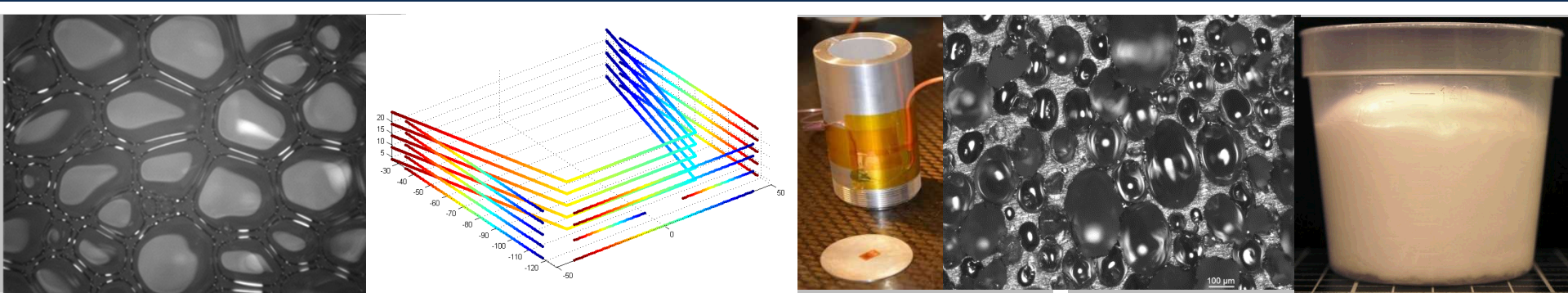


Exceptional service in the national interest



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

31st Polymer Processing Society, Seoul, South Korea

Session G9, June 11, 2015



The Challenge: Predicting How Manufacturing Conditions Impact Component Dimensional Stability

A Typical Process

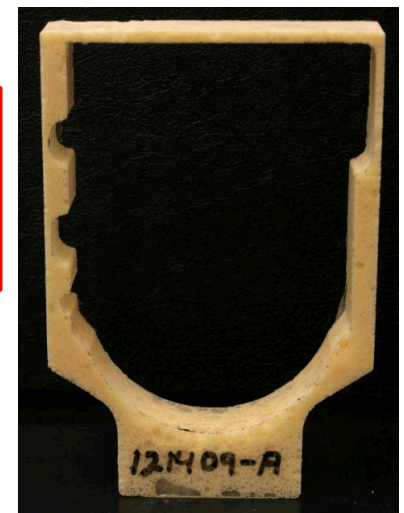
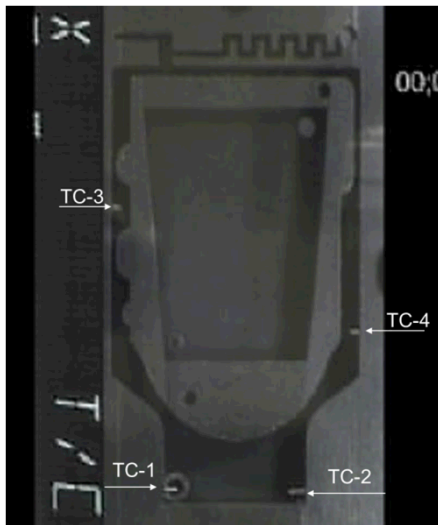
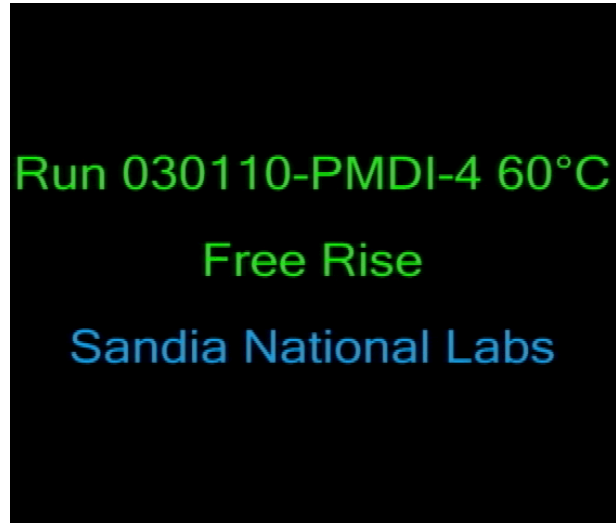
Injection,
foaming and
initial curing
at lower T

Run 030110-PMDI-4 60°C
Free Rise
Sandia National Labs

Oven time
at higher T
to make
sure it is
fully cured

Remove
from mold –
predict cure
and thermal
stresses

Predict
shape and
size over
years



Polyurethane (PMDI) Foams

Application Space

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

The Problems

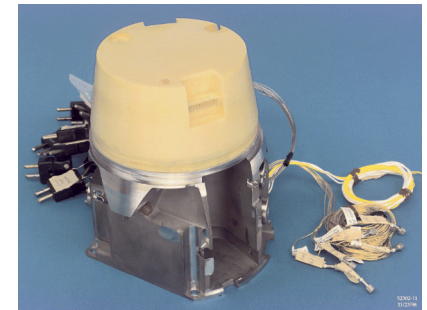
- Voids, Density Variations, **Residual Stress**
- **Short Term**: Meet Tight Geometric Specifications
- **Long Term**: Long term shape change/loss of component function

Objective

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



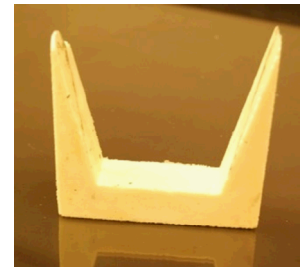
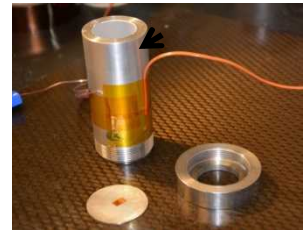
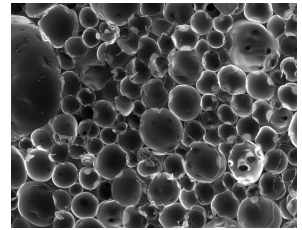
PU has a short pot-life: models can help reduce defects and improve filling process



Mock component encapsulated with PMDI from "KCP Encapsulation Design Guide" (Mike Gerding, UUR)

Outline

- Solid Model Overview
- “Basic” Solid Model Characterization
 - Shear Moduli, Viscoelastic Shear and Bulk Relaxation
 - Matrix Cure Kinetics and the Glass Transition
- Advanced Solid Model Characterization—Pop-off test
 - Deconvolute cure shrinkage, Modulus evolution (cure), and thermal expansion
 - Can we model this simple experiment?
- Validation Experiments – “Staple” mold
 - Manufacturing Conditions Measurements
 - Dimensional Stability Measurements and Calculations



Three Stages of Material Response

Stage I

Fluid

Pre-Gel

(0-10³ 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

(10³– 10⁴ 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

(10⁴ + seconds)

Residual stresses, density, and properties vary spatially

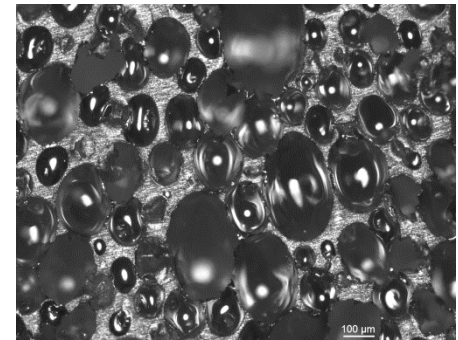
Both long and short term shape change is possible as different parts of the foam relax at different rates

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 CO₂
 - 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

Pressure

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

Shear Deformation
Matrix Cure

Glass Transition Evolution

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

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

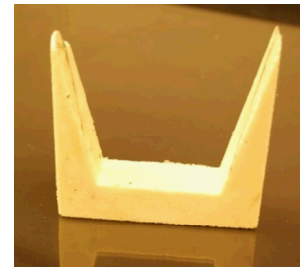
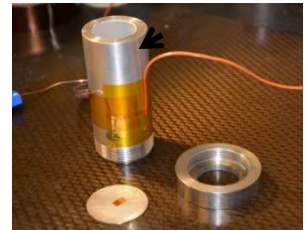
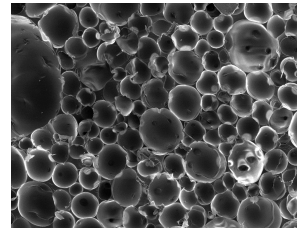
Shear Modulus

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

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

Outline

- Solid Model Overview
- “Basic” Solid Model Characterization
 - Shear Moduli, Viscoelastic Shear and Bulk Relaxation
 - Matrix Cure Kinetics and the Glass Transition
- Advanced Solid Model Characterization—Pop-off test
 - Deconvolute cure shrinkage, Modulus evolution (cure), and thermal expansion
 - Can we model this simple experiment?
- Validation Experiments – “Staple” mold
 - Manufacturing Conditions Measurements
 - Dimensional Stability Measurements and Calculations



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 T_g

2) Thermal Mechanical Analysis

Isofrequency

Temperature Sweep of a
“Fully Cured” Foam Bar

- Coefficients of Thermal Expansion
- Bulk/Thermal Relaxation Function

3) ATR Infrared Spectroscopy

Various Isothermal
Spectral Measurements
of the “Dry Foam”

- Matrix Cross-linking Reaction Kinetics

4) DSC

Isothermal and Cyclic
Temperature Sweeps of
“Dry Foam”

- Isothermal Reaction Kinetics
- Glass Transition Evolution

5) Uniaxial Compression

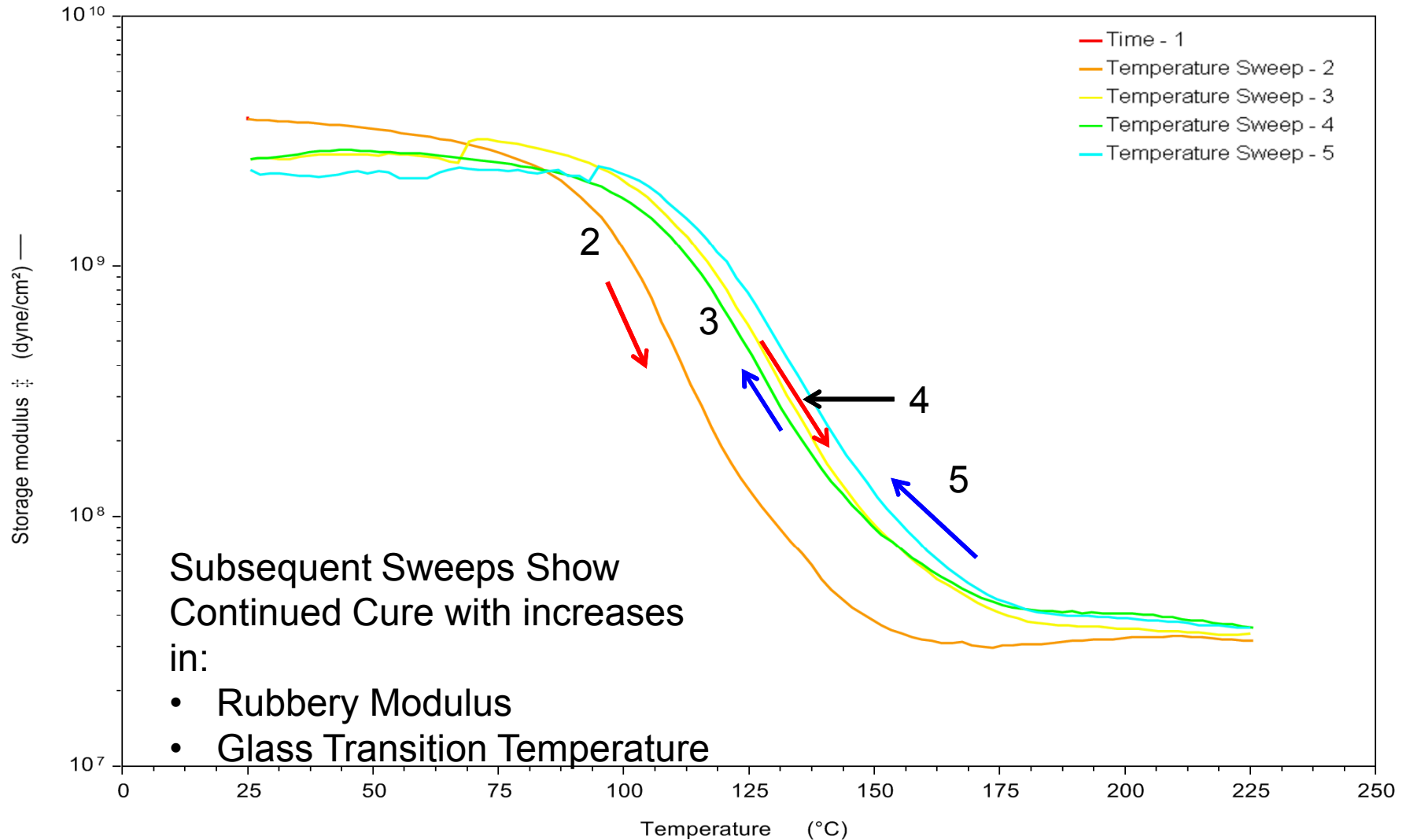
Isothermal and Cyclic
Temperature Sweeps of
“Dry Foam”

- Yield phenomena (Deformation Induced Mobility)

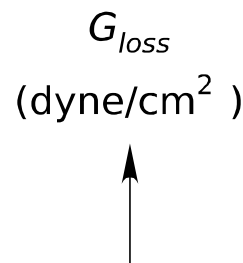
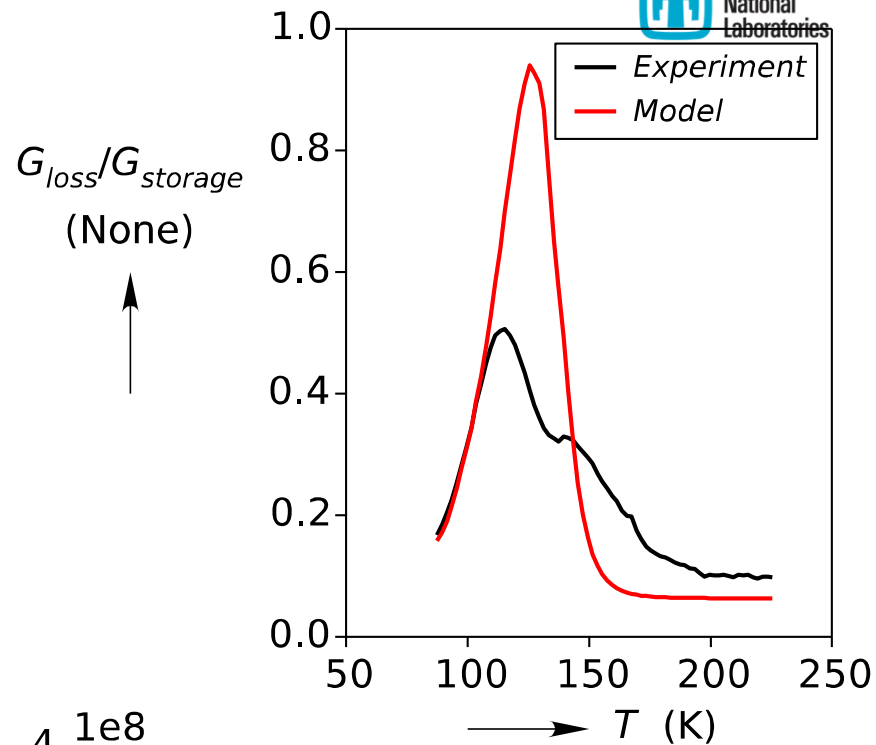
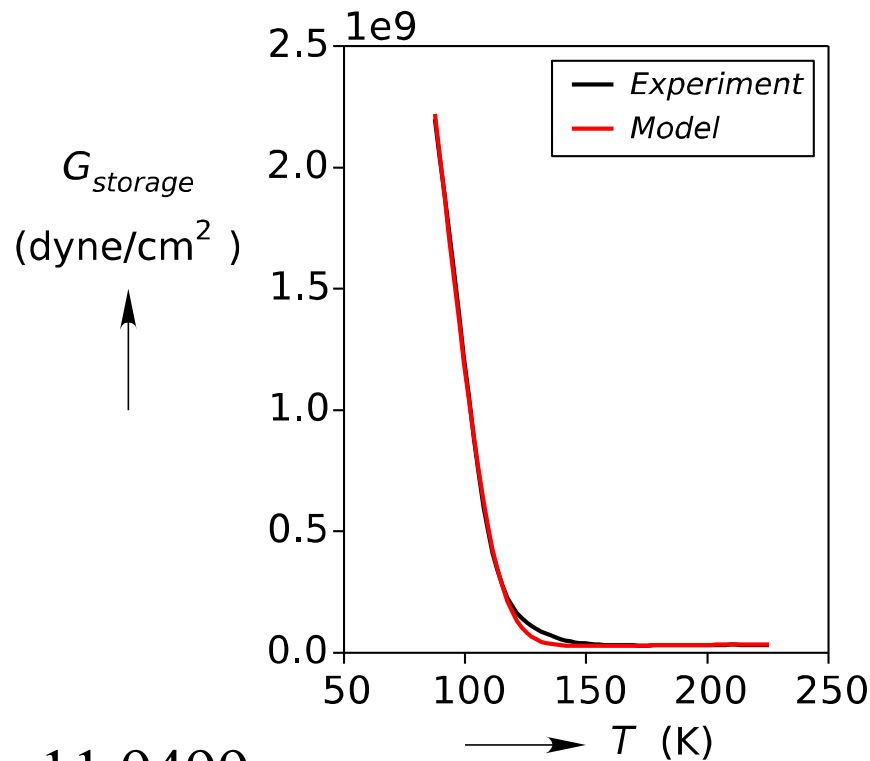
6) Cure Shrinkage and
Rubbery Shear Modulus
Evolution during Cure
“Dry Foam” Dimensional
change measurements
during cure

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



$$C_1 = 11.9499$$

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

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

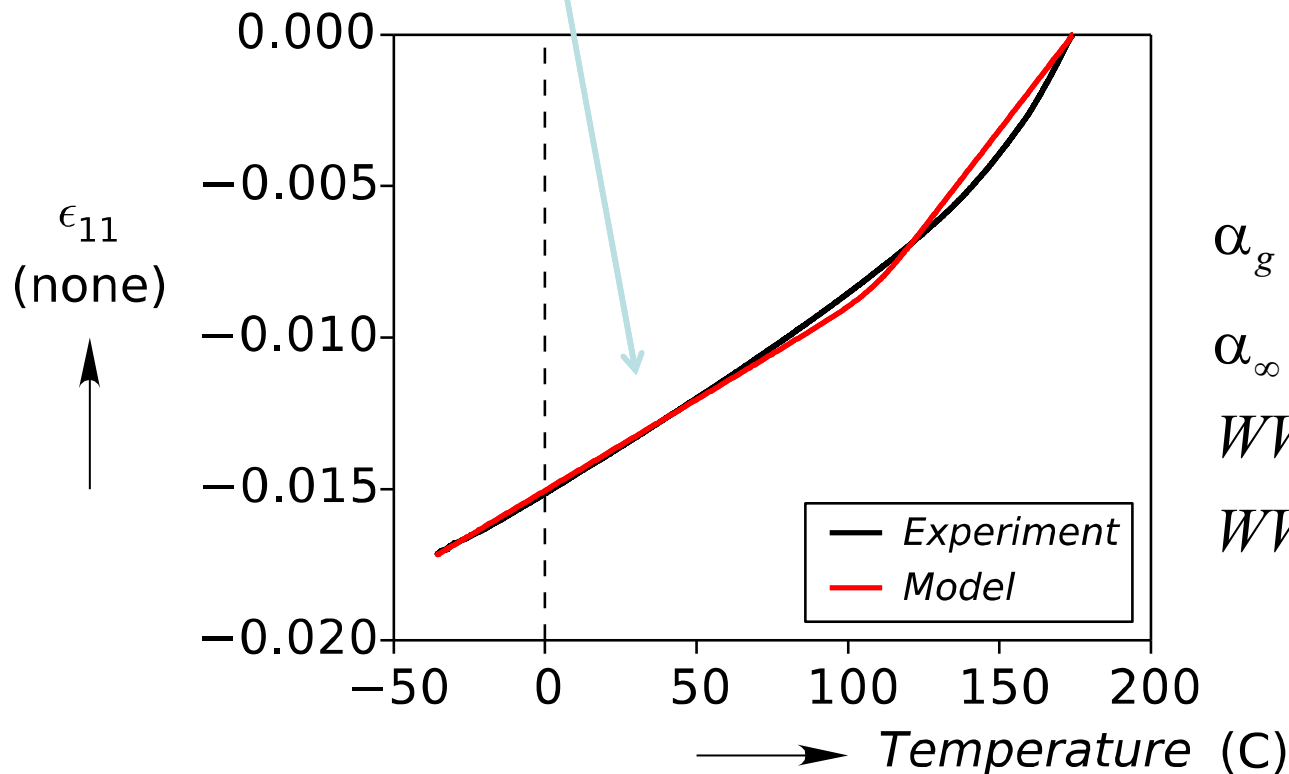
$$WW_\tau = 0.9216 \times 10^{-3} \text{ s}$$

$$WW_\beta = 0.181$$

2) Brute Force TMA Fitting

Stable Glassy Response

“Curve” Shows evidence of Additional Matrix Cure (shrinkage)



$$\alpha_g = 188E-6 \quad K^{-1}$$

$$\alpha_\infty = 408E-6 \quad K^{-1}$$

$$WW_\tau = 0.018336 \quad \text{sec}$$

$$WW_\beta = 0.176101$$

3) Single Extent of Reaction Calibration from ATR IR Spectroscopy

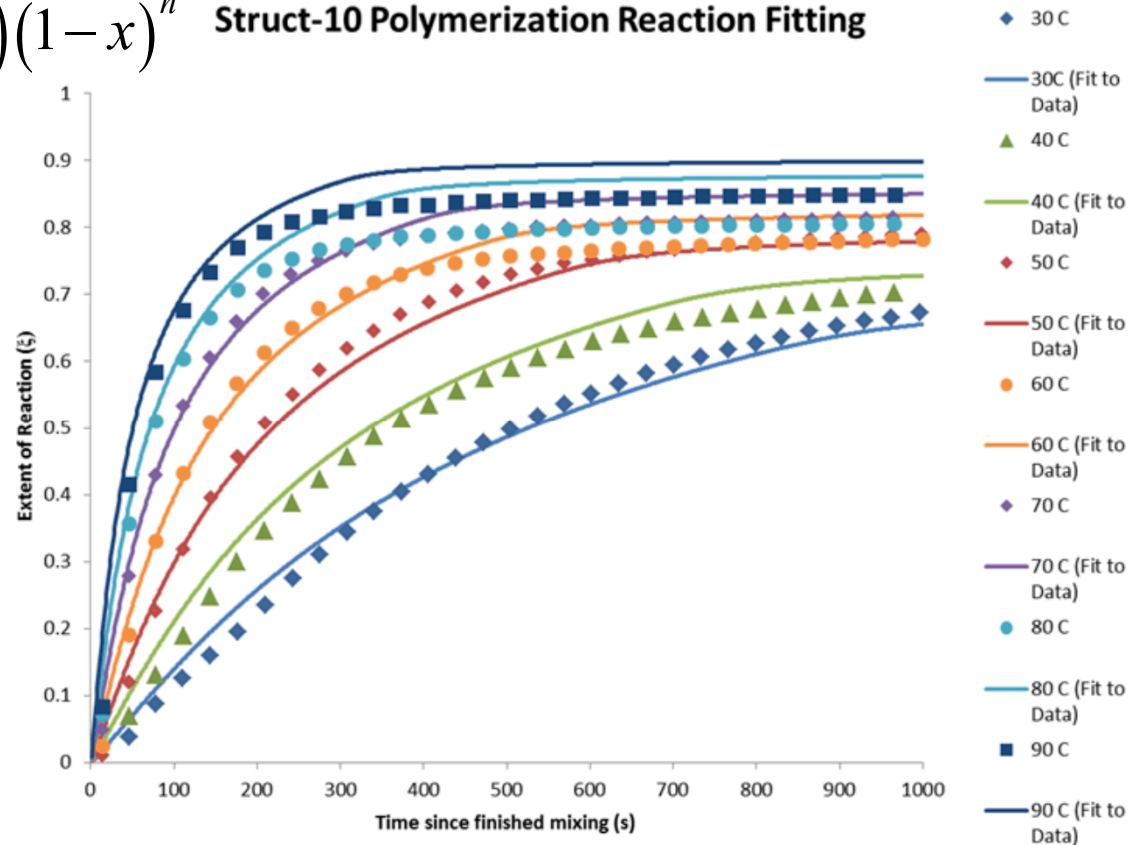
Reaction Kinetics Follow a Modified Kamal 1974 Single Reaction Extent Description.
Vitrification arresting of the cure kinetics is assumed to follow the simple Debenidetto Form

$$\frac{\partial x}{\partial t} = \frac{\left(k_0 \exp\left(-\frac{E_a}{RT}\right) \right)}{(1 + wa)^\beta} (b + x^m)(1 - x)^n$$

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

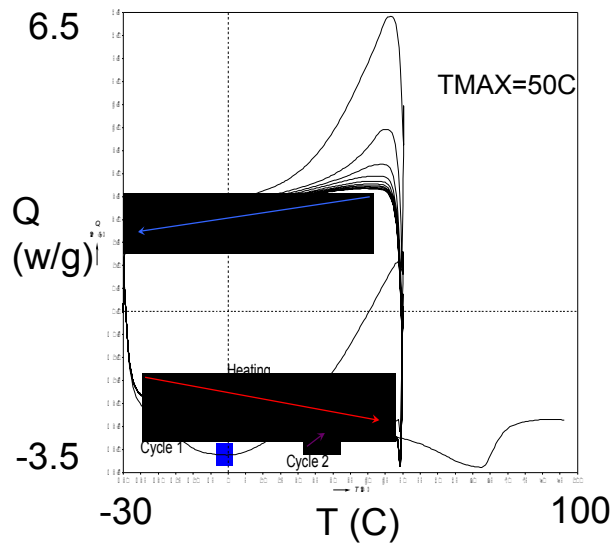
$$Tg[x] = \frac{Tg_0 (1 - x) + x \Lambda Tg_\infty}{1 - x + \Lambda x}$$

Struct-10 Polymerization Reaction Fitting

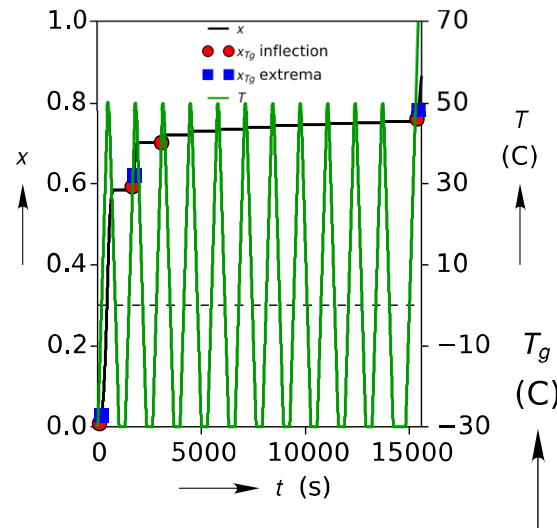


4) Differential Scanning Calorimetry to Estimate vs. x T_g vs. x

- 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**

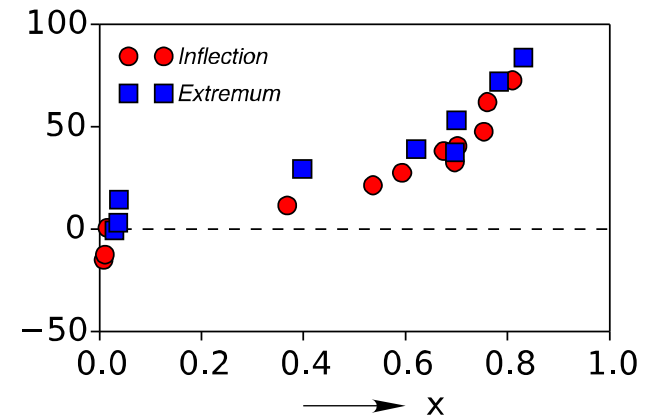


- 10 mg sample
- Cycle the temperature between -30 C and TMAX
- Ramp up to 100+C at end of test (10 cycles)



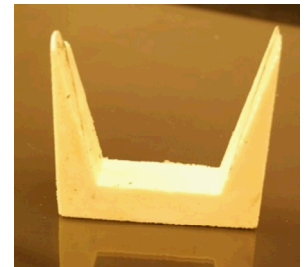
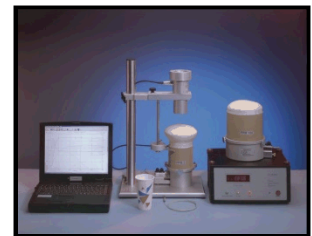
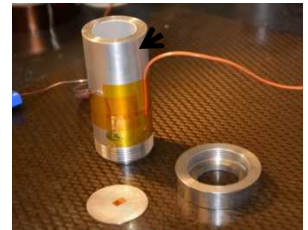
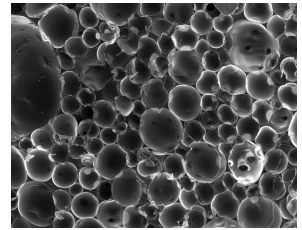
- Each test (TMAX varies) gives several point for T_g as $f(t)$
- Integrate the t-T history with assumed kinetic reaction fit to translate t to extent of cure x .

Collection of Data from 3 Tests with different TMAX cycle temperatures



Outline

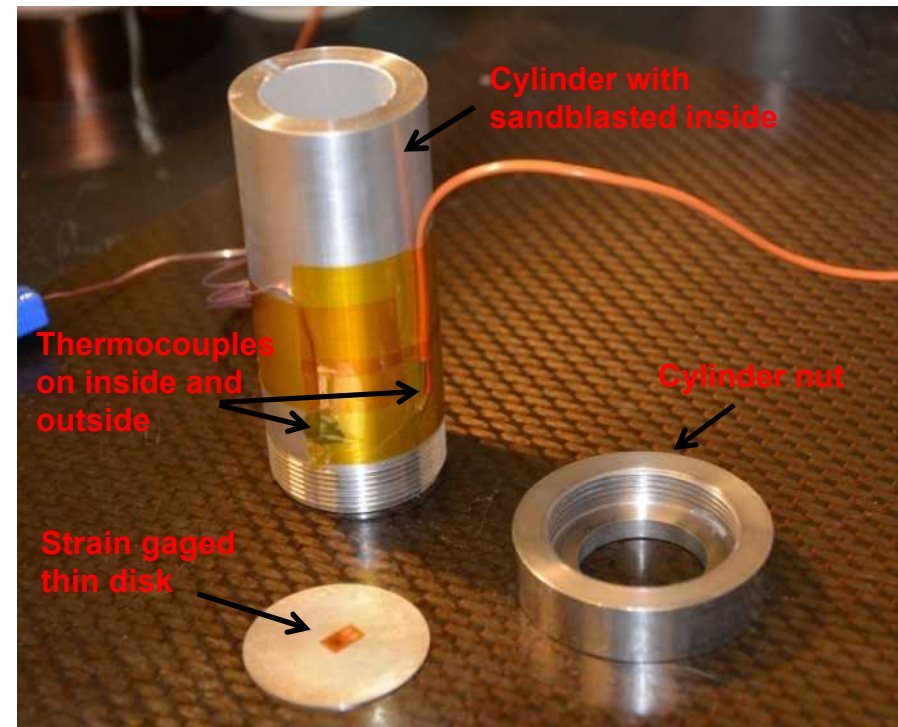
- Solid Model Overview
- “Basic” Solid Model Characterization
 - Shear Moduli, Viscoelastic Shear and Bulk Relaxation
 - Matrix Cure Kinetics and the Glass Transition
- Advanced Solid Model Characterization—Pop-off test
 - Deconvolute cure shrinkage, Modulus evolution (cure), and thermal expansion
 - Can we model this simple experiment?
- Validation Experiments – “Staple” mold
 - Manufacturing Conditions Measurements
 - Dimensional Stability Measurements and Calculations



We Tried for a Simple Experiment

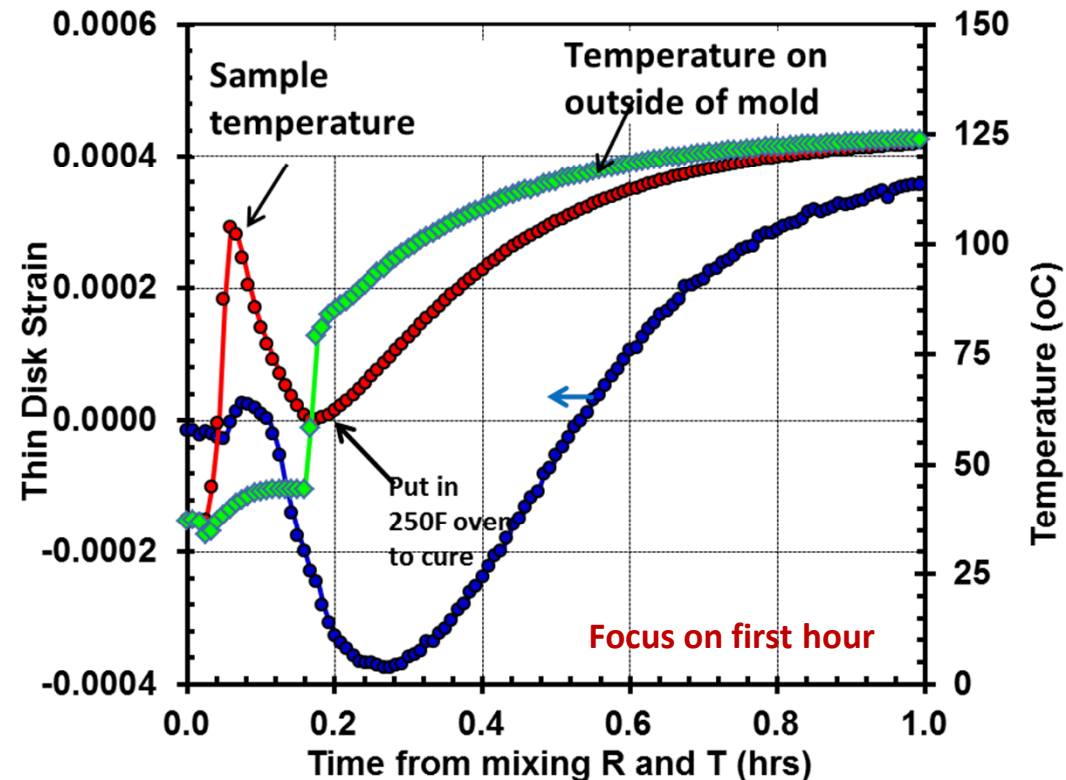
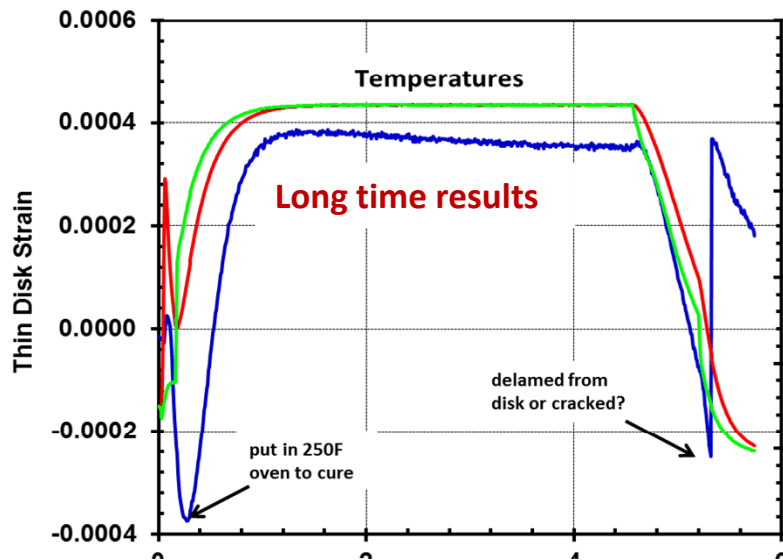
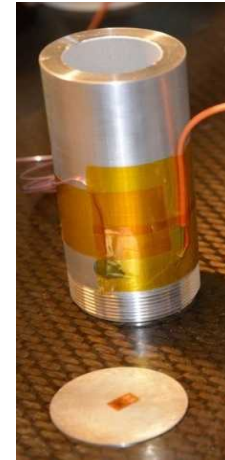
- Previously used at Sandia to look at stresses from curing epoxies.
- Dry Foam. Foam precursors removed of water – No foaming reaction
 - Shrinkage of polyurethane only, no effects of gas diffusion
 - Assume matrix shrinkage is the same for the “dry” and “wet” foams
- Cure schedule (Approximated from 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?

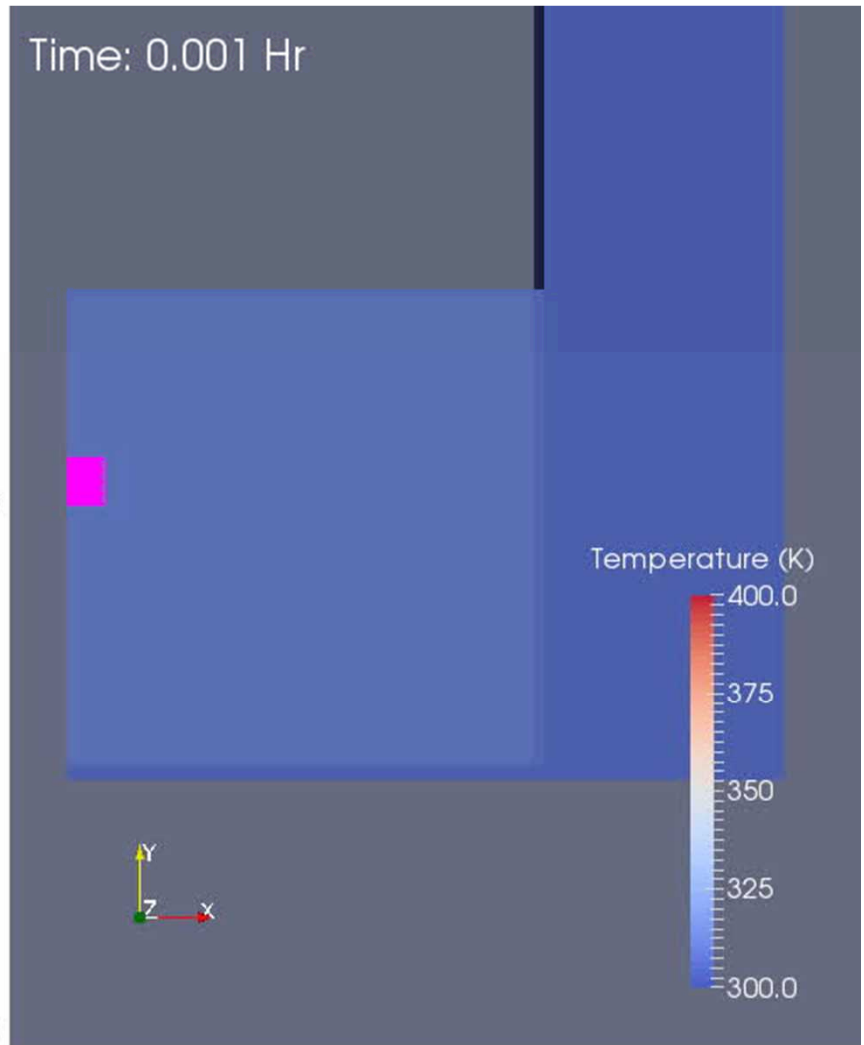
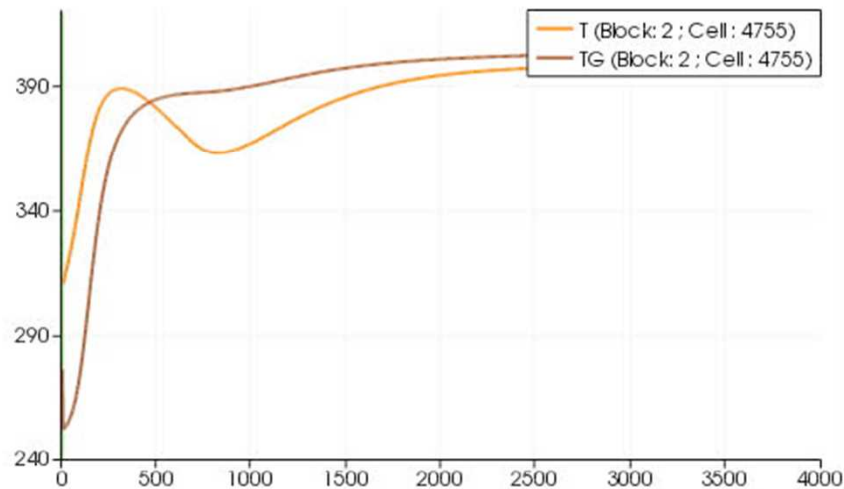
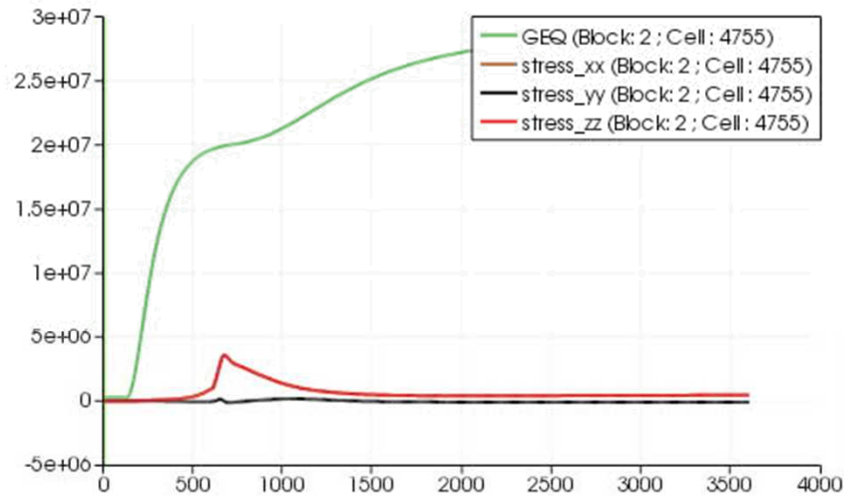


Pop-Off Test Results

- 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

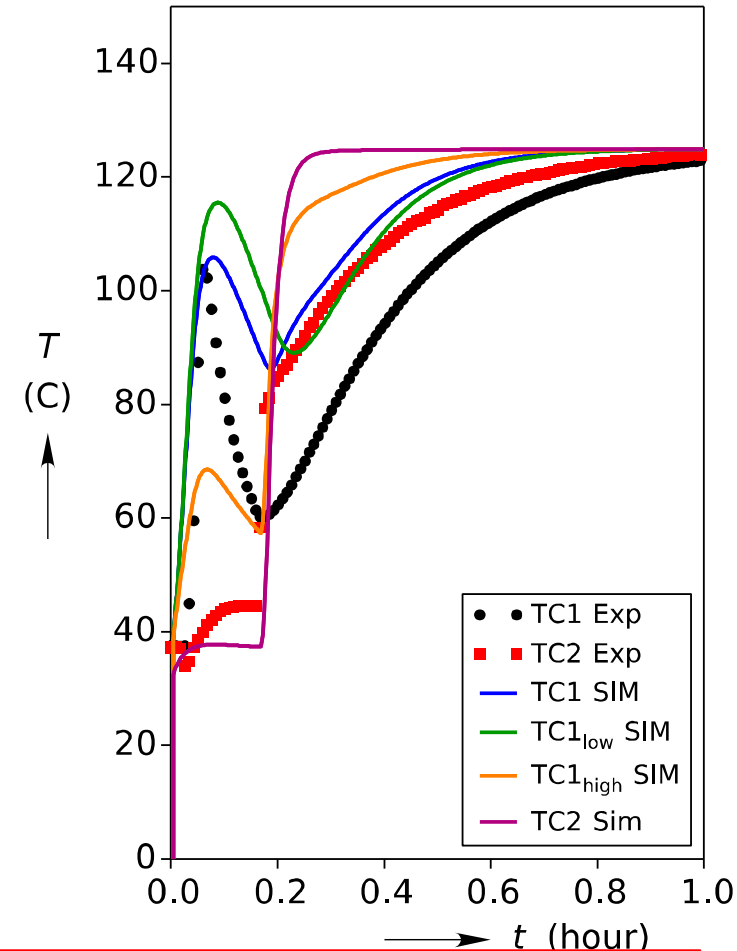
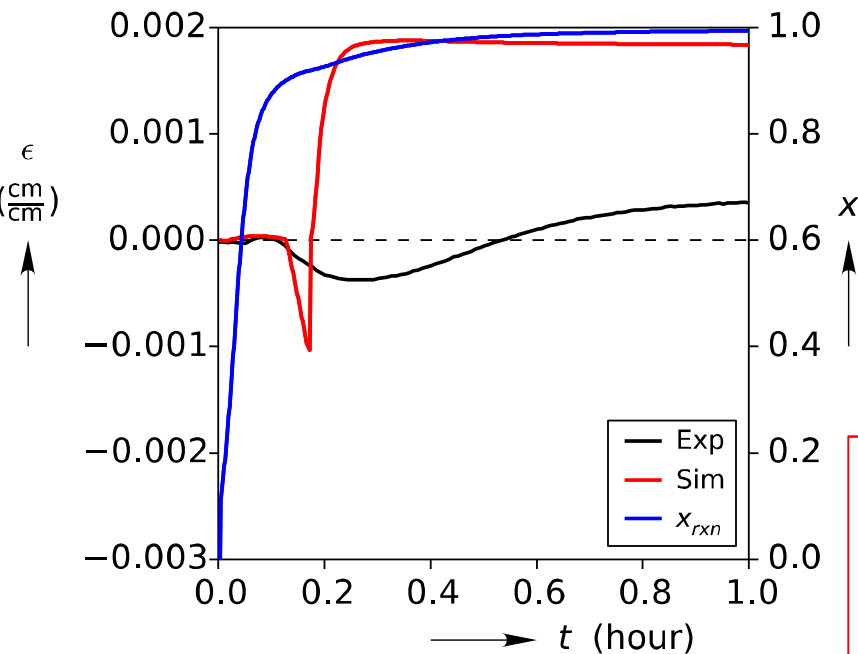


Pop-Off Test: Comparison to Experiment

Qualitative thermal behavior predicted

Uncertainty in thermocouple location creates
large uncertainty in model fidelity

Experimental cooling rates faster than predicted

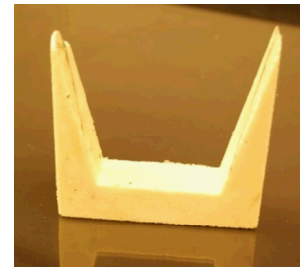
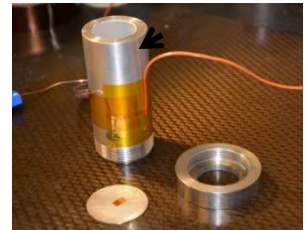
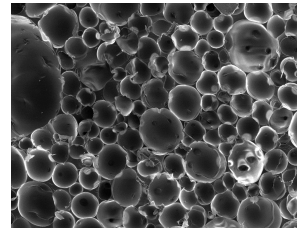


Qualitative strain behavior captured. Quantitative predictions
require thermal, curing, and modulus evolutions to be accurate

Question equivalence between dry foam
and true foam material parameters

Outline

- Solid Model Overview
- “Basic” Solid Model Characterization
 - Shear Moduli, Viscoelastic Shear and Bulk Relaxation
 - Matrix Cure Kinetics and the Glass Transition
- Advanced Solid Model Characterization—Pop-off test
 - Deconvolute cure shrinkage, Modulus evolution (cure), and thermal expansion
 - Can we model this simple experiment?
- Validation Experiments – “Staple” mold
 - Manufacturing Conditions Measurements
 - Dimensional Stability Measurements and Calculations



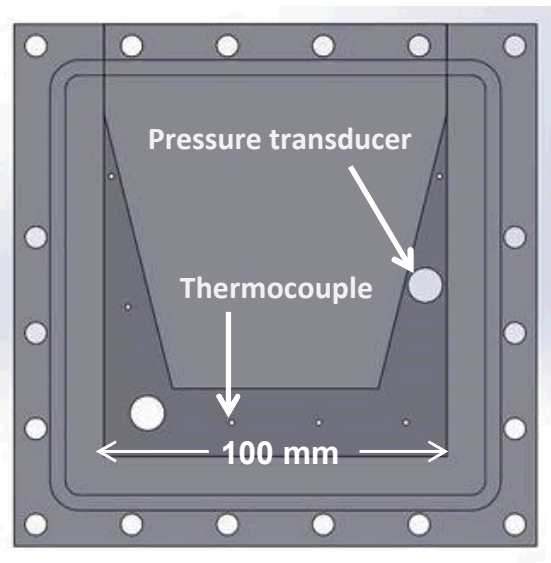
Cure Shrinkage Monitoring

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/ft³
 - 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

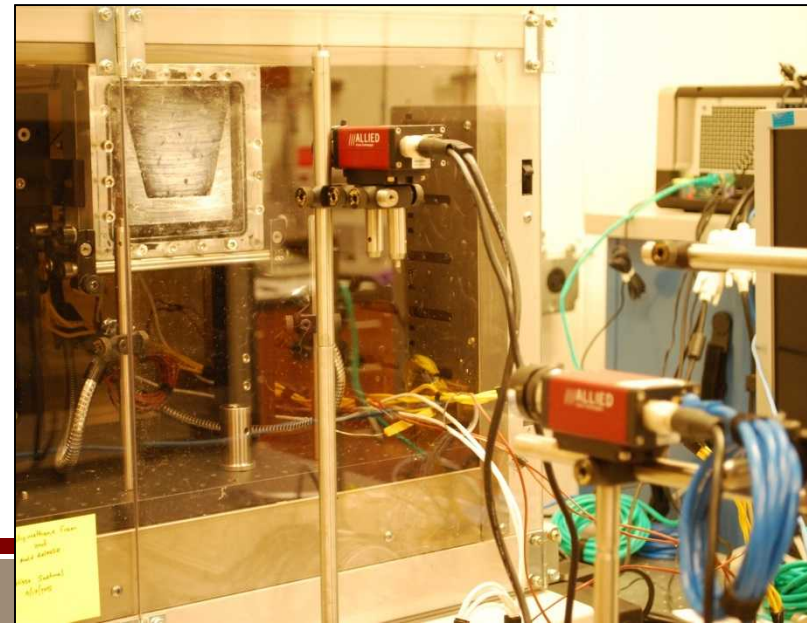


CMM measures dimensional changes



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

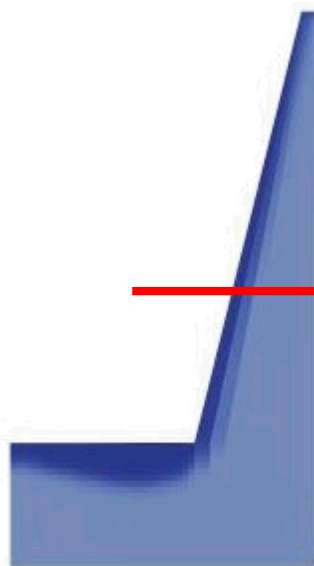
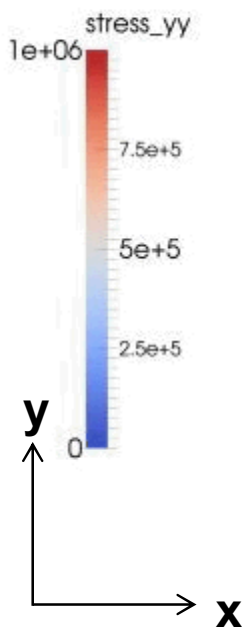
**1% Volume Strain on
100% Cure**

**10% Volume Strain
on 100% Cure**

**15% Volume Strain on
100% Cure**

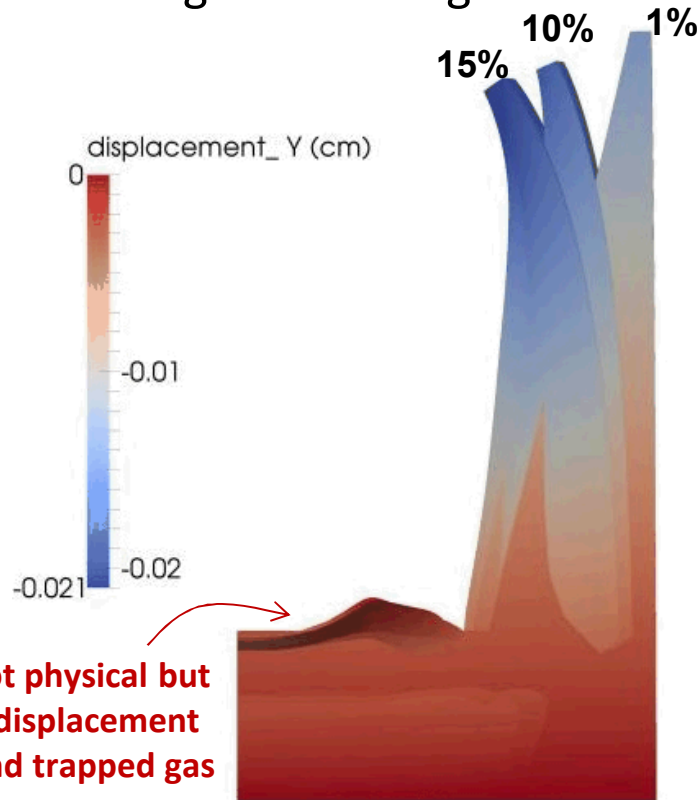
Increasing
Stress
Magnitude

Low stress region due to filling model
over-predicting trapped gas, creating
spurious low density area

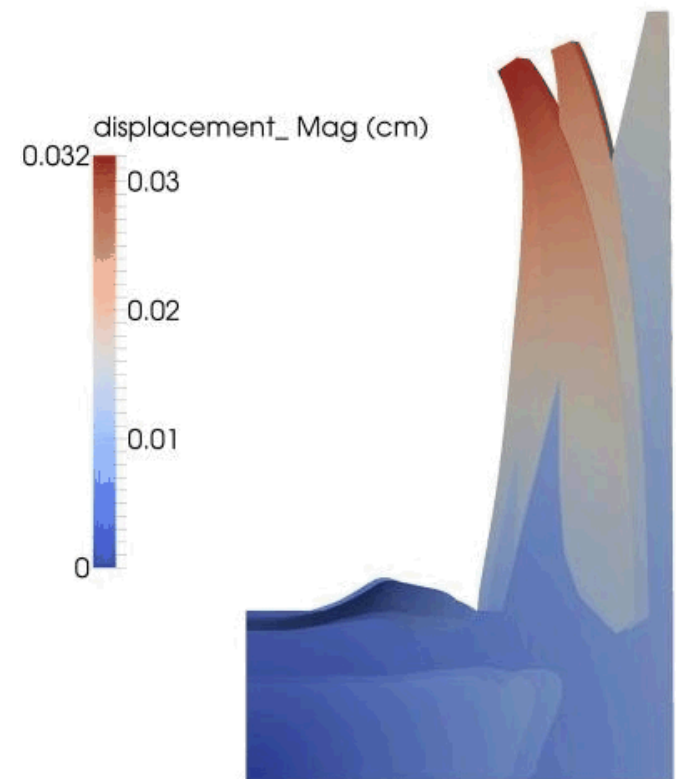


Staple Mold Predictions: Dimensional Stability

- 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



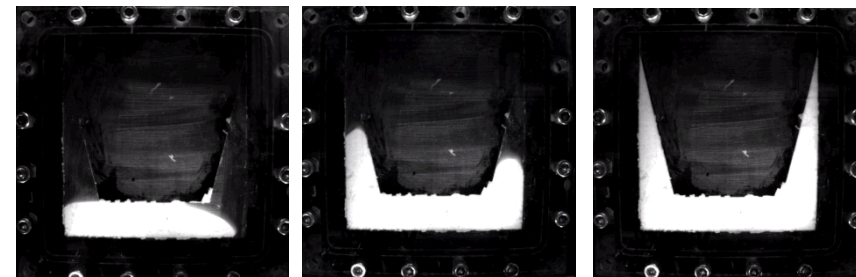
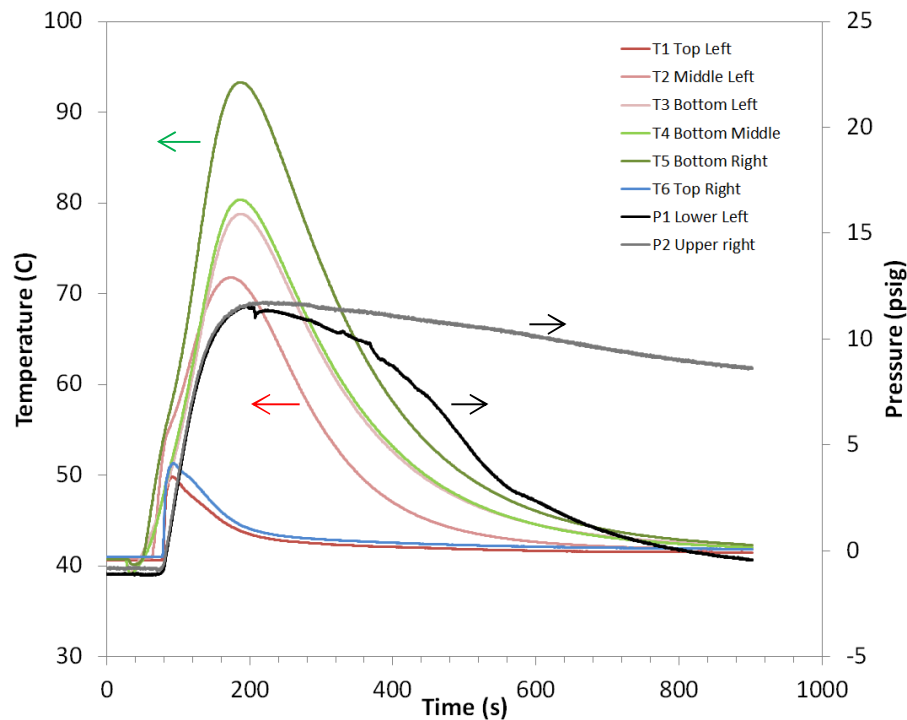
Displacements (cm) amplified by 100



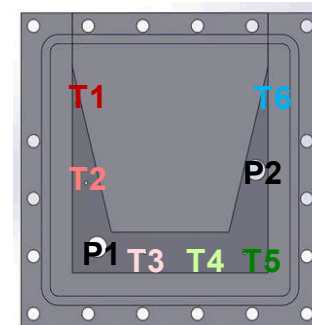
Displacements of 0.03 cm correspond to about 0.3% of the initial long side of the staple

Foaming U-shaped staple mold

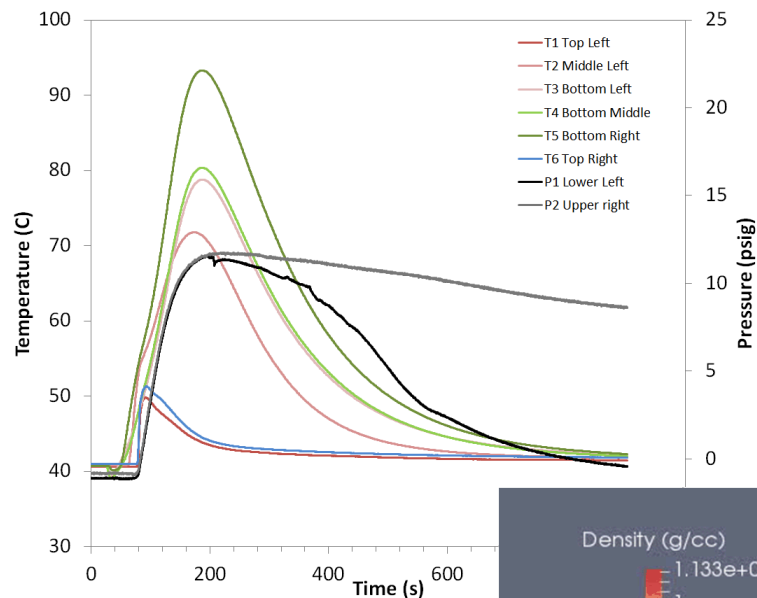
- Over many repeats, temperature, pressure, and flow profile are remarkably repeatable
- Imperfectly symmetric fill common
- Pressure rises as foam expands, relaxes at lower corner and stays positive at P2.



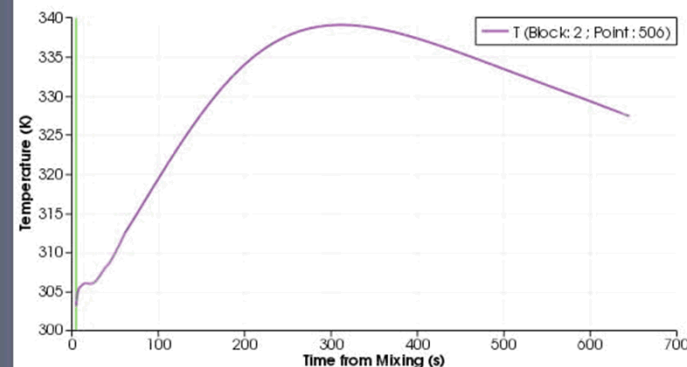
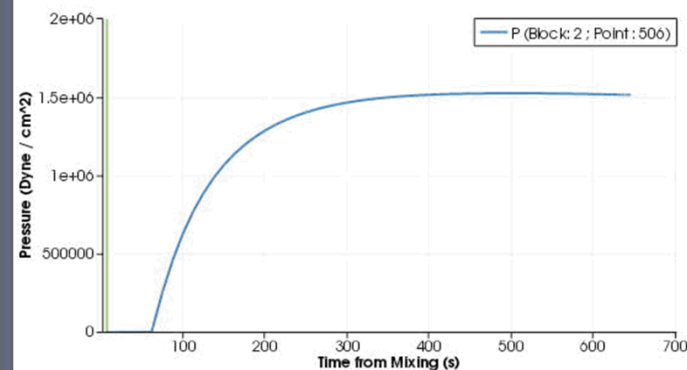
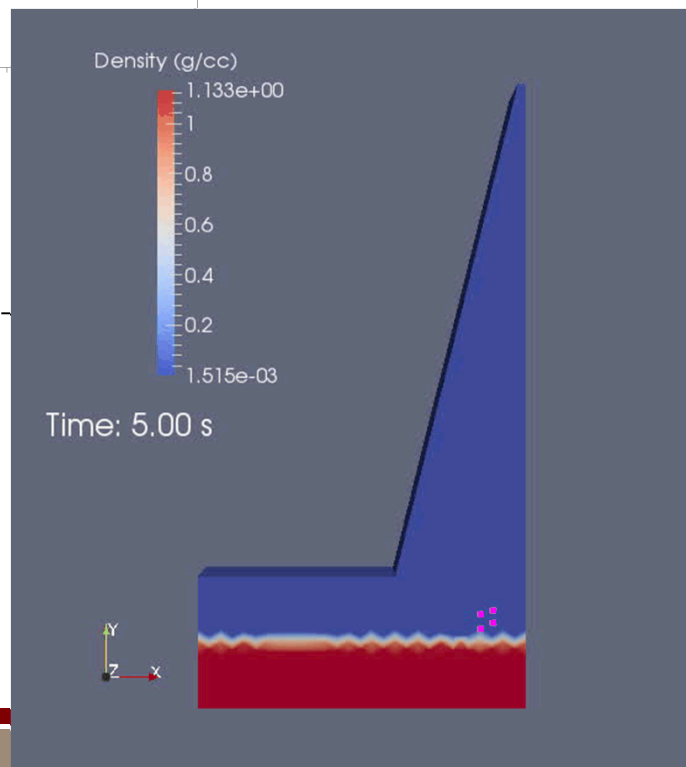
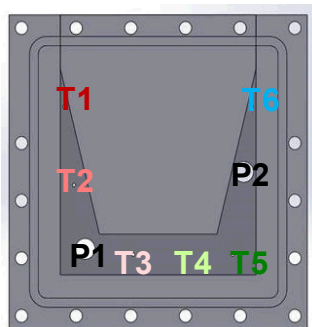
Some slight asymmetry due to bias of initial injection



U Staple Simulation Comparison

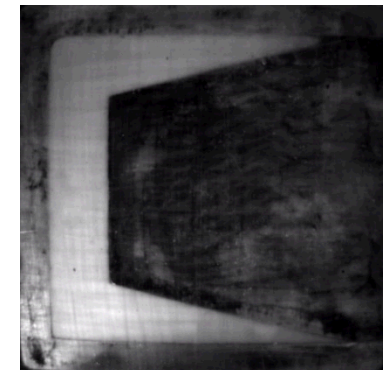
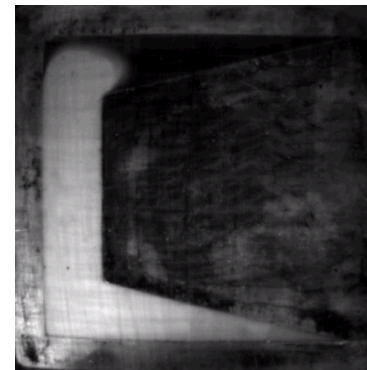
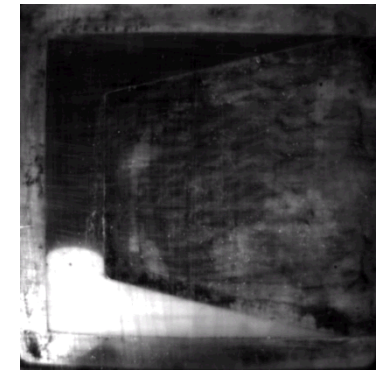
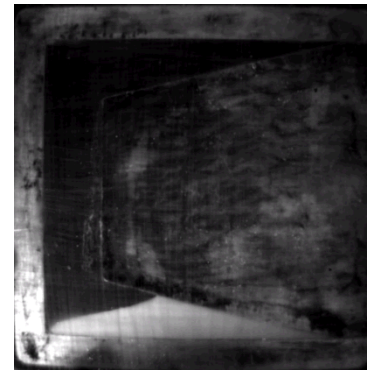
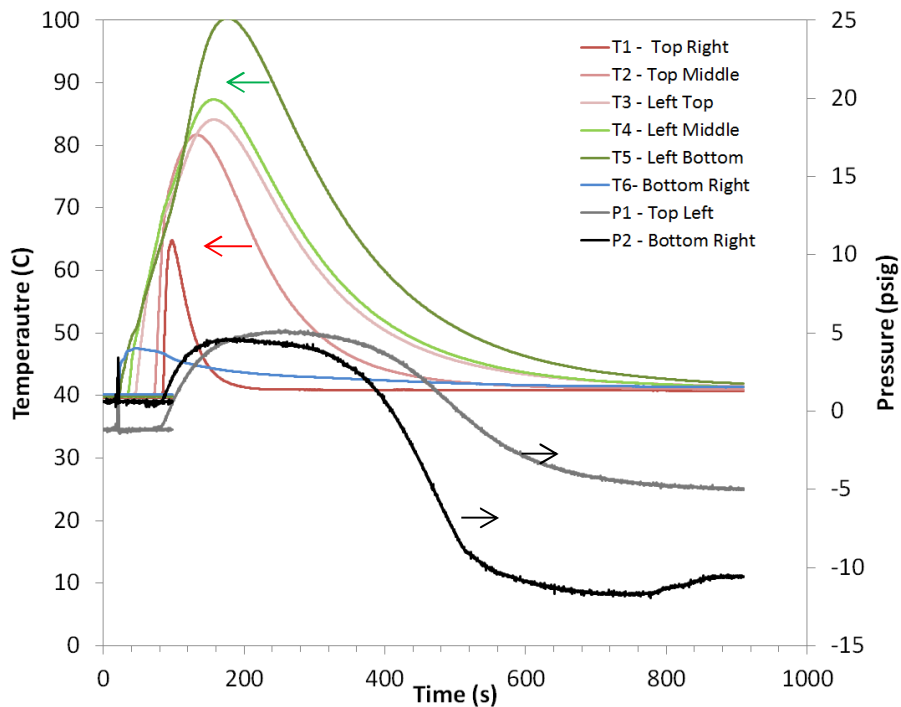
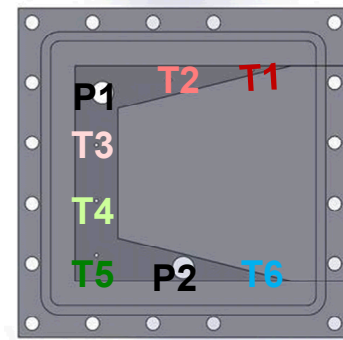


- Simulation Temperature at the hot spot is $\sim 40^{\circ}\text{C}$ instead of 50°C above the initial resin temperature. Cool down is much slower.
- Pressure rise is reasonable, but simulation pressure is roughly 21 psi compared with the experiments 12 psi



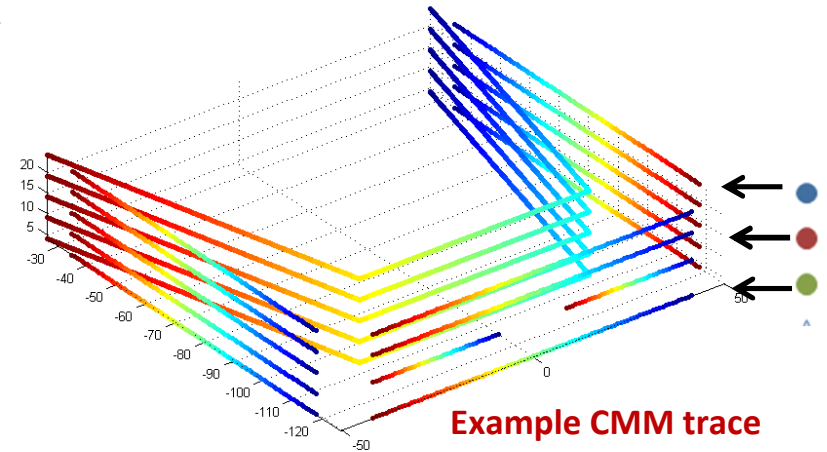
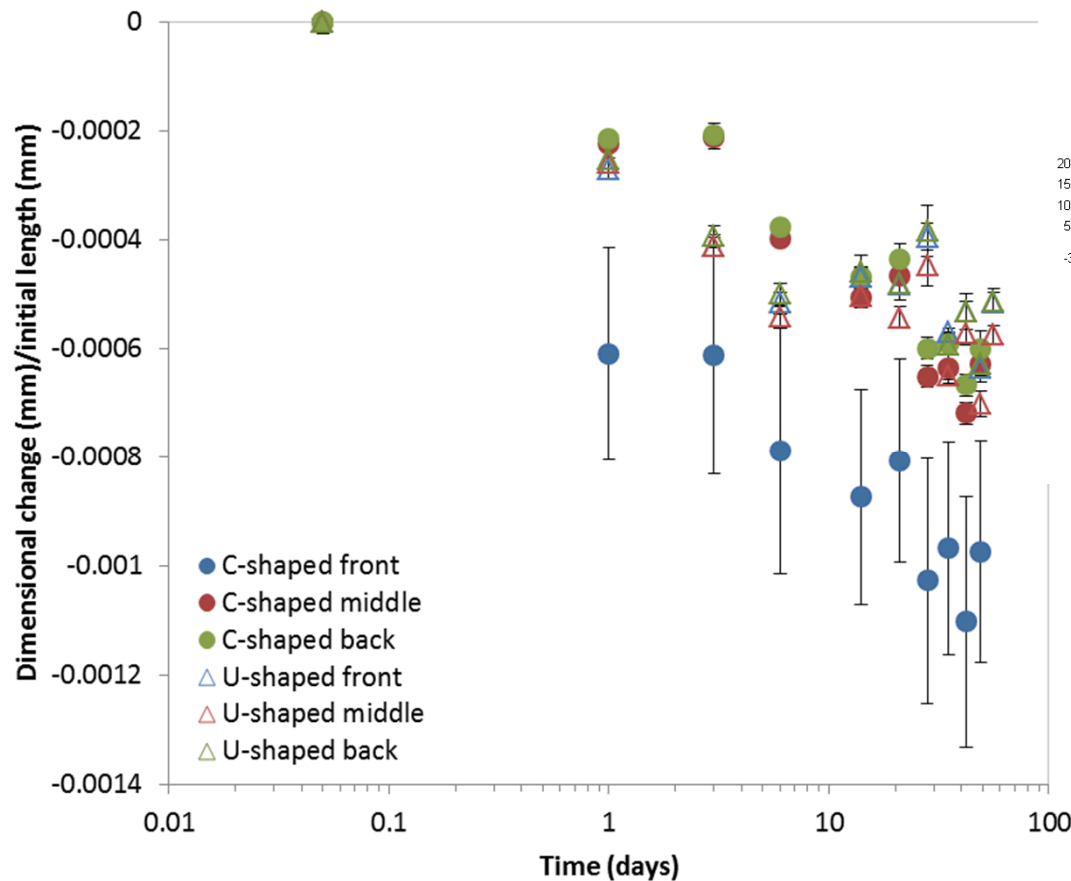
Foaming C-Shaped Staple Mold

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



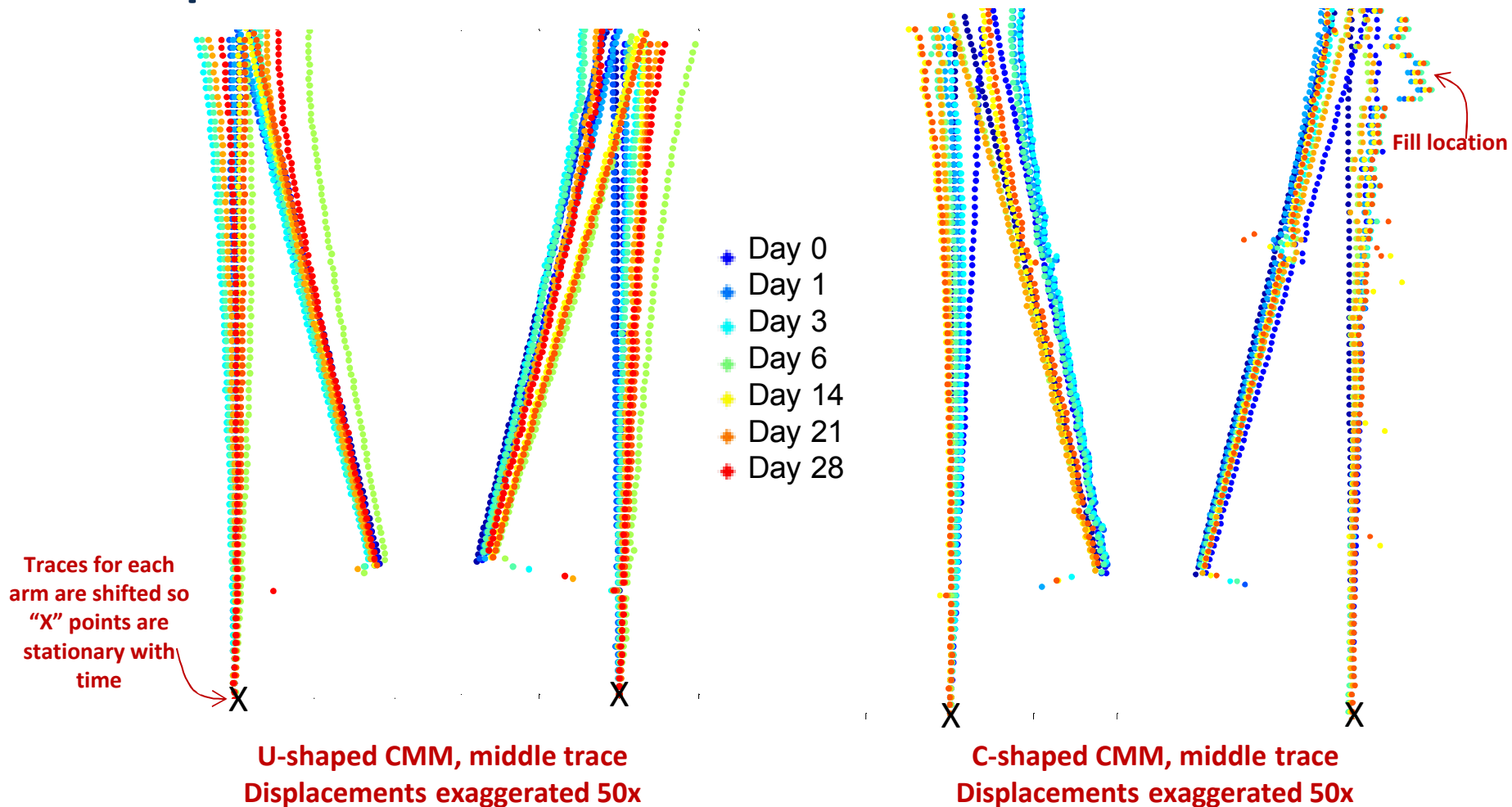
Long-Time Shrinkage

- 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

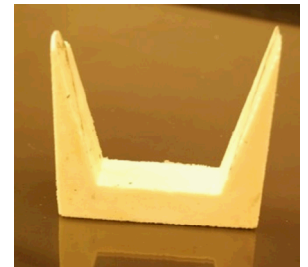
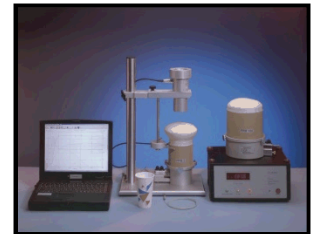
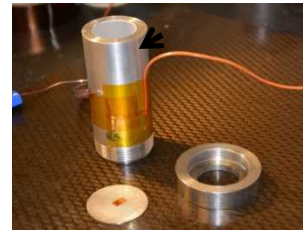
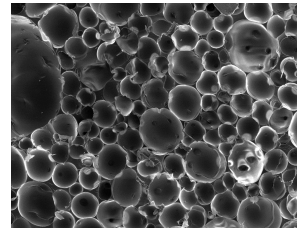
- Initial experiment/model comparisons show that the model matches experiments qualitatively
 - Improvements to experiments will target sensitive parameters identified by model (thermocouple location, ranges of foam density)
 - Improvements to model will target improved material parameters, boundary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

Acknowledgements

Melissa Soehnel, SNL, Experimental assistance

Henry Lorenzo, SNL, CMM measurements

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.



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

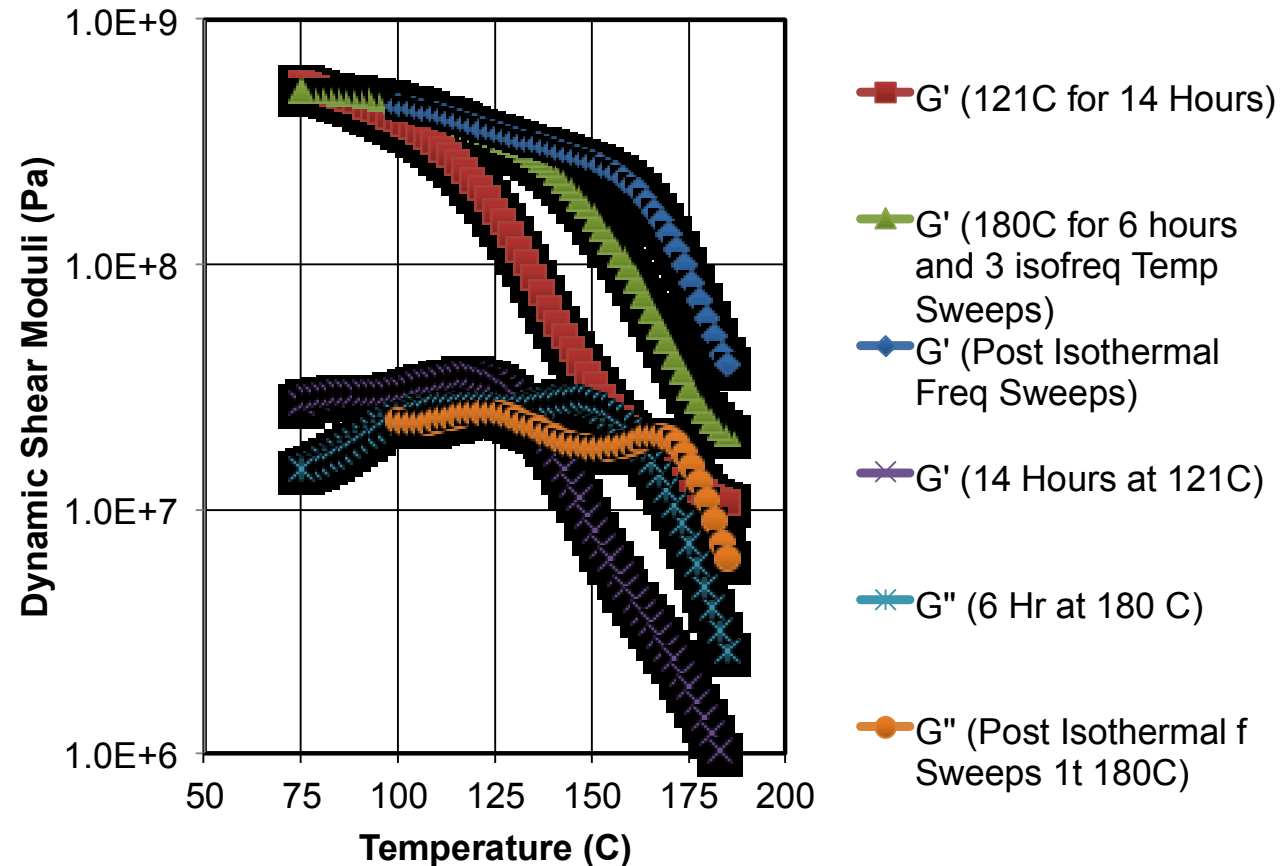
- Iso-frequency temperature sweep in oscillatory shear
 - T_g and Transition Width
 - Isothermal frequency sweeps in oscillatory shear above T_g
 - Shear WLF characterization
 - Shear relaxation function
- TMA sweeps across the glass transition
 - Bulk/Thermal relaxation function

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



Curing continues up to 225 C, where we observe decomposition. No stable rubbery state

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

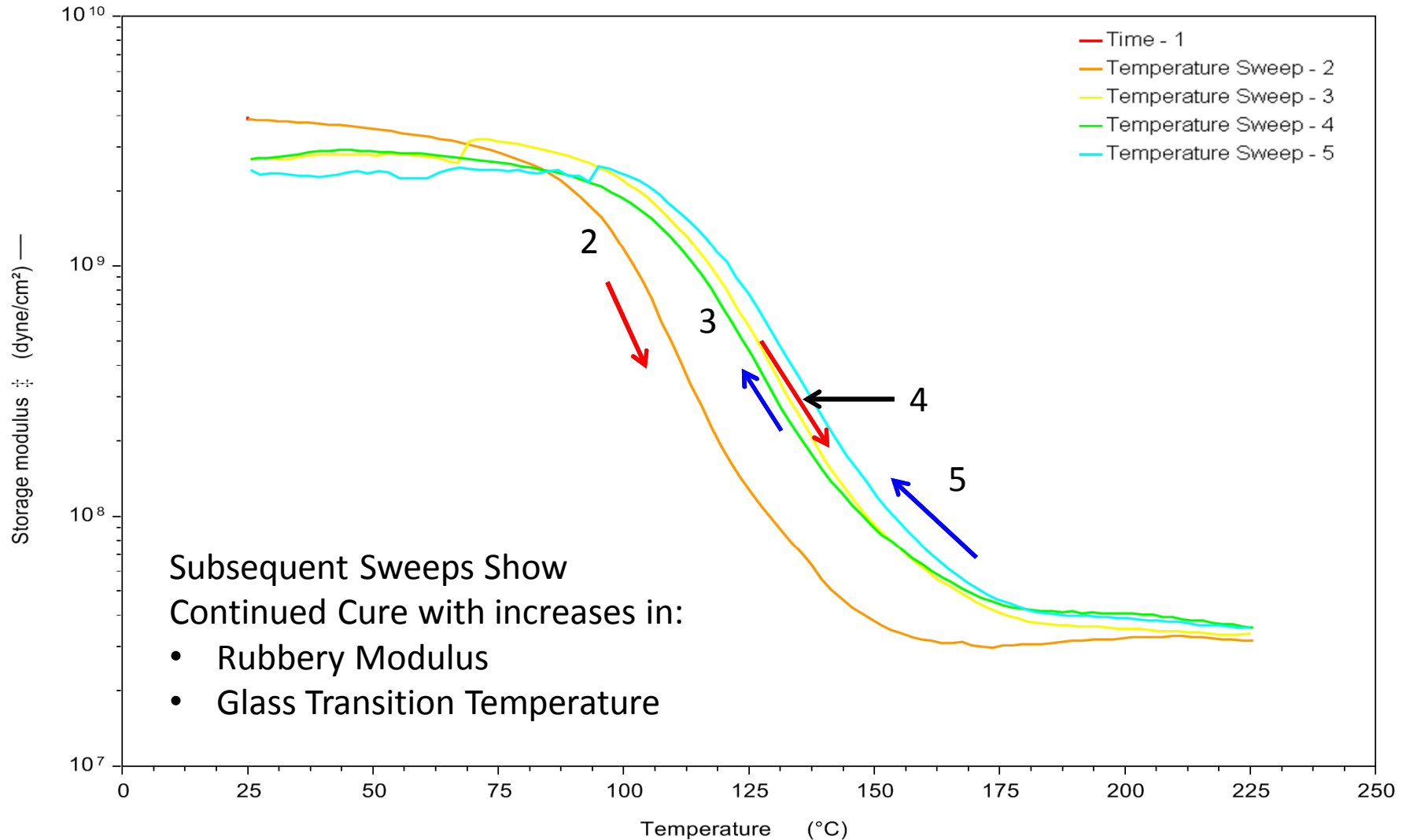
**BRUTE FORCE FITTING THE SHEAR
RELAXATION FUNCTION, GLASSY SHEAR
MODULUS, AND RUBBERY SHEAR
MODULUS FROM KCP-PROTOCOL FOAM**

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

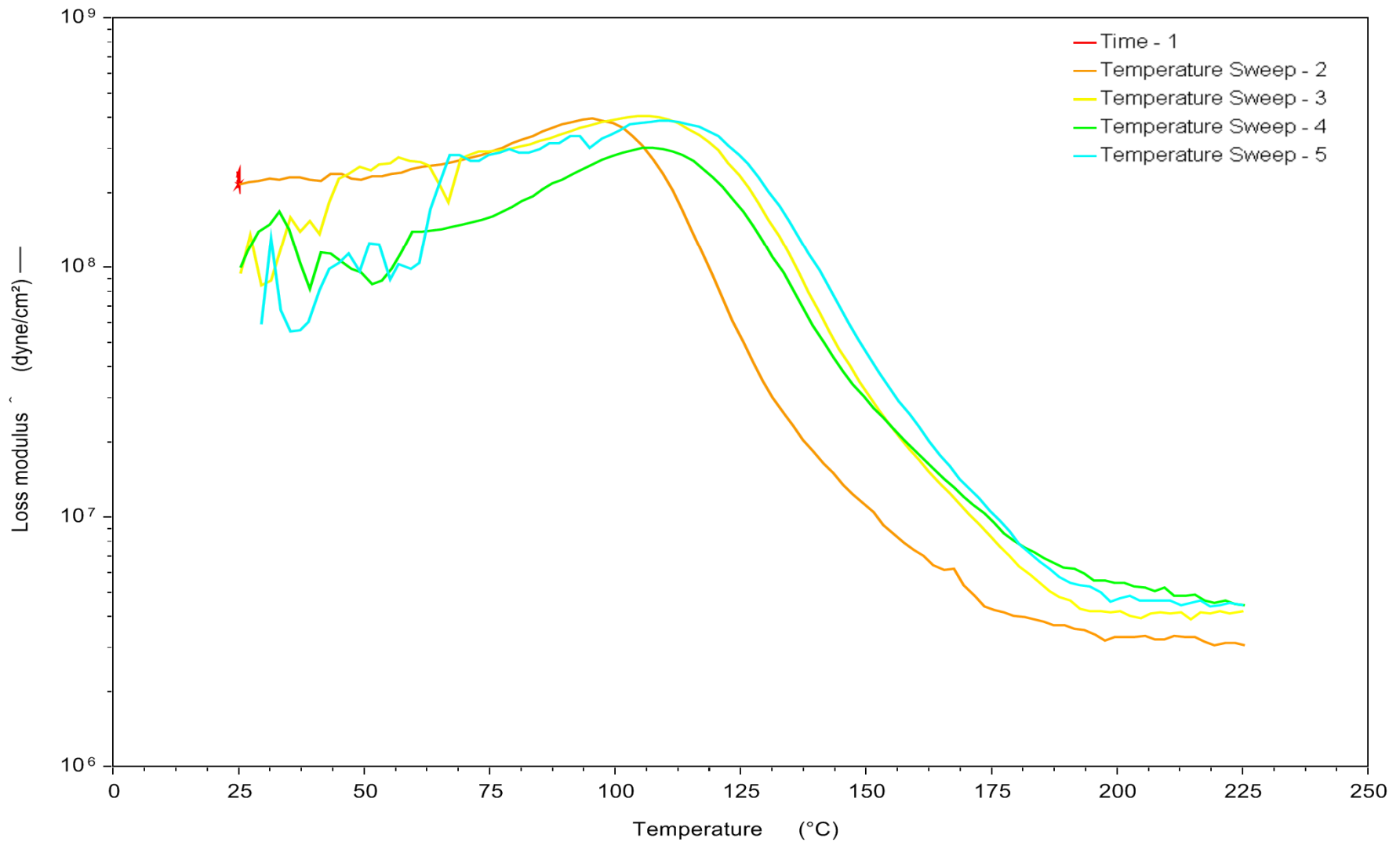
KCP Cure Schedule—Cool to RT—Cut Torsion Bars—Isofrequency Sweep Up—Sweep Down—Sweep Up—Sweep Down

Structural 10 lbs. Foam bar (1)

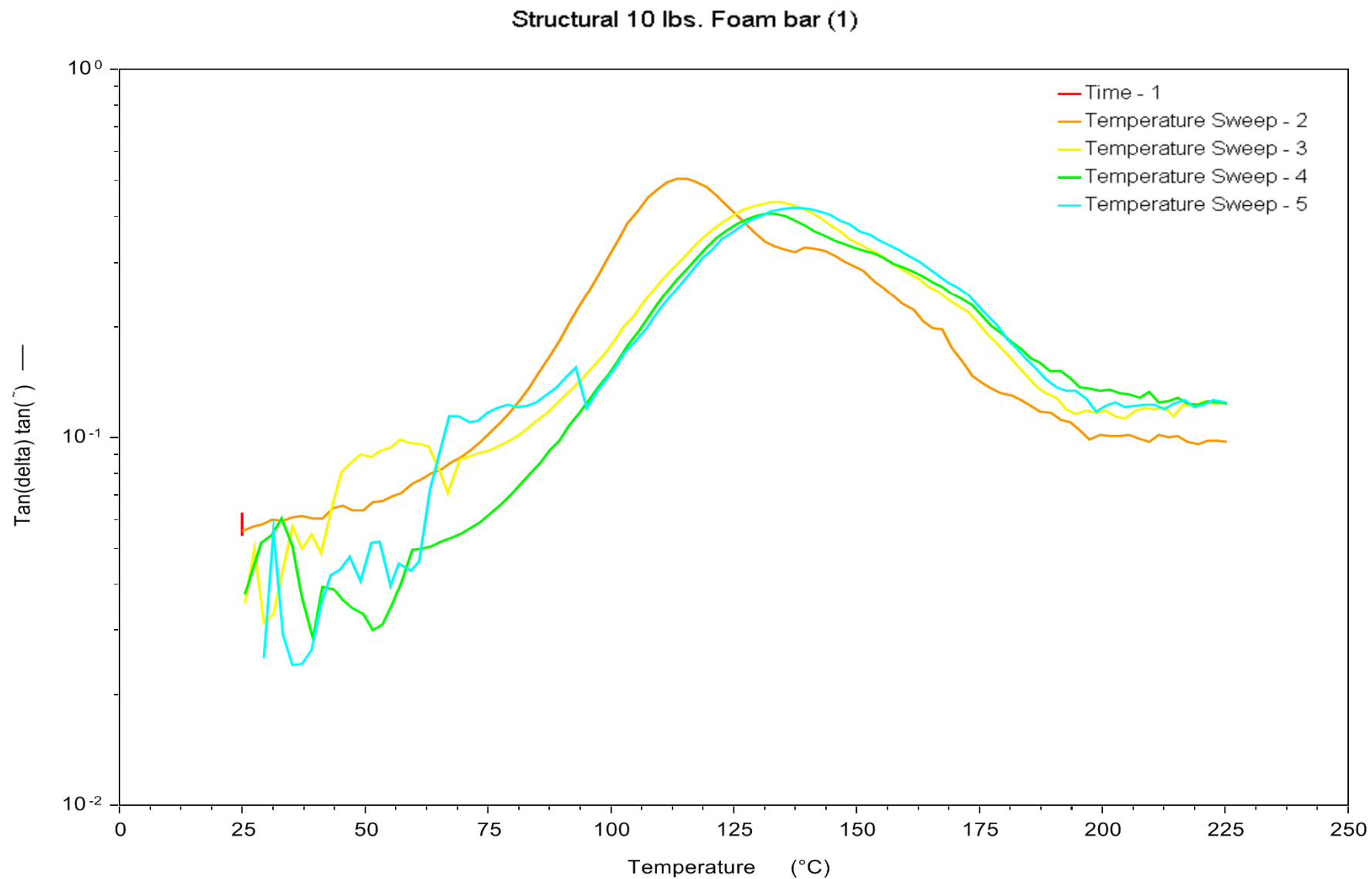


Raw Data from the ARES 2 Rheometer

Structural 10 lbs. Foam bar (1)



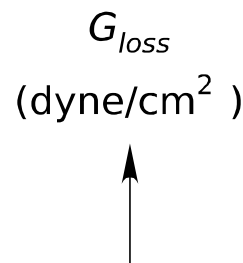
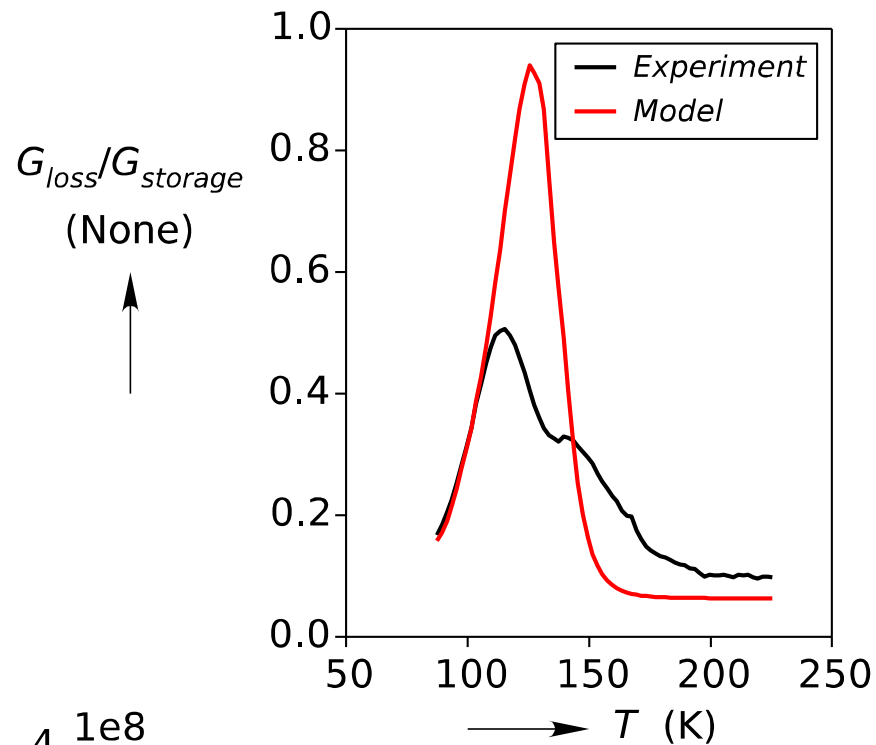
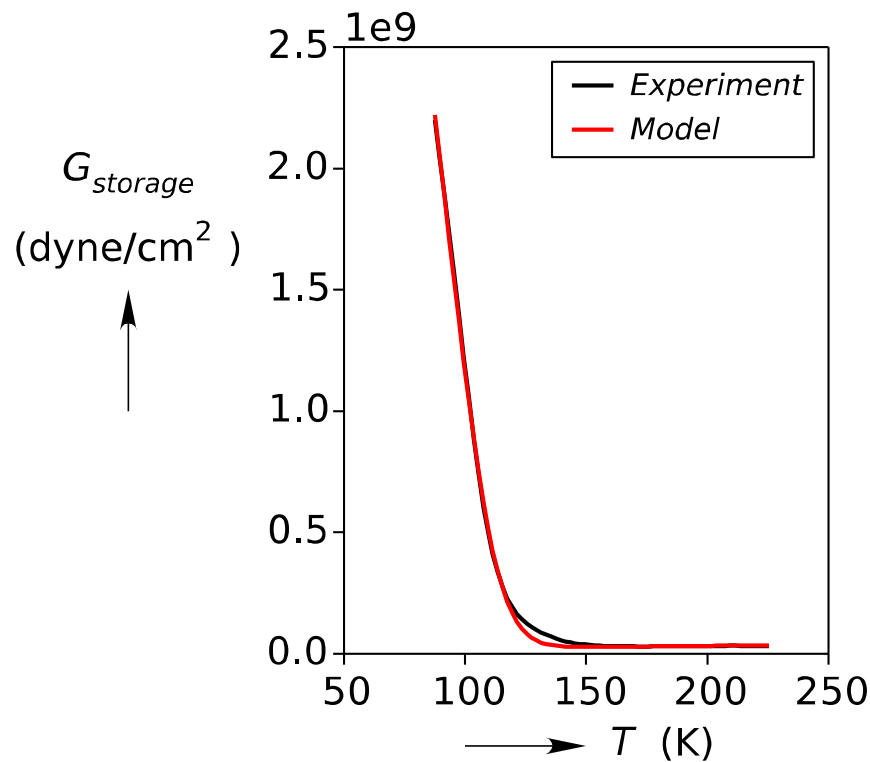
Raw Data from the ARES 2 Rheometer



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 , τ , and β 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



$$C_1 = 11.9499$$

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

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

$$WW_\tau = 0.9216 \times 10^{-3} \text{ s}$$

$$WW_\beta = 0.181$$

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:**
 - $T_0, C_1, C_2 = 283 \text{ K}, 8.86, \text{ and } 101.6 \text{ K}$
 - $T_0, C_1, C_2 = 231 \text{ K}, 16.7, \text{ and } 68.0 \text{ K}$ for a PU material cross-linked with toluene diisocyanate and trimethylol propane
- **Our Fit**
 - $T_0, C_1, C_2 = 388 \text{ K}, 11.9, \text{ and } 98.6 \text{ K}$

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 , τ , and β 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

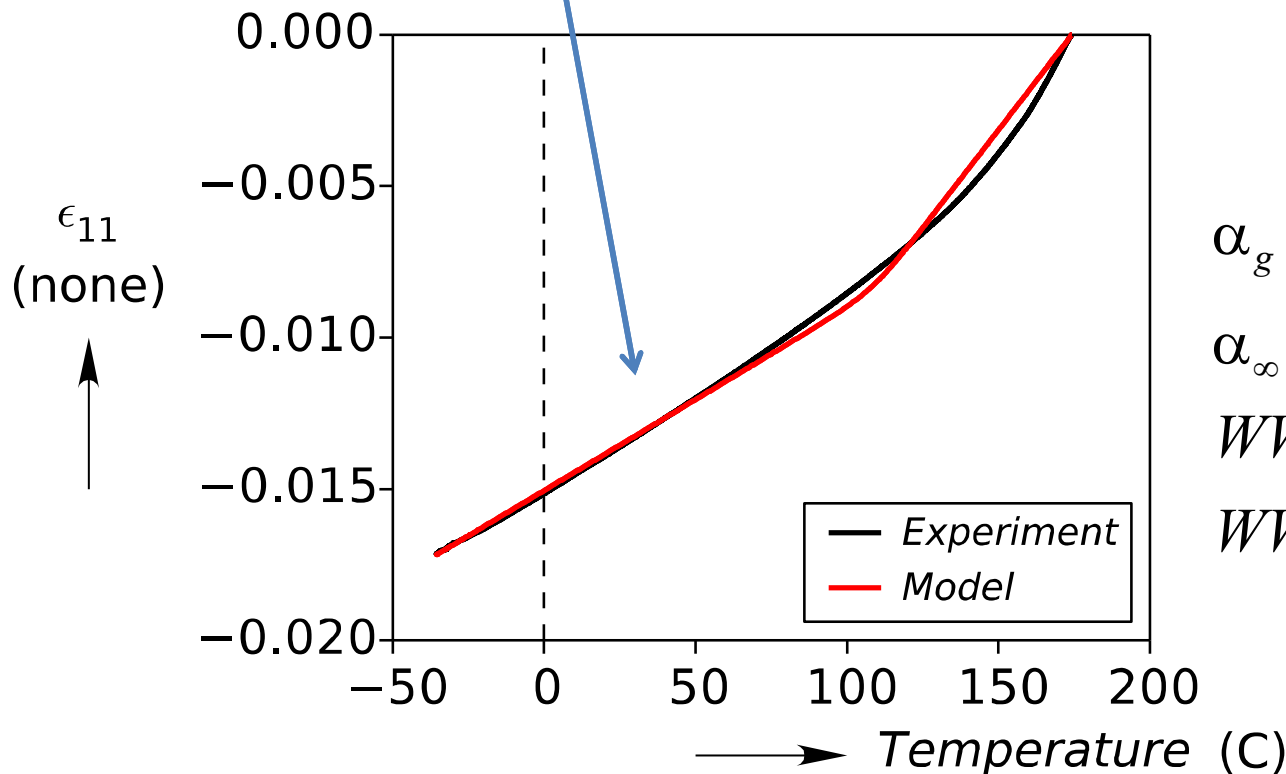
Brute Force Fitting the Bulk/Thermal Relaxation Function and Coefficients of Thermal Expansion using a Thermal-Mechanical Analyzer

- **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 τ , β 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

Stable Glassy Response

“Curve” Shows evidence of Additional Matrix Cure (shrinkage)



$$\alpha_g = 188E-6 \quad K^{-1}$$

$$\alpha_\infty = 408E-6 \quad K^{-1}$$

$$WW_\tau = 0.018336 \quad \text{sec}$$

$$WW_\beta = 0.176101$$

