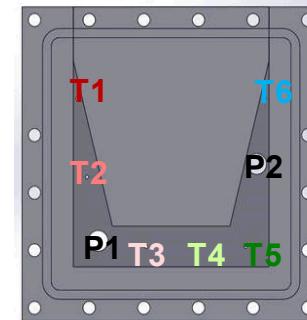
Displacements of 0.03 cm correspond to about 0.3% of the initial long side of the staple

# Foaming U-shaped staple mold

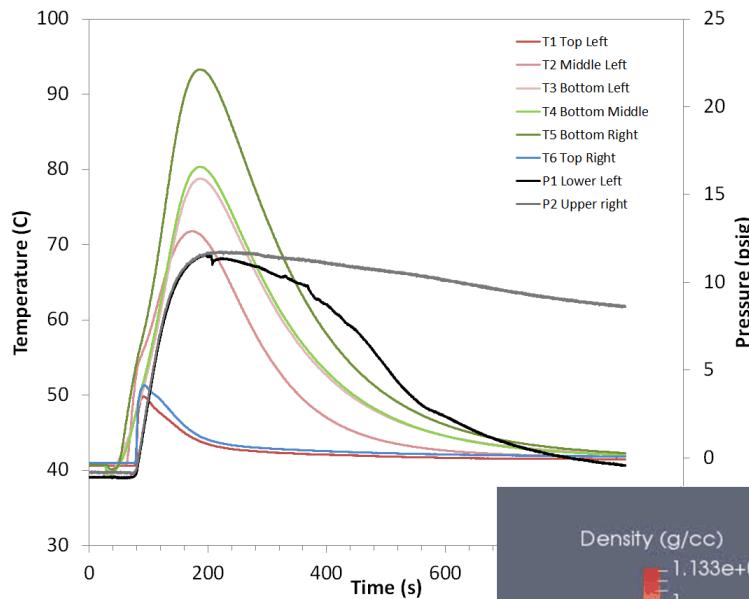
- Over many repeats, temperature, pressure, and flow profile are remarkably repeatable
- Imperfectly symmetric fill common
- Pressure rises as foam expands, relaxes at lower corner and stays positive at P2.



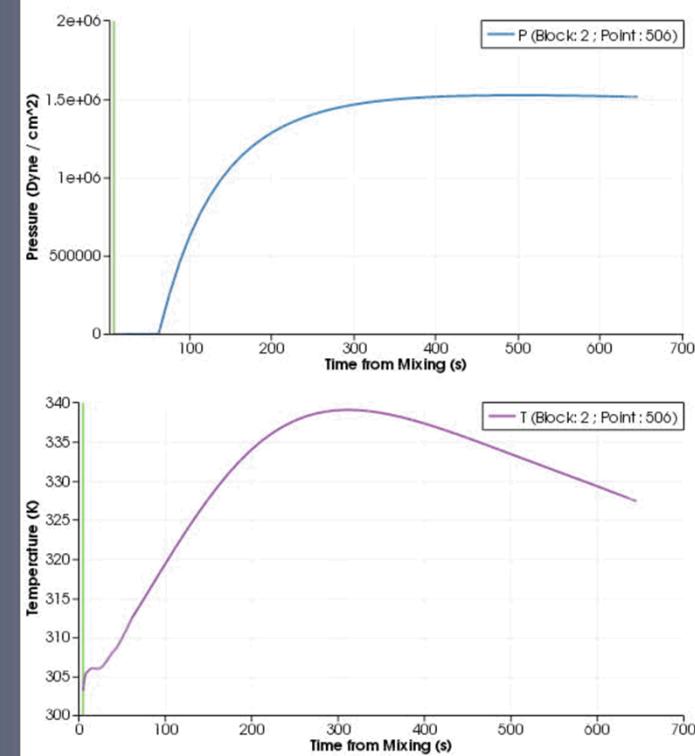
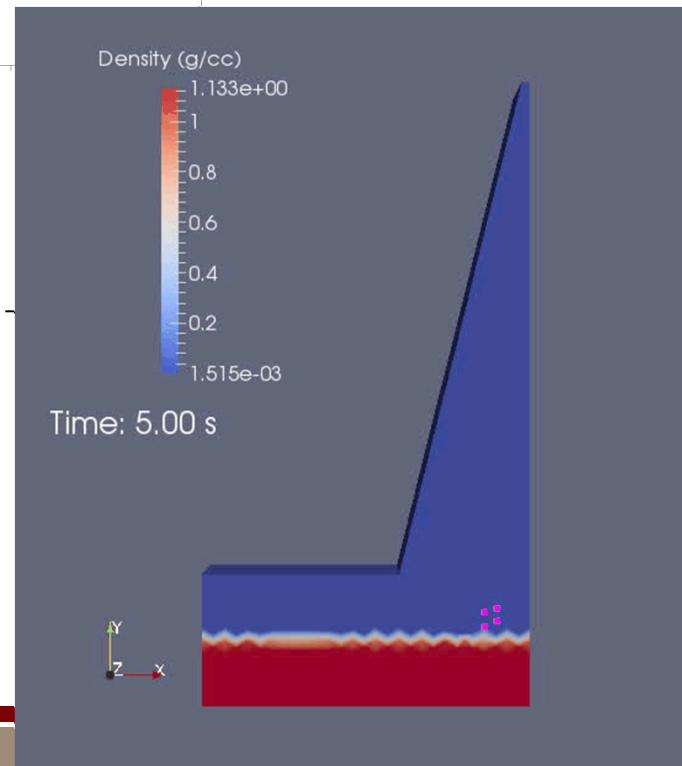
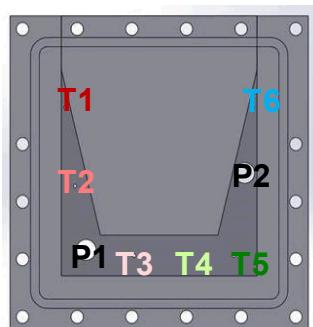
Some slight asymmetry due to bias of initial injection



# U Staple Simulation Comparison

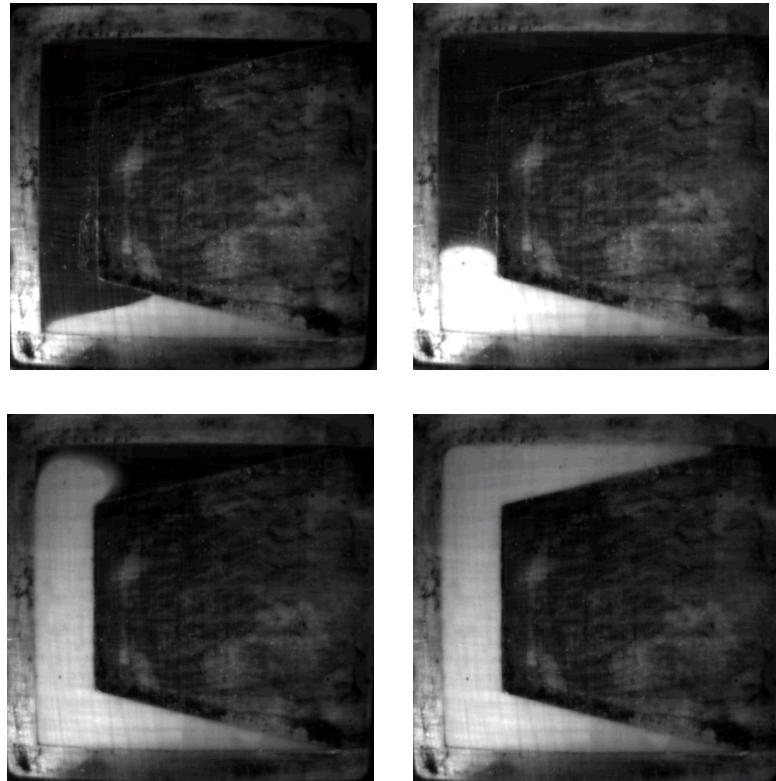
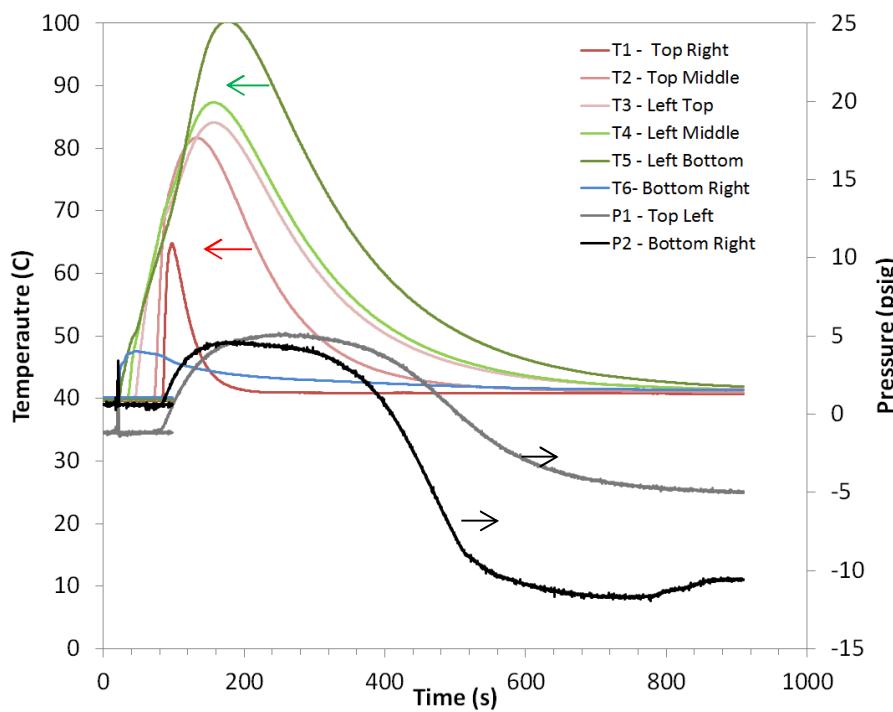
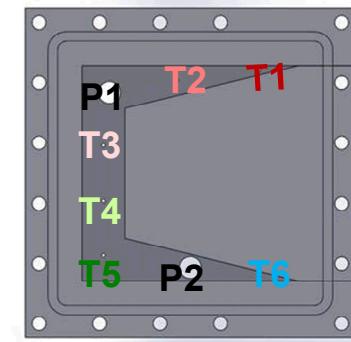


- Simulation Temperature at the hot spot is  $\sim 40\text{C}$  instead of  $50\text{C}$  above the initial resin temperature. Cool down is much slower.
- Pressure rise is reasonable, but simulation pressure is roughly 21 psi compared with the experiments 12 psi



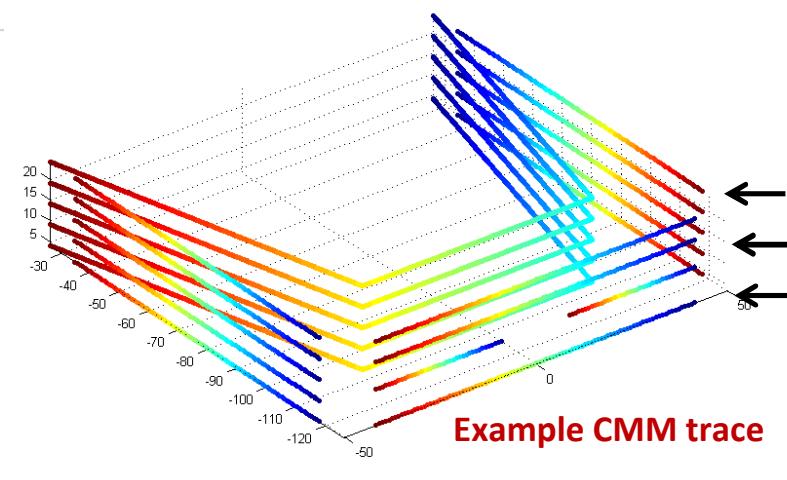
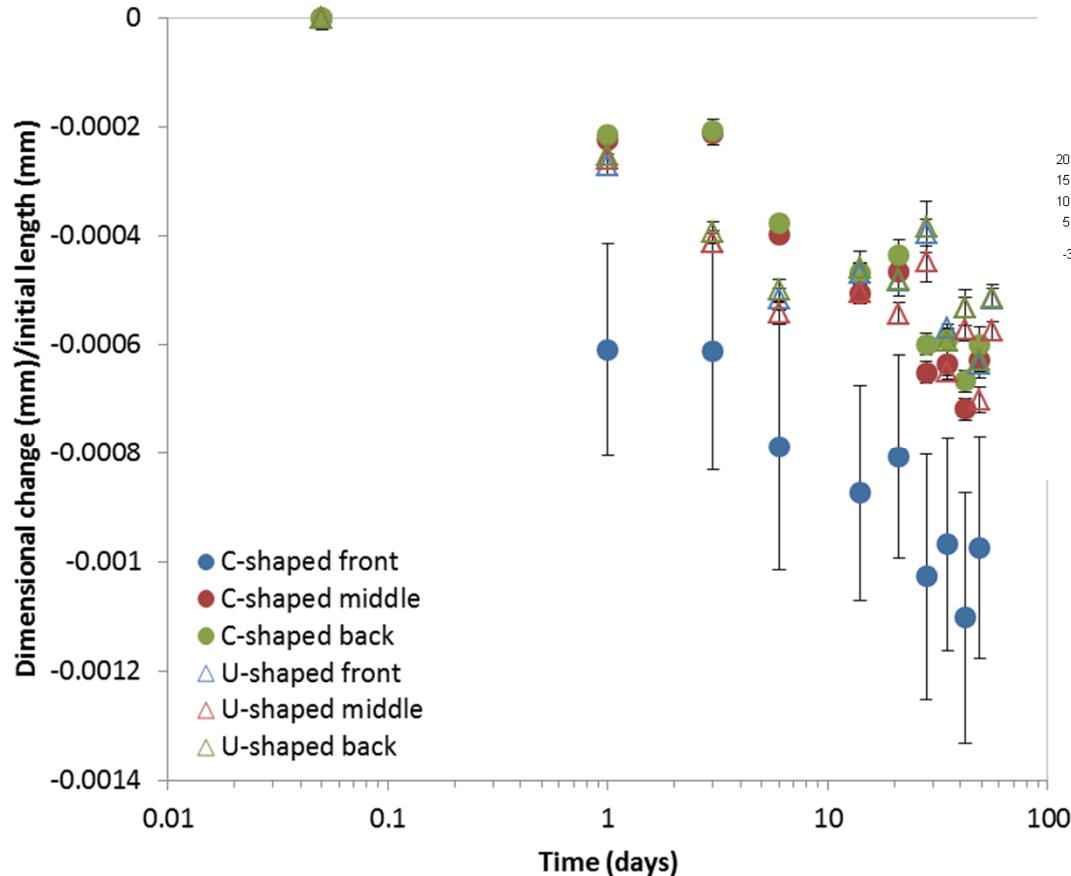
# Foaming C-Shaped Staple Mold

- Higher maximum temperature compared to U-shaped
- Stress rises then becomes tensile at both P1, P2 locations
  - Delamination often seen at P1



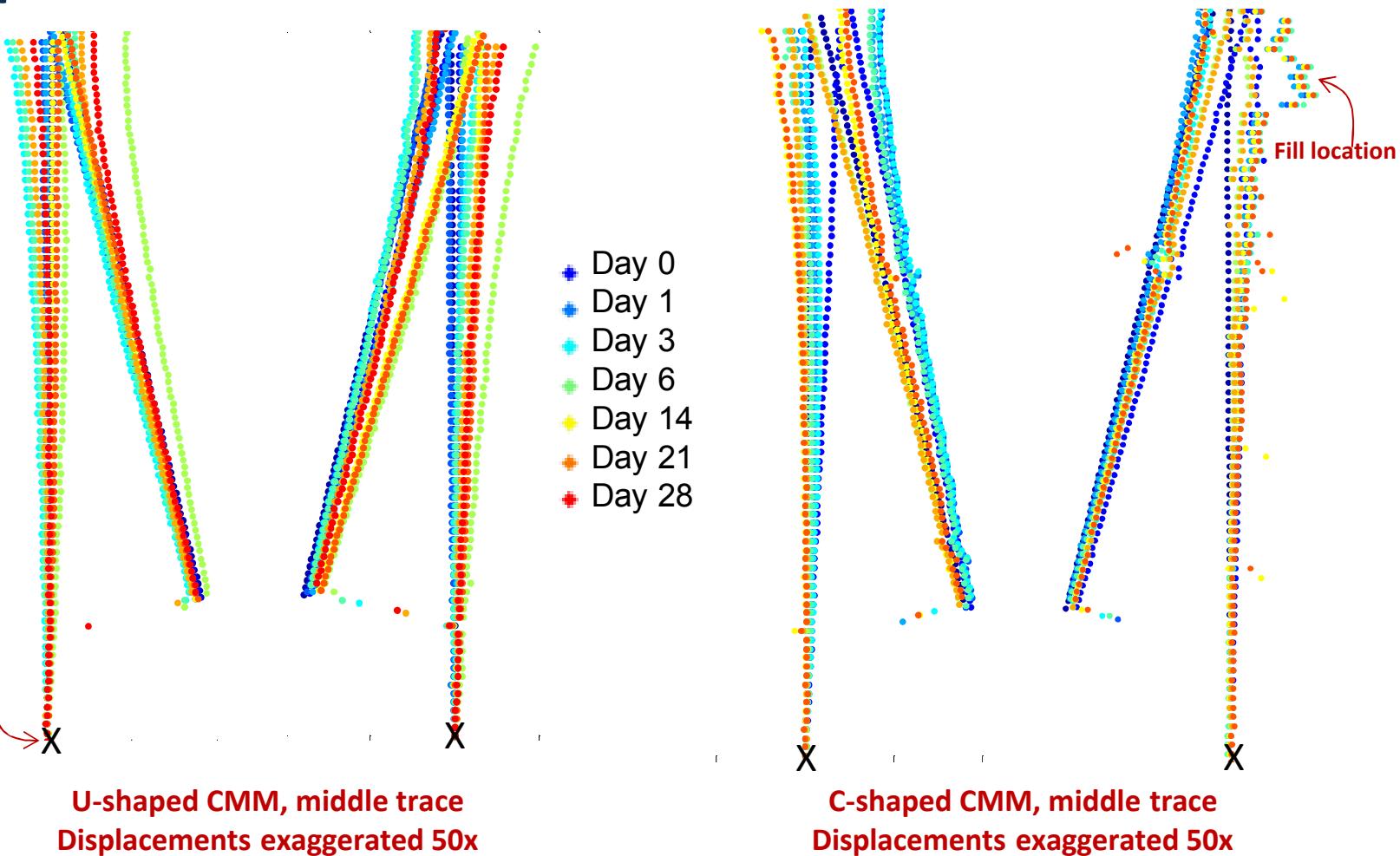
# Long-Time Shrinkage

- C- and U- shaped staple foam pieces cured 120 °C, 4 hours in mold
- Mounted upright, measured using CMM weekly (100 mN probe force)
- All surfaces move in time – defining point “(0,0,0)” a challenge



Shrinkage measured with respect to initial foam dimensions hours after removal from curing oven.

# Staple Mold CMM: Arm movement



- Arm movement not consistent, following AWE observations
- Density (CT scan), extent-of-cure spatial variations to be measured
- Possible that 100 mN CMM probe force could still move tips

# Conclusions

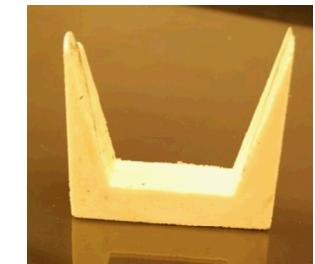
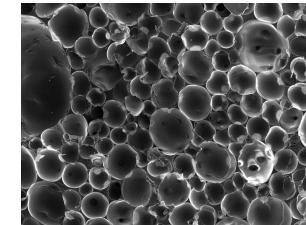
**A model was developed to predict stress relaxation and warpage during foam aging, taking property gradients predicted with a filling model into account**

- Initial experiment/model comparisons show that the model matches experiments qualitatively
  - Improvements to experiments will target sensitive parameters identified by model (thermocouple location, ranges of foam density)
  - Improvements to model will target improved material parameters, boundary conditions
- The model is very sensitive to thermal and curing conditions.

## Acknowledgements

Melissa Soehnel, SNL, Experimental assistance

Henry Lorenzo, SNL, CMM measurements



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# BACKUP SLIDES

# Calibration for the NLVE Curing Model to Represent the Post-Gelled Solid Foam

## I. Thermal-Mechanical Properties on as-received foam specimens

- Shear measurements
  - Shear moduli and temperature dependencies in the glassy state
- Uniaxial Compression in the glassy state
  - Yield (localization) strength of the material (Clock C4 Parameter)

## II. Viscoelastic Characterization on Fully Cured Neat Polymer (Dry Foam) Specimens

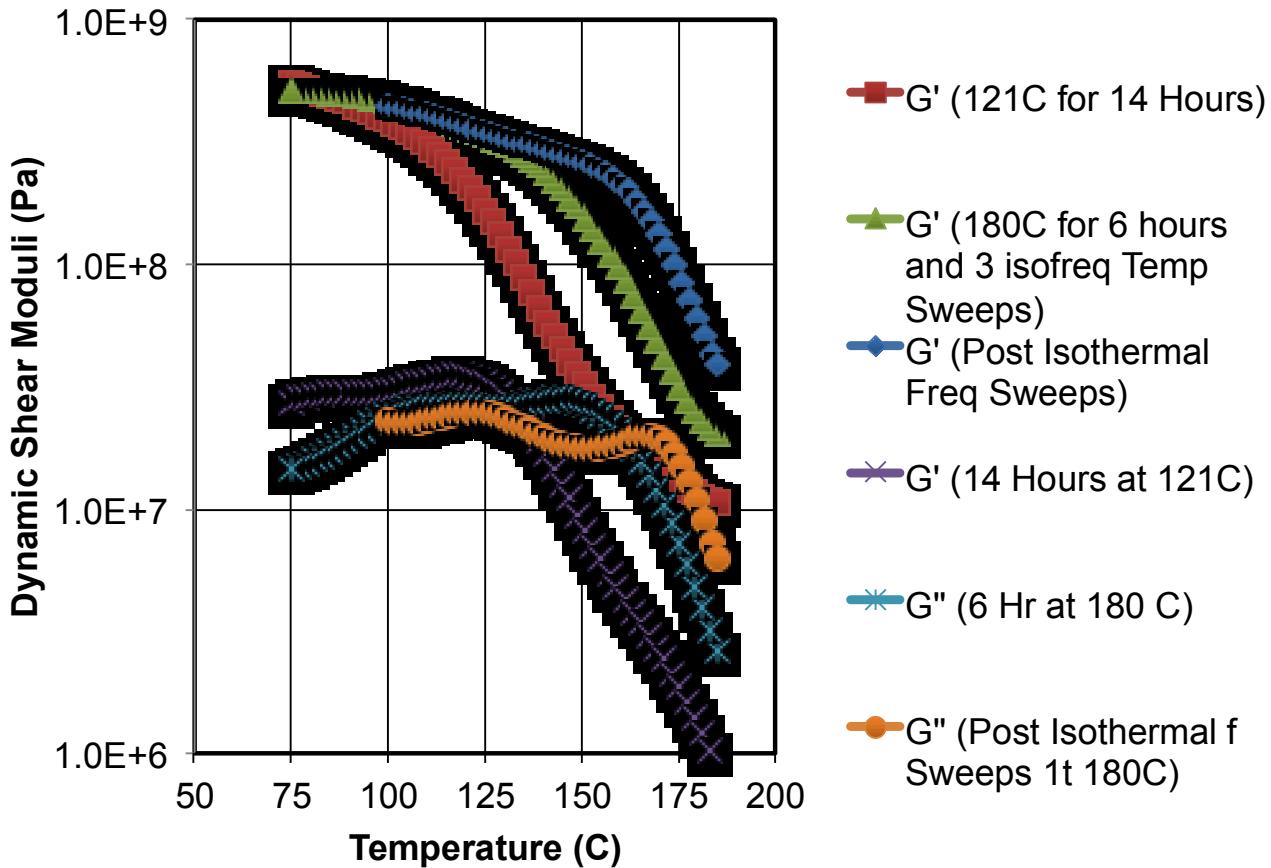
- Iso-frequency temperature sweep in oscillatory shear
  - $T_g$  and Transition Width
  - Isothermal frequency sweeps in oscillatory shear above  $T_g$
  - Shear WLF characterization
  - Shear relaxation function
- TMA sweeps across the glass transition
  - Bulk/Thermal relaxation function

## III. Cure Effects on Neat Polymer Specimens and Foams

- Digital Scanning Calorimetry (DSC)
  - Successive sweeps to determine  $T_g$  vs. extent of cure
  - Method assumes the cure kinetics have already been fully calibrated (FT-IR)
- Cure shrinkage measurements
  - Pop Off Tube

# Evidence of Continued Cure After High Temperature Annealing/Aging

- We cannot reach a stable (no further curing) rubbery state without incurring decomposition and/or other side reactions
- Instead of fully cured dry foam specimens, we characterize above the cure schedule (between 120 and 180 C)
  - Viscoelastic measurements are convoluted by additional cure



# U-Staple Physical Aging Simulation (1 Year from Mixing)

# Color Change Accompanying High Temperature Aging



Start



End of Ramp  
up to 200°C



End of Ramp  
down to 40°C



End of Ramp  
up to 200°C



End of Ramp  
down to 40°C

Difficult to fully cure without decomposing the polymer matrix

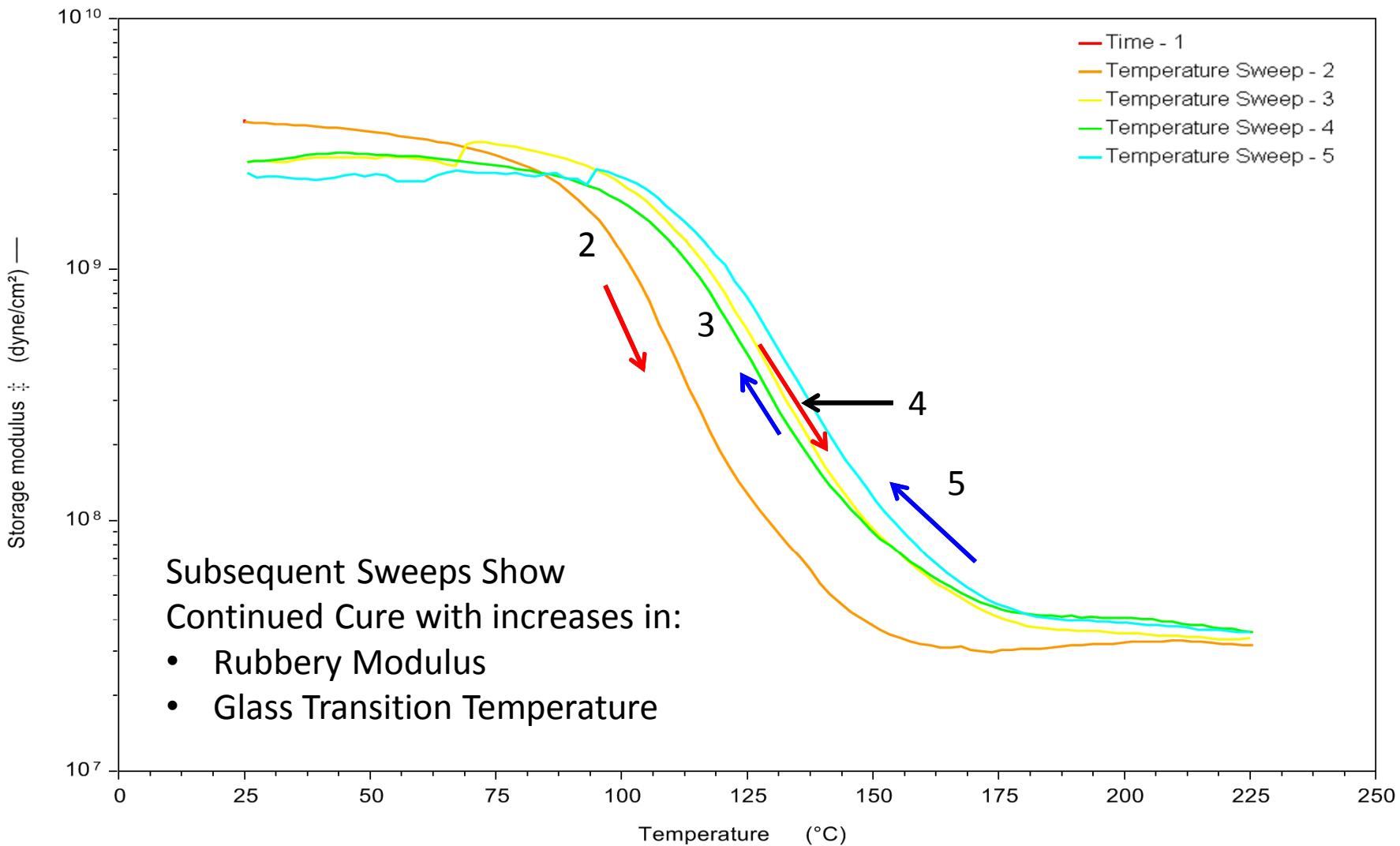
**BRUTE FORCE FITTING THE SHEAR  
RELAXATION FUNCTION, GLASSY SHEAR  
MODULUS, AND RUBBERY SHEAR  
MODULUS FROM KCP-PROTOCOL FOAM**

# Brute Force Fitting the shear relaxation function, glassy shear modulus, and rubbery shear modulus from KCP-Protocol Foam

- **Torsion Bar Preparation**
  - Cure at 120 C for 4 hours. Foam rise and fill occurs initially at 38 C preheated mold, but that mold is immediately inserted into the 120 C oven
  - Mold is cooled to room temperature
  - Specimen is released from the mold and machined down to the target torsion bar geometry
- **Oscillatory Shear Test Protocol**
  - First Temperature Cycle
    - 0.2 % shear strain. 1 Hz oscillation
    - Sweep from 25 C to 225 C and then back to 25C at 2 C per minute
  - Second, and Third Temperature Cycles
    - 0.1 % shear strain. 1 Hz oscillation
    - Sweep from 25 C to 225 C and then back to 25C at 2 C per minute

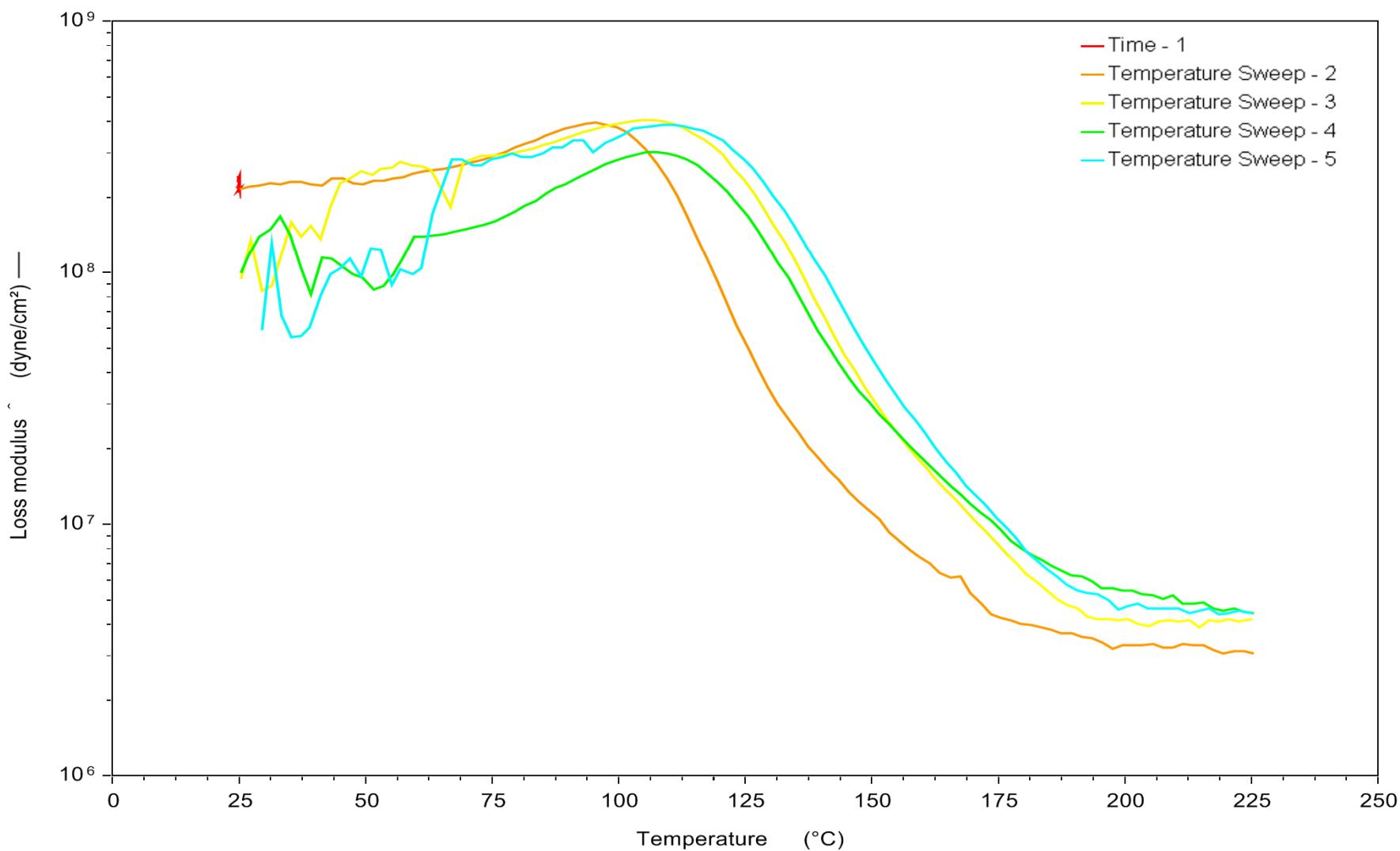
# KCP Cure Schedule—Cool to RT—Cut Torsion Bars—Isofrequency Sweep Up—Sweep Down—Sweep Up—Sweep Down

Structural 10 lbs. Foam bar (1)



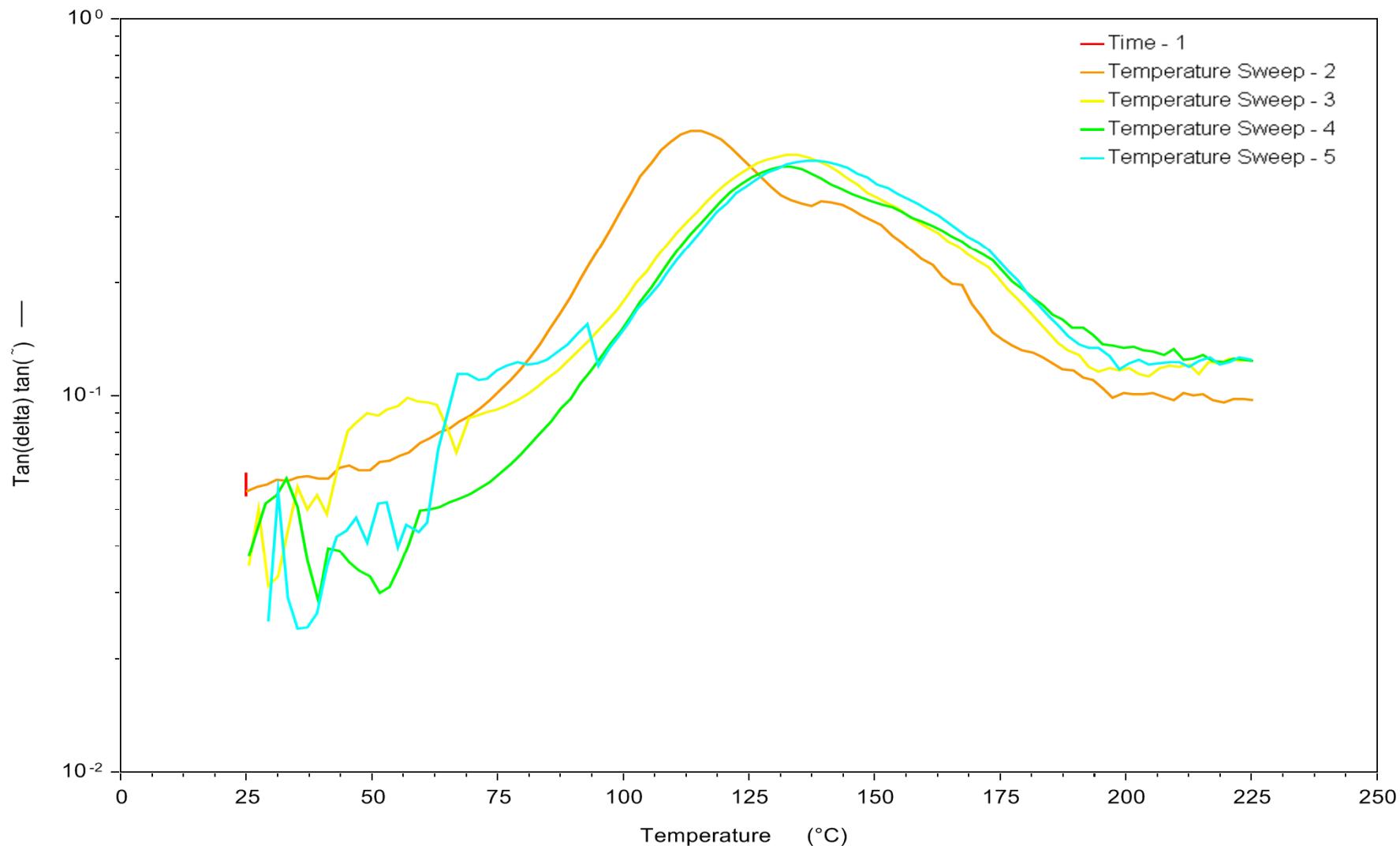
# Raw Data from the ARES 2 Rheometer

Structural 10 lbs. Foam bar (1)



# Raw Data from the ARES 2 Rheometer

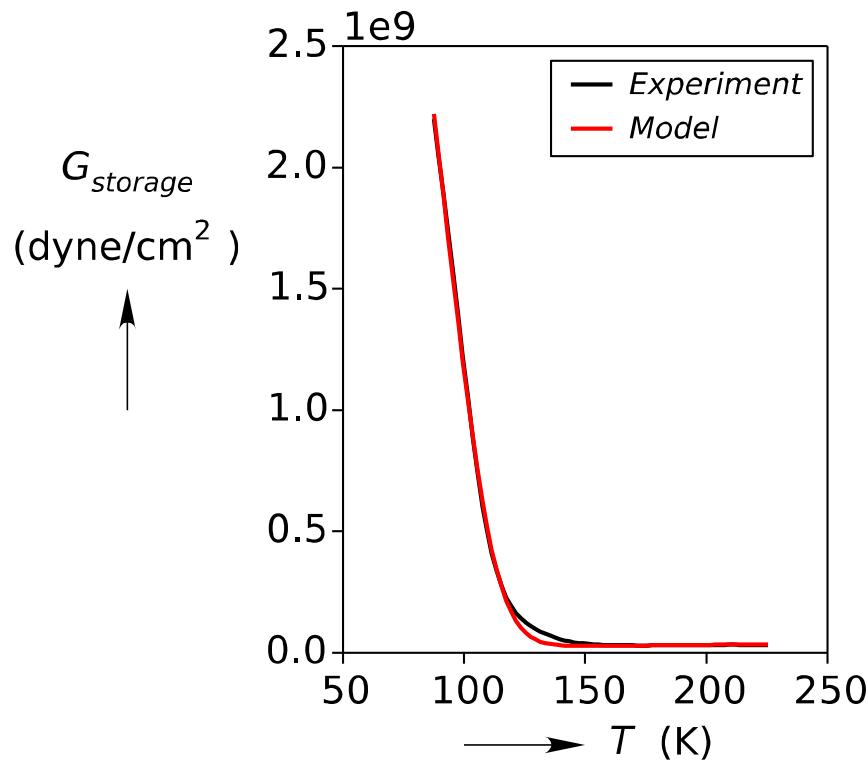
Structural 10 lbs. Foam bar (1)



# Viscoelastic Model Fitting Approach

- Define  $T_g$  as the peak of the  $G''/G'$  ( $\tan \delta$ )
- Focus on Data At and Above the Glass Transition Temperature  
Assume:
  - Linear Viscoelastic Behavior
  - Time-Temperature Superposition (TTS)
  - Rheological Simplicity
  - WLF Form of the TTS
  - No Temperature dependences of the rubbery and glassy storage shear moduli
- Fitting Procedure 1:
  - Fit rubbery and glassy shear moduli from  $G'$
  - Fit WLF  $C_1$ ,  $C_2$ ,  $\tau$ , and  $\beta$  directly to the  $G'$  vs.  $T$  curve using sierra or a semi-analytic code
    - Assumed a fixed number and distribution of prony series times for fitting the Williams-Watts representation of the shear relaxation function

# Fitting Results



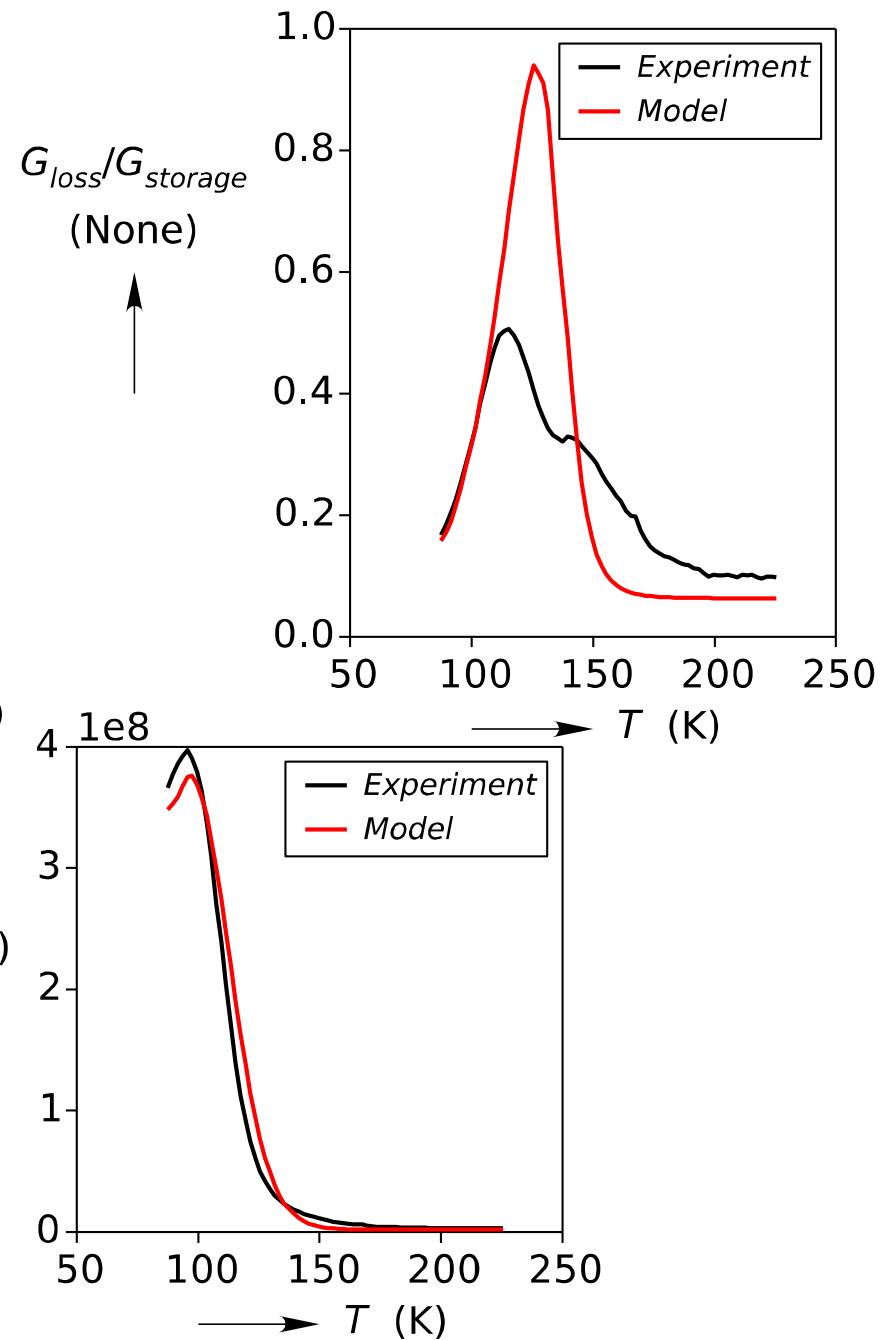
$$C_1 = 11.9499$$

$$C_2 = 98.591 \text{ } C$$

$$T_{ref0} = 115.47 \text{ } C$$

$$WW_{\tau} = 0.9216E-3 \text{ } s$$

$$WW_{\beta} = 0.181$$



# Concerns

- **Model Assumptions:**
  - We are deep in the glass below 70C, so fitting this region of the data is probably not a good idea
    - Ignore  $T < 100$  C during fits?
  - Curing matrix. Is the behavior sufficiently stable during the test?
- **Ferry's Data on Neat PU:**
  - $T_0, C_1, C_2 = 283$  K, 8.86, and 101.6 K
  - $T_0, C_1, C_2 = 231$  K, 16.7, and 68.0 K for a PU material cross-linked with toluene diisocyanate and trimethylol propane
- **Our Fit**
  - $T_0, C_1, C_2 = 388$  K, 11.9, and 98.6 K

## Two Possible Viscoelastic Model Fitting Approach

- Define  $T_g$  as the peak of the  $G''/G'$  ( $\tan \delta$ )
- Focus on Data At and Above the Glass Transition Temperature  
Assume:
  - Linear Viscoelastic Behavior
  - Time-Temperature Superposition (TTS)
  - Rheological Simplicity
  - WLF Form of the TTS
  - No Temperature dependences of the rubbery and glassy storage shear moduli
- Fitting Procedure 1:
  - Fit rubbery and glassy shear moduli from  $G'$
  - Fit WLF  $C_1$ ,  $C_2$ ,  $\tau$ , and  $\beta$  directly to the  $G'$  vs.  $T$  curve using sierra or a semi-analytic code
    - Assumed a fixed number and distribution of prony series times for fitting the Williams-Watts representation of the shear relaxation function

# Brute Force Fitting the Bulk/Thermal Relaxation Function and Coefficients of Thermal Expansion using a Thermal-Mechanical Analyzer

- **Specimen Preparation**
  - KCP Curing Schedule
- **TMA Protocol**
  - Hold at 180 C for 30 minutes to reach physical equilibrium
  - Cool at 3 C/min holding a reference force to -40 C
  - Reheat at 3 C/min to 180C
  - Measure the height as a function of time
- **Fitting Procedure**
  - Fit the reheat curve
  - **Simultaneously fit:** The Williams-Watts  $\tau$ ,  $\beta$  directly associated with the volumetric/thermal relaxation function and the glassy and rubbery thermal expansion coefficients

# Brute Force Fitting the Bulk/Thermal Relaxation Function and Coefficients of Thermal Expansion using a Thermal-Mechanical Analyzer

