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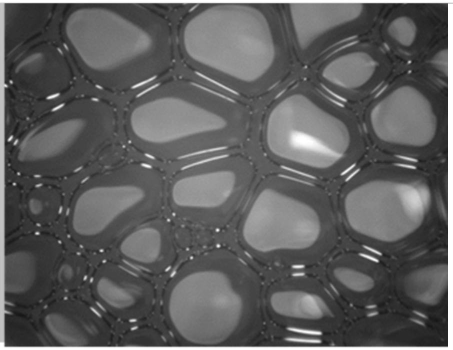

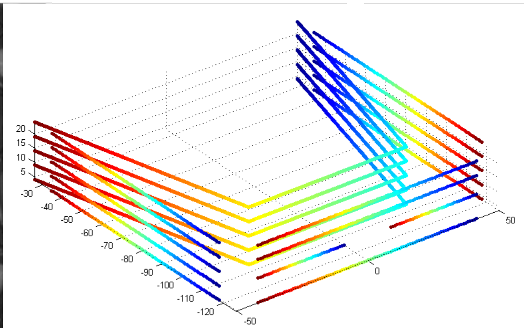

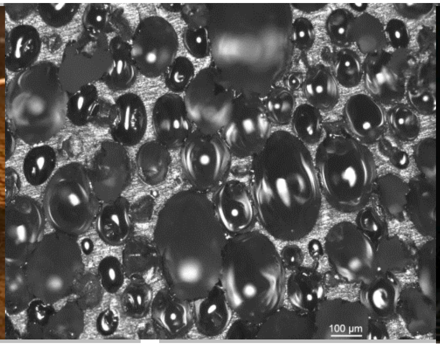

# Measuring and Modeling the Dimensional Stability of High Density Polyurethane Foams

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Society of Rheology Annual Meeting, Baltimore, MD

**SG23**

October 13, 2015

U.S. DEPARTMENT OF ENERGY

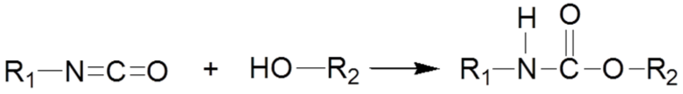
NNSA National Nuclear Security Administration

# Introduction

***Polyurethane foams are used as an encapsulant and a structural material to mitigate against shock and vibration***

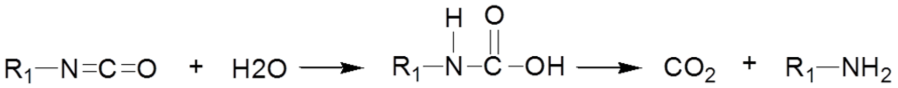
*Overarching Goal: Cradle-to-grave model for foaming, vitrification, cure, aging*

Focus on high density PMDI foams BKC44306, BKC44307



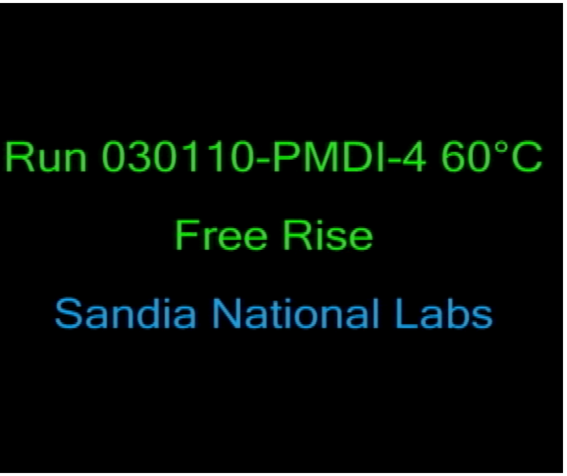
$$R_1{-}N{=}C{=}O + HO{-}R_2 \longrightarrow R_1{-}\overset{\overset{H}{|}}{N}{-}\overset{\overset{O}{\|}}{C}{-}O{-}R_2$$

**Urethane formation, crosslinking**



$$R_1{-}N{=}C{=}O + H2O \longrightarrow R_1{-}\overset{\overset{H}{|}}{N}{-}\overset{\overset{O}{\|}}{C}{-}OH \longrightarrow CO_2 + R_1{-}NH_2$$

**Foaming reaction yields $CO_2$ and amine**



Run 030110-PMDI-4 60°C

Free Rise

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*Curative and polyol are mixed, injected into mold or part. Foaming and initial curing begin. Reactions are exothermic.*

*Higher temperature cure in an oven*
*Frustrated cure shrinkage*

*Mold removal, cooling*

*Aging over years*

# Introduction

## Stage I

Fluid

**Pre-Gel**

($0\text{-}10^3$ 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

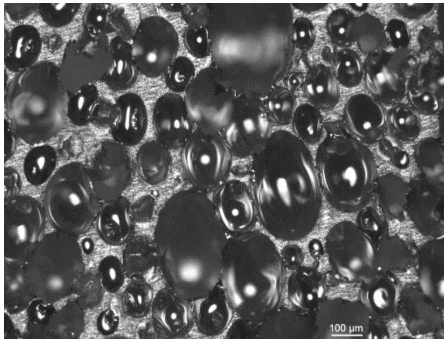
Boundary conditions strongly influence residual stresses

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

*Modeling first stage: See Rao et al., Thursday 9:30, CR18*

# Focus on Stage II, 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
  - Other suspects: Skins, bubble size, shape and orientation
- **Many possible sources for dimensional changes**
  - Response to residual stress
  - Continued cure of material
  - Bubble pressure, loss of $CO_2$
  - Hydration/Dehydration (controlled??)



**Goal:** ***Develop, calibrate, and validate a predictive model framework to describe stress relaxation and warpage of high-density polyurethane foam over short and long time periods, given physical property gradients developed during the manufacturing process***

# Modeling The Curing Solid State (II and III)

**Balance Laws and Solution Fields:**

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

Lagrangian FEM

ALE FEM

**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)

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

Logarithmic Strain

Temperature

Extent of matrix cure

*Material and Laboratory Time Relation*

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

*Density Scaling*

$$\sigma \sim \rho^2$$

$$\psi[\rho_0] = \left(\frac{\rho_0}{\rho_{ref\,0}}\right)^p \psi[\rho_{ref\,0}]$$

Free Energy

$$\underline{\underline{\sigma}}[\rho_0] = \left(\frac{\rho_0}{\rho_{ref\,0}}\right)^p \underline{\underline{\sigma}}[\rho_{ref\,0}]$$

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

$$N = \left\{ \left[ T(t) - T_{ref} \right] - \int_0^t ds\ f_1\left(t^* - s^*\right) \frac{dT}{ds}(s) \right\} + C_3 \left\{ I_1(t)_{ref} - \int_0^t ds\ f_1\left(t^* - s^*\right) \frac{dI_1}{ds}(s) \right\}$$

$$+ C_4 \left\{ \int_0^t \int_0^t ds\, du\, f(t^* - s^*, t^* - u^*) \frac{d\underline{\underline{\varepsilon}}_{dev}(s)}{ds} : \frac{d\underline{\underline{\varepsilon}}_{dev}(u)}{du} \right\} + C_5\left(x(t)\right) \left\{ \left[ x(t) - x_{ref} \right] - \int_0^t ds\ f_1\left(t^* - s^*\right) \frac{dx}{ds}(s) \right\}$$

Shear Deformation

Matrix Cure

## *Glass Transition Evolution*

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

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

## *Shear Modulus*

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

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

# Calibration of NLVE Model

**1) Oscillatory Shear**
Isofrequency Temperature Sweep of a "Fully Cured" Foam Torsion Bar

- Shear moduli
- Shear Relaxation Function
- Time, temperature superposition above Tg

**2) Thermal Mechanical Analysis**
Isofrequency Temperature Sweep of a "Fully Cured" Foam Bar

- Coefficients of Thermal Expansion
- Bulk/Thermal Relaxation Function

**3) 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) Cure Shrinkage**
"Dry Foam" Dimensional change measurements during cure

*Still work in progress*

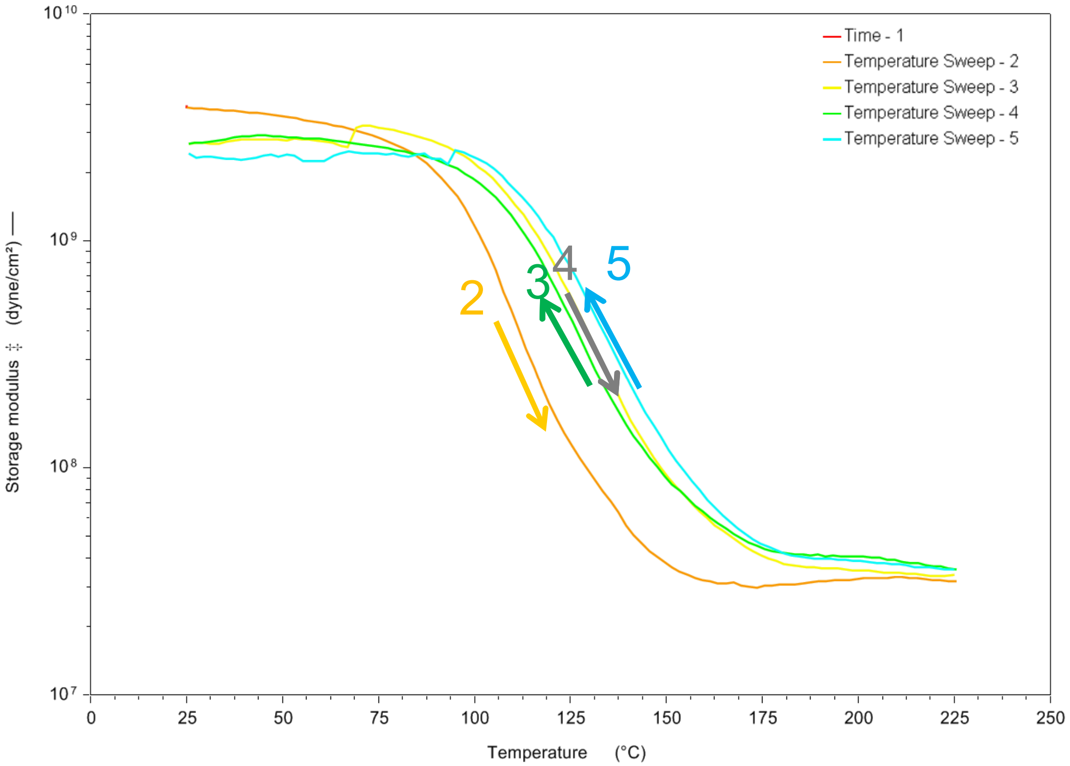
**6) Uniaxial Compression**
Isothermal and Cyclic Temperature Sweeps of "Dry Foam"

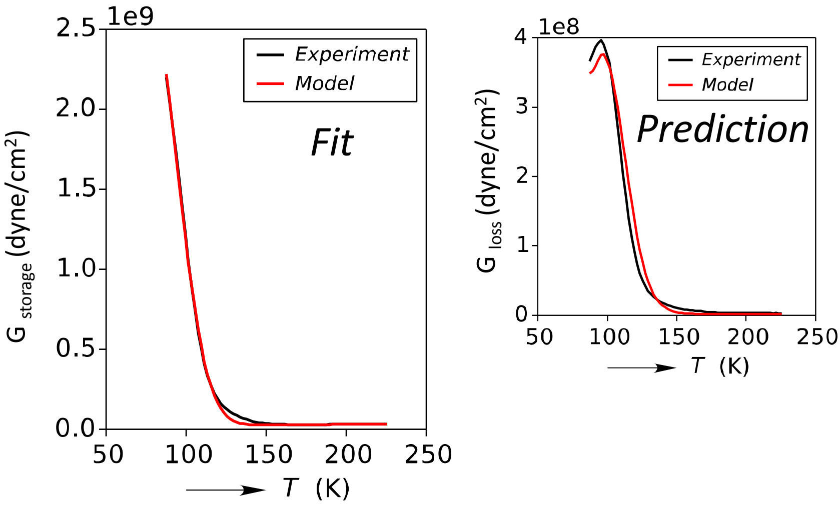
- Yield phenomena (Shear Deformation Induced Mobility)

*"Dry foam" = foam precursors without water, "no" bubble formation*

# Modulus Evolution

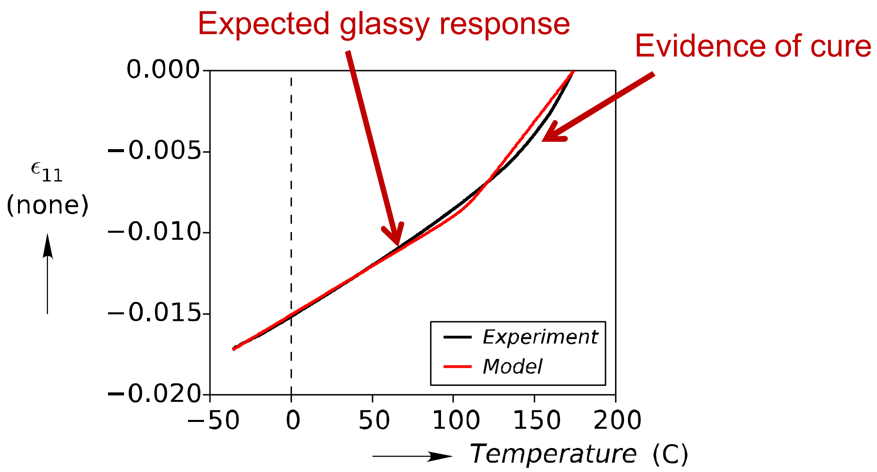
- Oscillatory shear of a cured foam bar
  - Cured using normal production cure schedule (121 $^{o}$C, 4 hrs)
- Subsequent sweeps in temperature show continuing cure
  - Increases in shear modulus, glass transition temperature
- Production cure schedule does not fully cure material





Near Tg, fit the Time-Temperature WLF Shift Factors and Williams-Watts Shear Relaxation Function via Optimization to the Storage Modulus Behavior

# Thermal expansion, Cure Kinetics



***Thermal expansion*** measured with the dry foam using a thermal mechanical analyzer

Expansion seems quite high compared with literature values. Evidence of continued cure at high temperatures.

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

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

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

$$WW_\beta = 0.176101$$

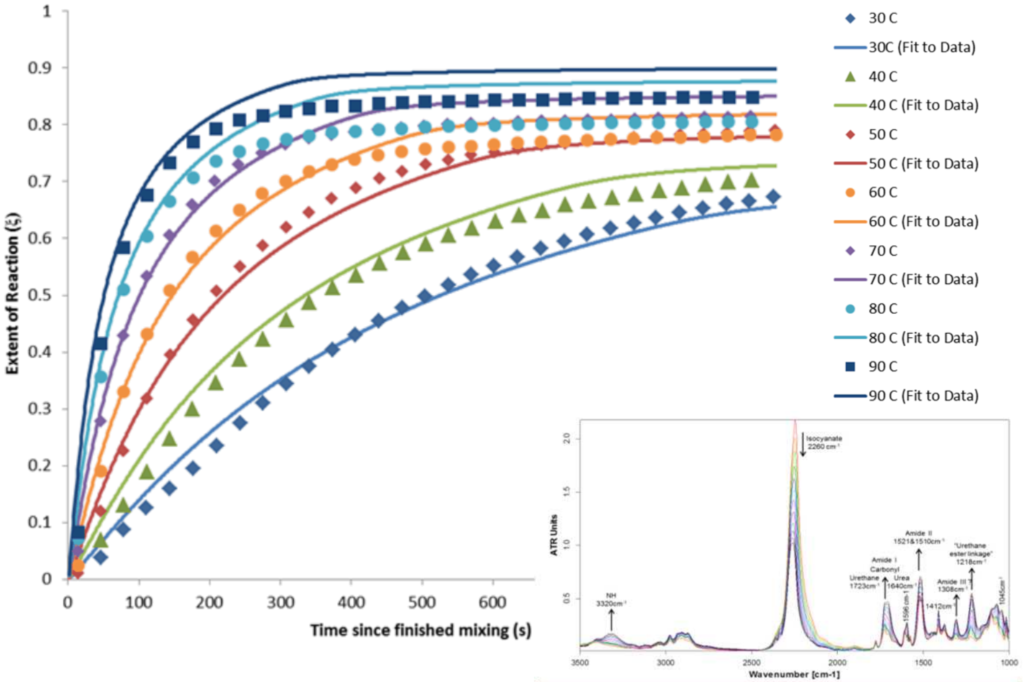
***Isothermal micro-attenuated total reflection IR spectroscopy measurements*** provide cure kinetics vs. temperature

Urethane ester linkage (1218 cm$^{-1}$) used to measure extent of reaction with time.

Model using Kamal cure kinetics approach. Vitrification slows curing reaction

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

$$T_g[x] = \frac{T_{g0}(1-x)+xAT_{g\infty}}{1-x+Ax} \qquad \log_{10} a = \frac{-C_1\left(T-T_g[x]\right)}{C_2+T-T_g[x]}$$



Sourer and Kamal, Thermochimica Acta, V 14, 1976

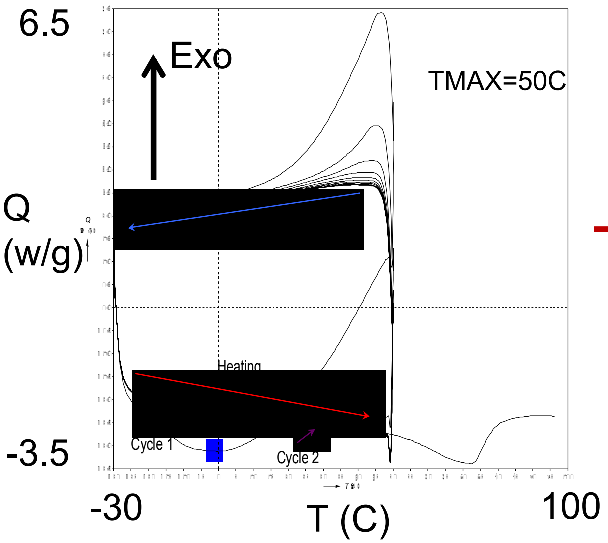
# Relate Extent of Reaction to Tg

**We require Tg as a function of the extent of reaction (Di Benedetto form)**

**Problem:** Measuring Tg involves heating the material, which provokes more cure.

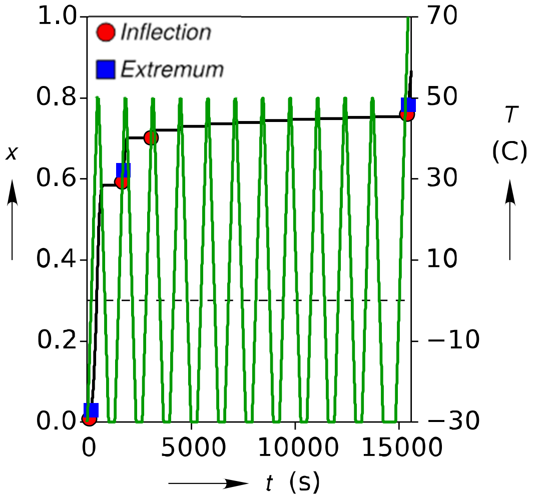
**Solution:** Model the curing of the sample during the measurement to find x at $T_g$.

Differential Scanning Calorimetry identifies $T_g$ over a series of temperature ramps



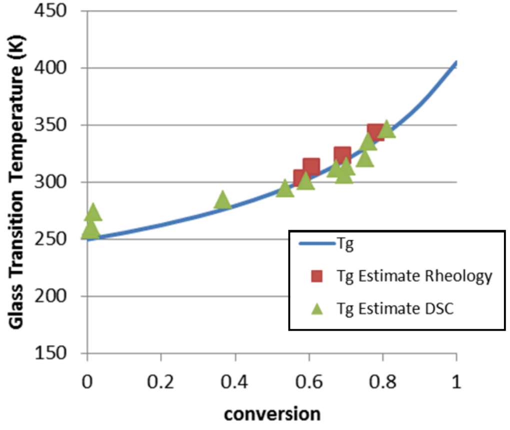
- ~10 mg samples
- Cycle the temperature between -30 C and $T_{MAX}$
- Ramp up to 100+C at end of test (10 cycles)

Calculate extent of rxn vs. time for DSC sample, given kinetics obtained based on IR measurements



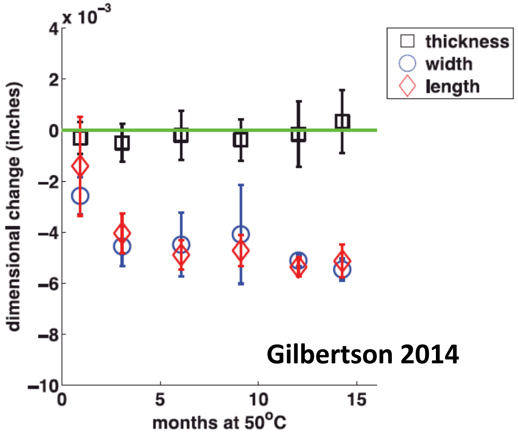
- Using either the inflection or the extremum gives very similar estimations of Tg.

Tg vs x relationship agrees very well with relationship created independently using rheology



# Validation Experiment

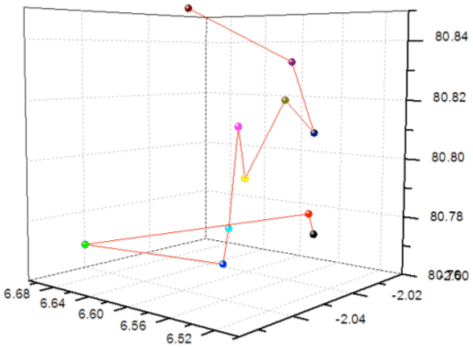
- Validation data set desired using a more realistic geometry
- Previous studies have had some success:



**Gilbertson 2014**

Figure 10: Dimensional change in blocks aged at 50 °C. Green line at 0 is a visual reference.

**Pockett, Warriner (2013)**



**Extent of cure heterogeneities noted**

**“Consistency of movement between measurements is hard to conclude”**

- Decision: Model Pockett, Warriner experiment. Repeat experiment using CMM as measuring tool, using PDMI foam formulation of interest

**Gilbertson, R. D, B. M. Patterson, Z. Smith, LA-UR-14-20007, 2014**

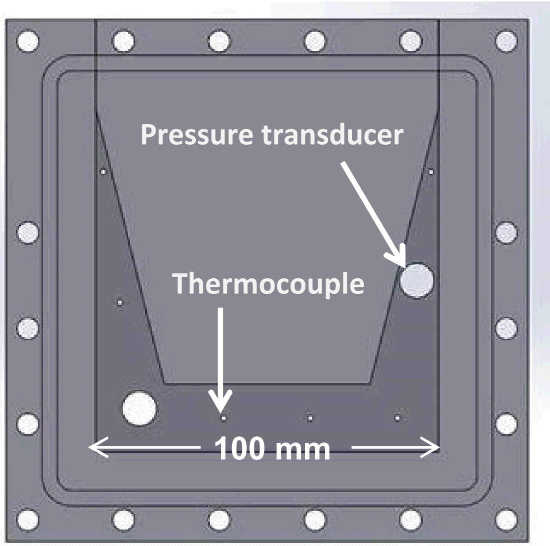
**Pockett, K., C. Warriner, AWE Report 283/13, 2013**

# Cure Shrinkage Monitoring

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

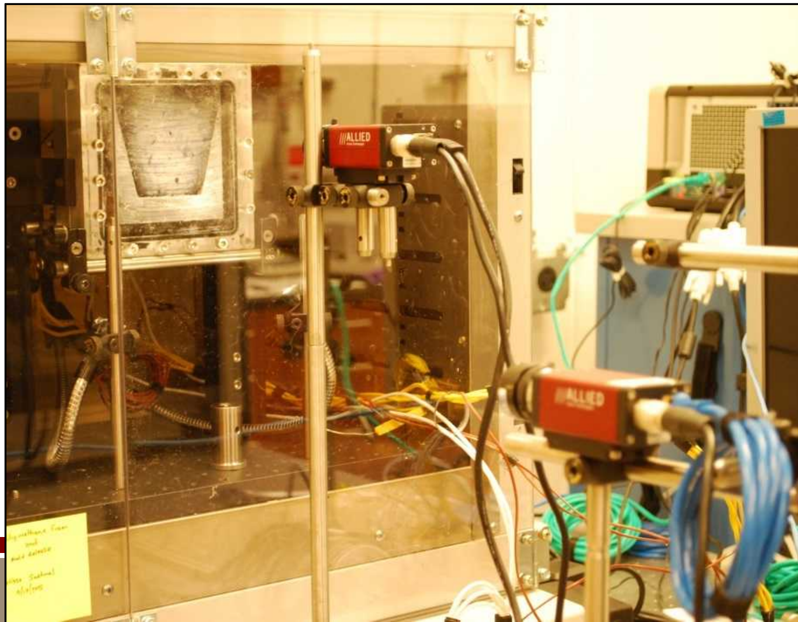
- Geometry inspired by AWE previous work (Pockett + Warriner)
- Initially, filling conditions approximate those at KCP
  - PMDI S10 foam injected at 40 °C, overpacked to 12.5 lb/ft$^3$
  - After 15 mins, cured in oven at 120 °C for 4 hrs
  - Two separate filling orientations "C" and "U"
- Coordinate Measurement Machine (CMM)
  - Calibrated to measure 100 mm length to +/- 3 µm accuracy
  - Parts stored in dry desiccator when not being measured

**CMM measures dimensional changes**



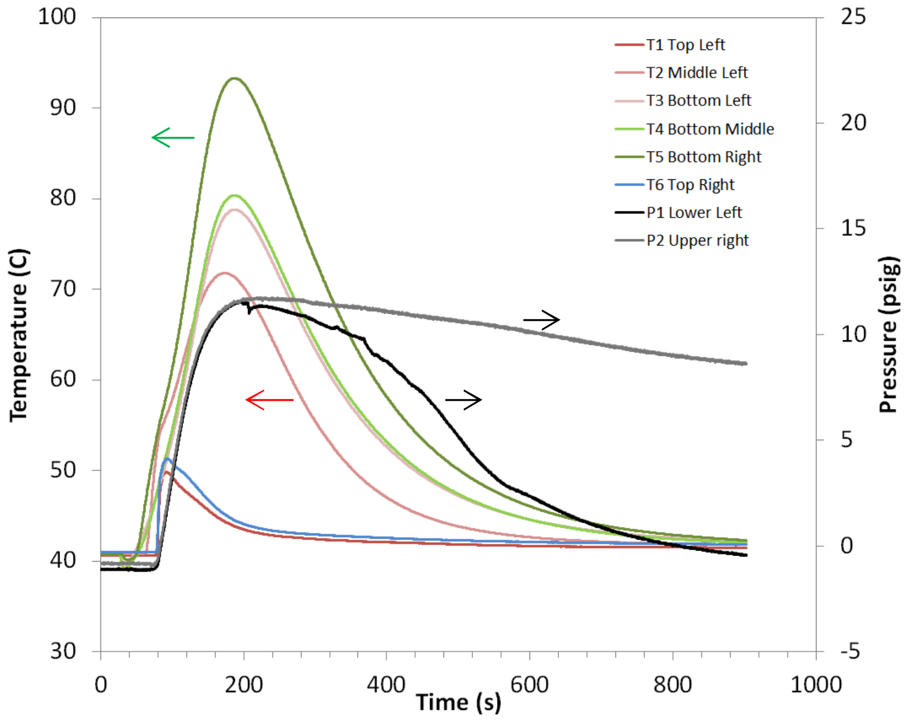
**Ports for thermocouples and pressure transducers to record parameters during foaming.**

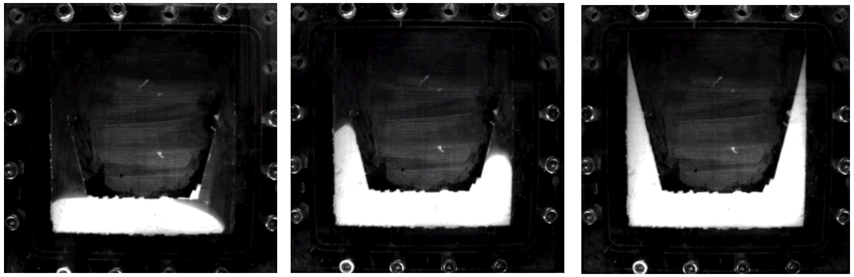
**Fill filmed using cameras, transparent oven door**



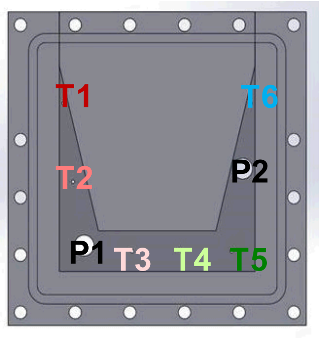
# Foaming U-shaped staple mold

- 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.

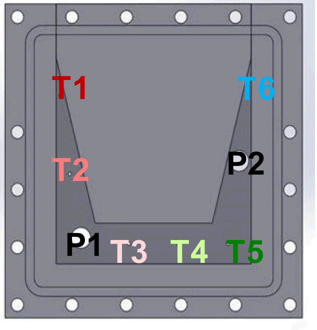




**Some slight asymmetry due to bias of initial injection**

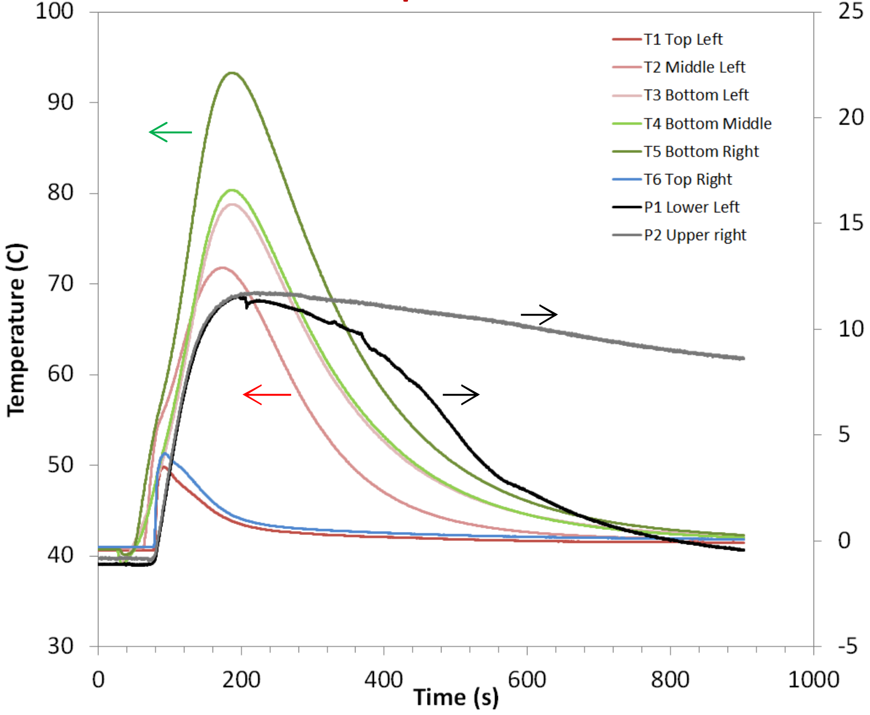


# Foaming U-shaped staple mold

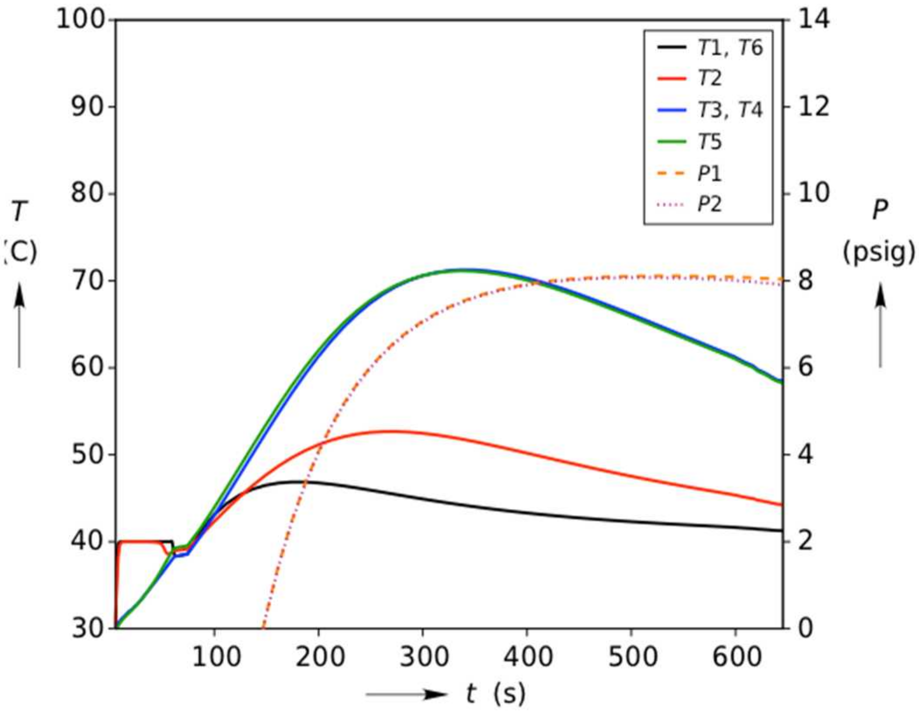


- Filling model (see talk by R. Rao, CR18) captures general behavior well
    - Slightly cooler, slightly slower
- Filling model simulation is initial conditions for aging model

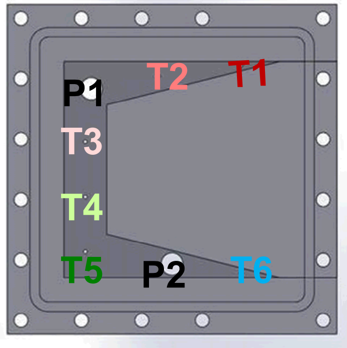
**Experiment**



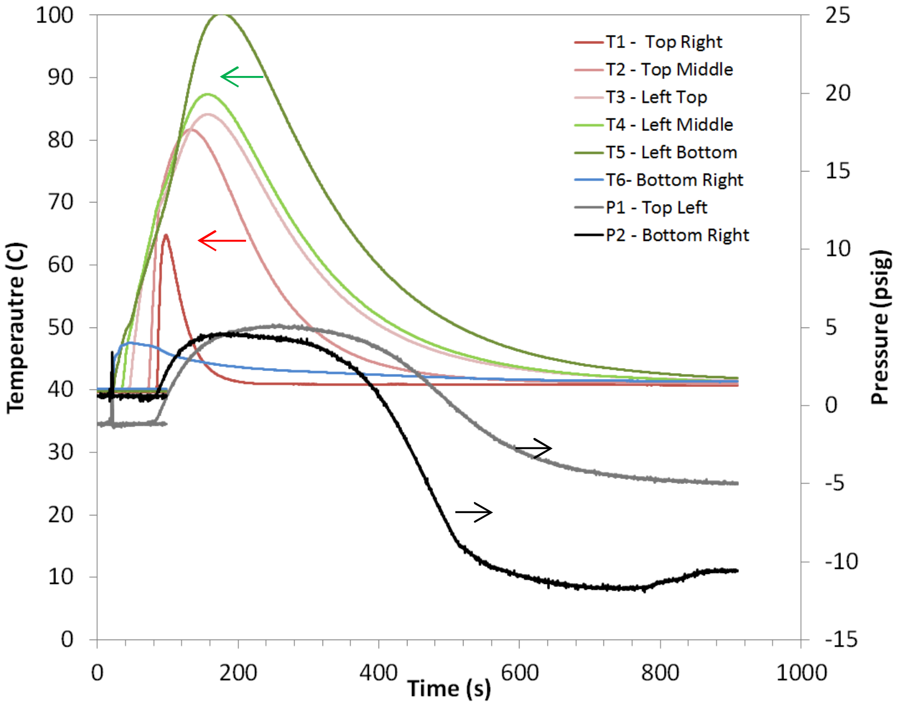
**Model Predictions**

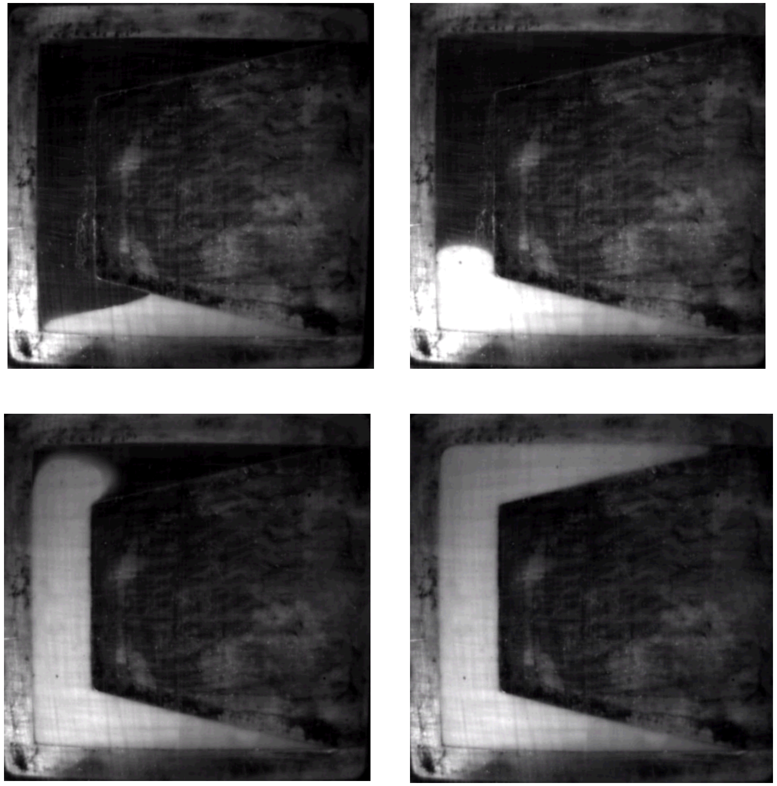


# Foaming C-Shaped Staple Mold

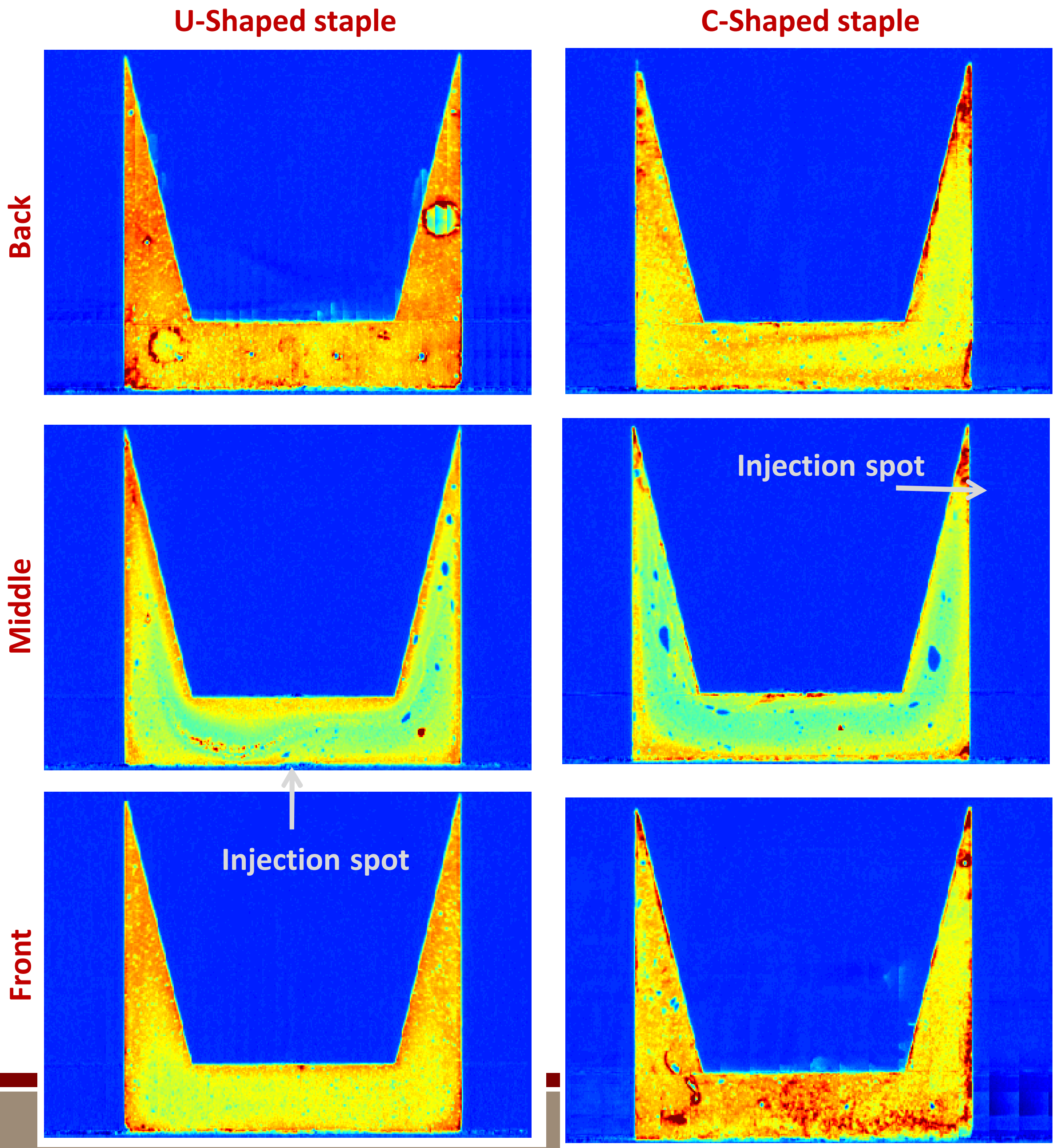


- Higher maximum temperature compared to U-shaped
- Stress rises then becomes tensile at both P1, P2 locations
  - Delamination often seen at P1





# Density of Staple Mold



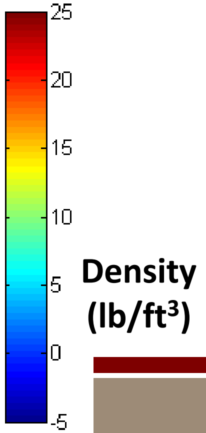
**A skin is apparent (25 lb/ft$^3$), whereas the interior density is as low as 7 lb/ft$^3$**

**Large voids-- primarily in the arms of the staple.**

- Coalescence seen in other thin PMDI samples
- Larger numbers of voids in C-shaped staple (more shear overall)

**Large bubbles could be source of pressure decay not predicted by model**

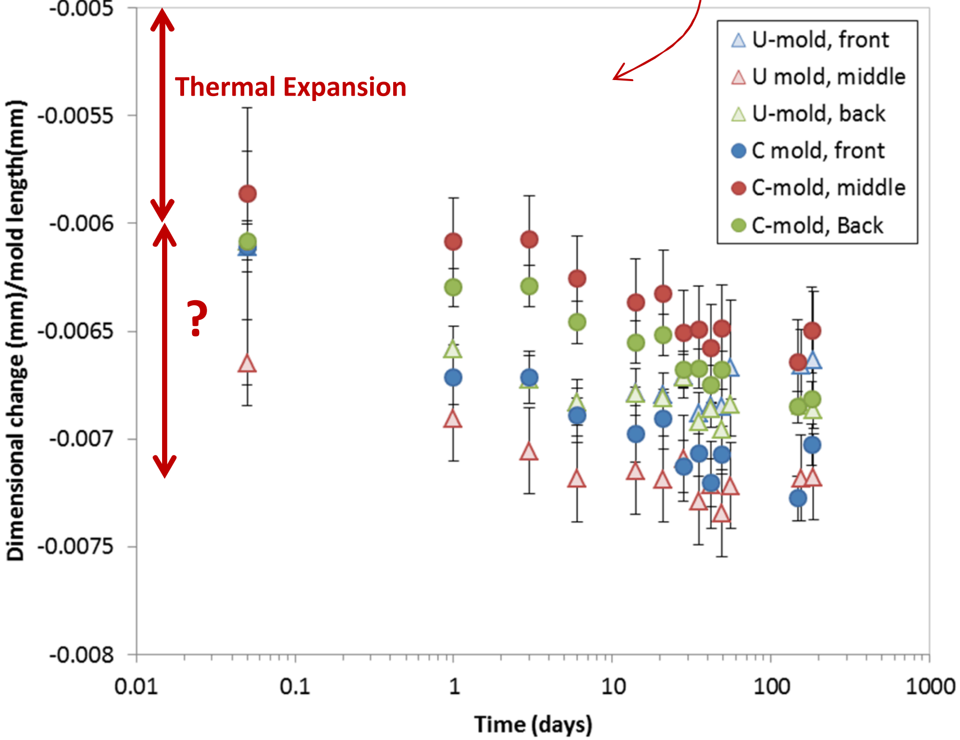
**Focus on bottom portion for shrinkage measurements**

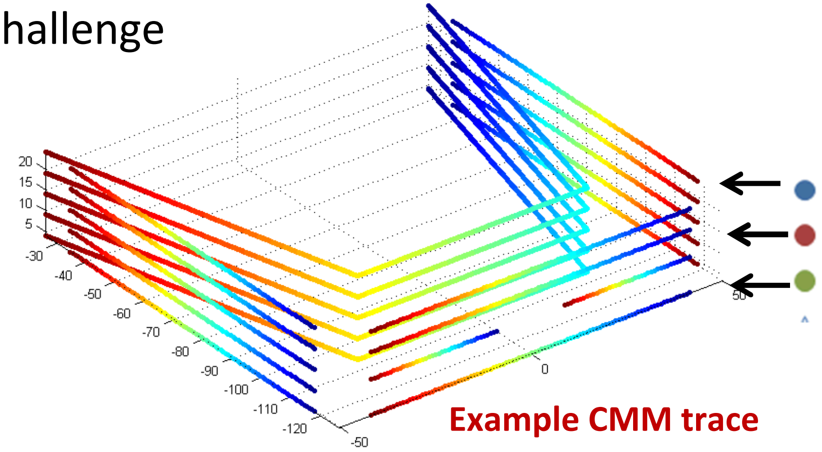


# Long-Time Shrinkage

- 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 origin a challenge

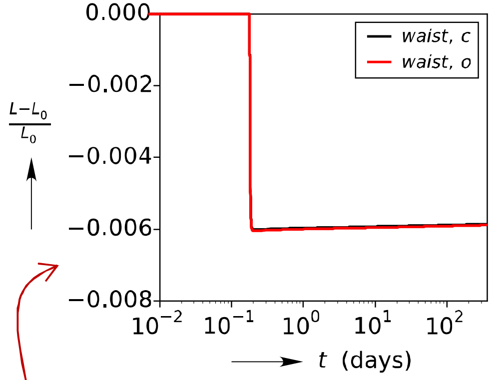
**Shrinkage measured with respect to hot (120 °C) mold dimensions**





**Example CMM trace**

**Model prediction**



**Model prediction captures thermal contraction well**
**Relaxation of residual stress is extremely slow (eons)**

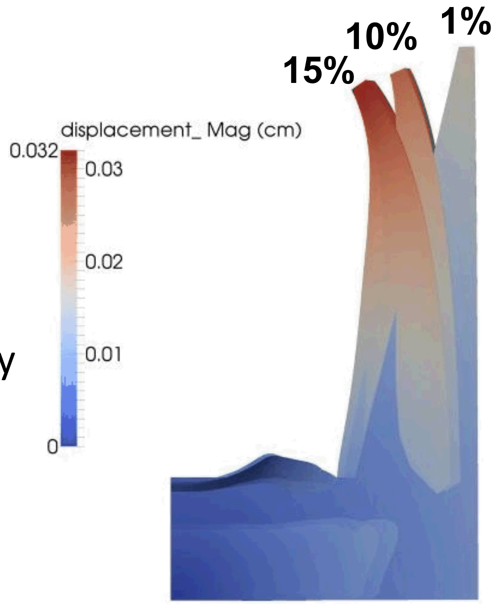
# Origin of Long-Time Shrinkage

## Idea 1: Continued Cure of Material

3% vol shrinkage/ 100% rxn extent implemented into model

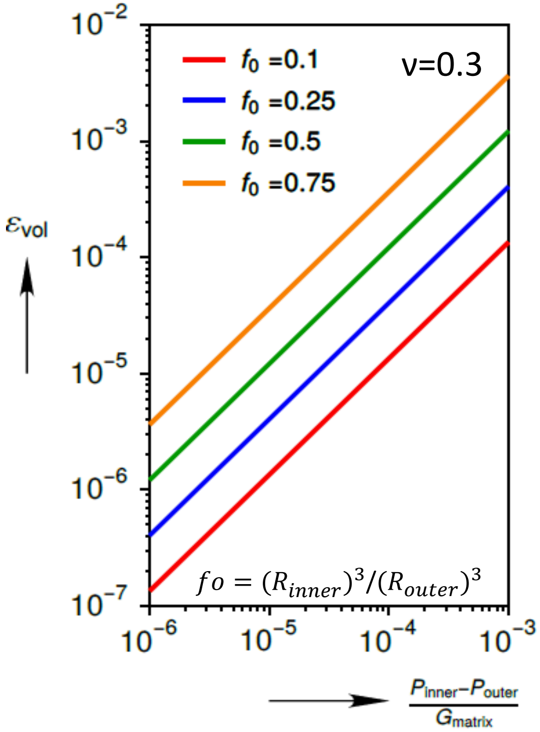
Experiments planned to obtain more accurate parameters

Initial results indicate that appreciable continued cure is very slow so far below $T_g$ of material



**Model predictions for various amounts of cure shrinkage**
**Displacements magnified x 100**

**Strain estimates for linear elastic shell as interior pressure decreases to 1 atm**



## Idea 2: Bubble Depressurization

Back-of-the-envelope calculations indicate:

Diffusion time scale is correct

Diffusion time ~ 160 days using

$D = 7\times10^{-8}\ cm^2/s$ measured for a PMDI foam*

Amount of strain is correct

Using Green and Shield solution for linear elastic spherical shell, the linear strain is on the order of 0.001 for reasonable values

---

*Bhattacharjee and Booth, 1995, J. Cellular Plastics

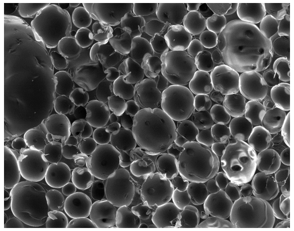
# Conclusions

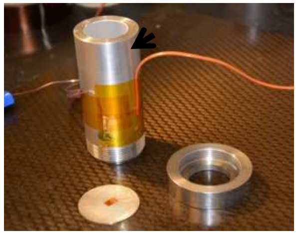
**A model framework was developed to predict stress relaxation and warpage during foam aging, taking property gradients predicted with a filling model into account**

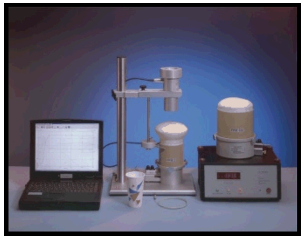
- Shear Modulus, cure kinetics, coefficient of thermal expansion discussed
- Dependence of these quantities with rxn extent, density, temperature

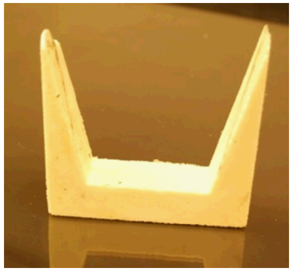
**Staple validation experiment was performed**

- Thermal contraction predicted well
- Long-term shrinkage possibly due to continued cure or bubble depressurization
- Future experiments will target identifying shrinkage physics









## Acknowledgements

Henry Lorenzo (SNL): CMM measurements

NNSA (WSEAT, PE+M, Enhanced Surveillance programs): Funding

# Backup Slides

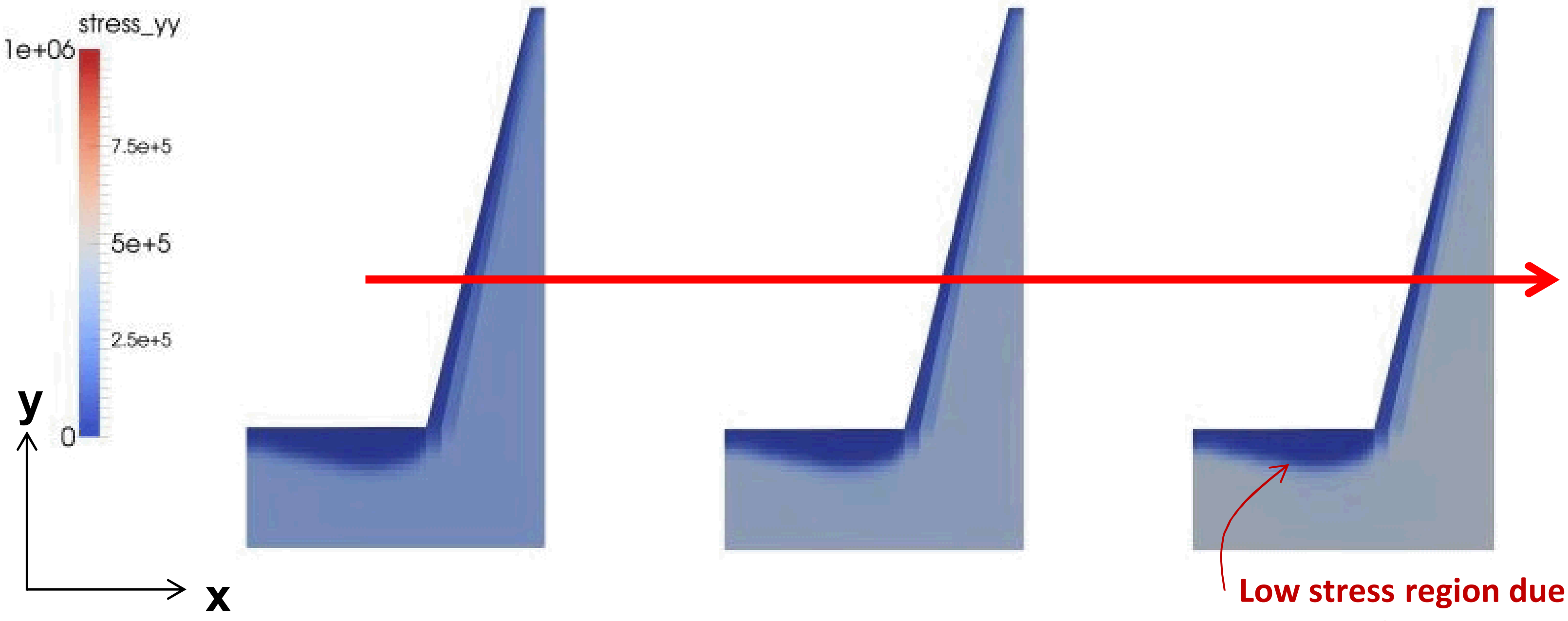
# Staple Mold Predictions: Stress in mold

- 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**

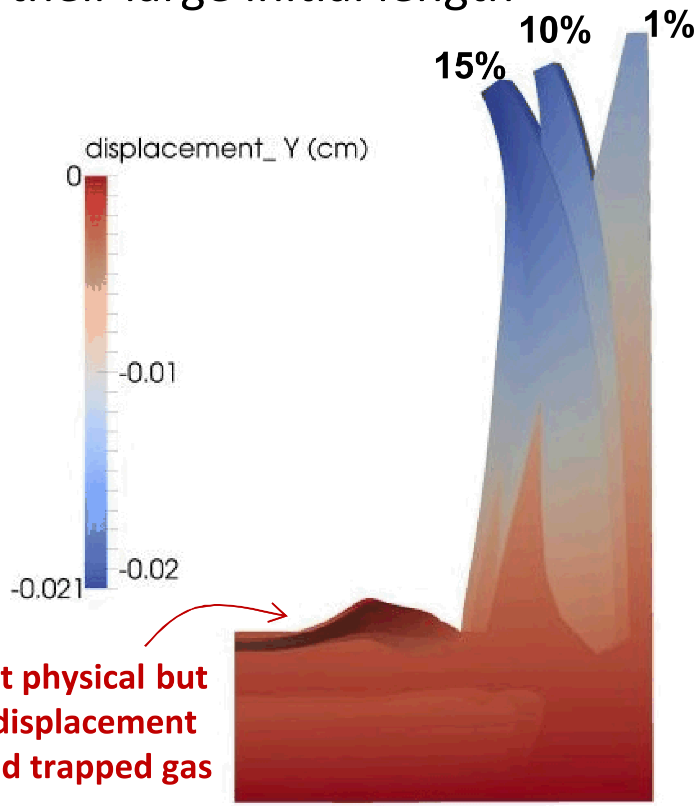


Increasing Stress Magnitude

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

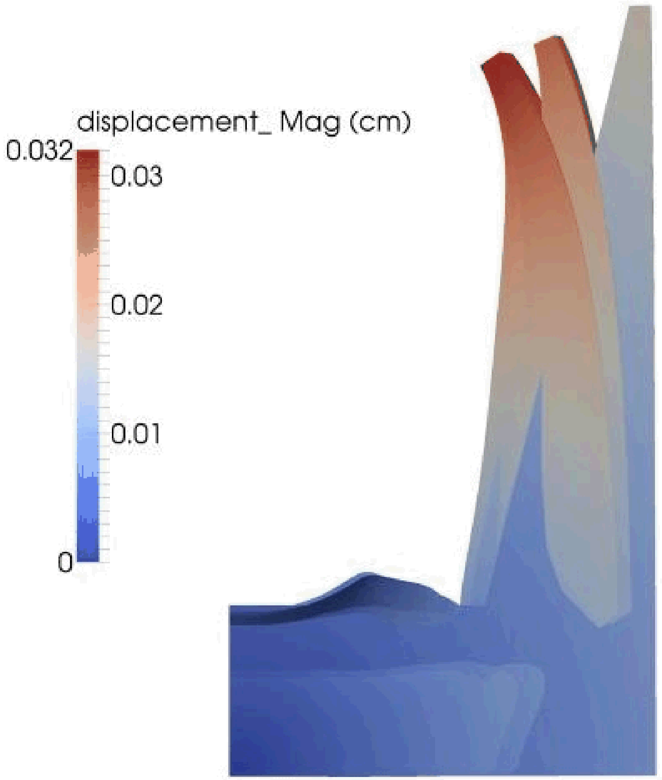
# Staple Mold Predictions: Dimensional Stability

- 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



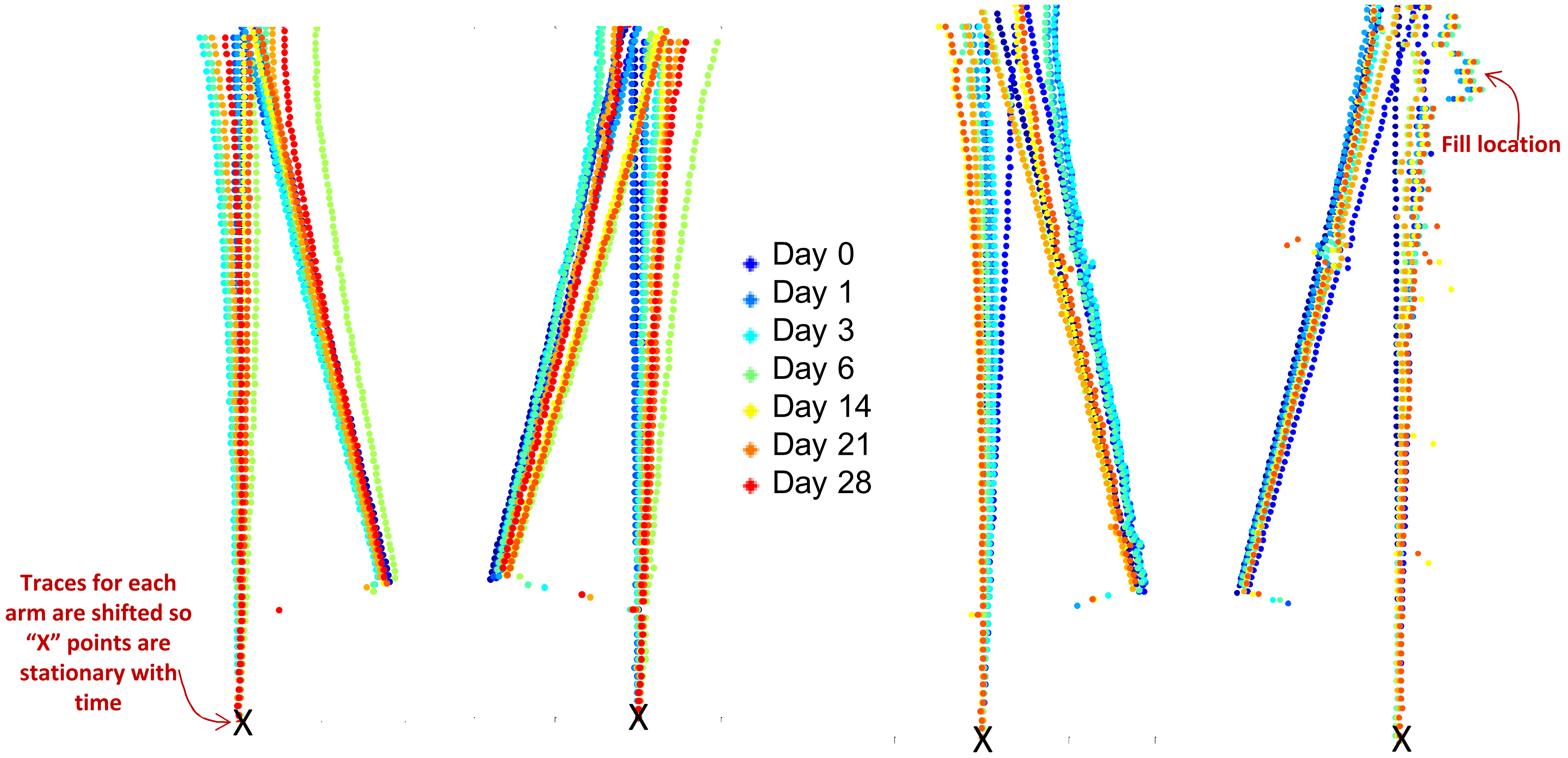
**“Ruffles” are not physical but arise from the displacement amplification and trapped gas**

**Displacements (cm) amplified by 100**



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

# Staple Mold CMM: Arm movement



Traces for each arm are shifted so “X” points are stationary with time

Fill location

U-shaped CMM, middle trace
Displacements exaggerated 50x

C-shaped CMM, middle trace
Displacements exaggerated 50x

- 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

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

### I. Thermal-Mechanical Properties on <u>as-received foam specimens</u>

- 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 <u>Neat Polymer (Dry Foam) Specimens</u>

- 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

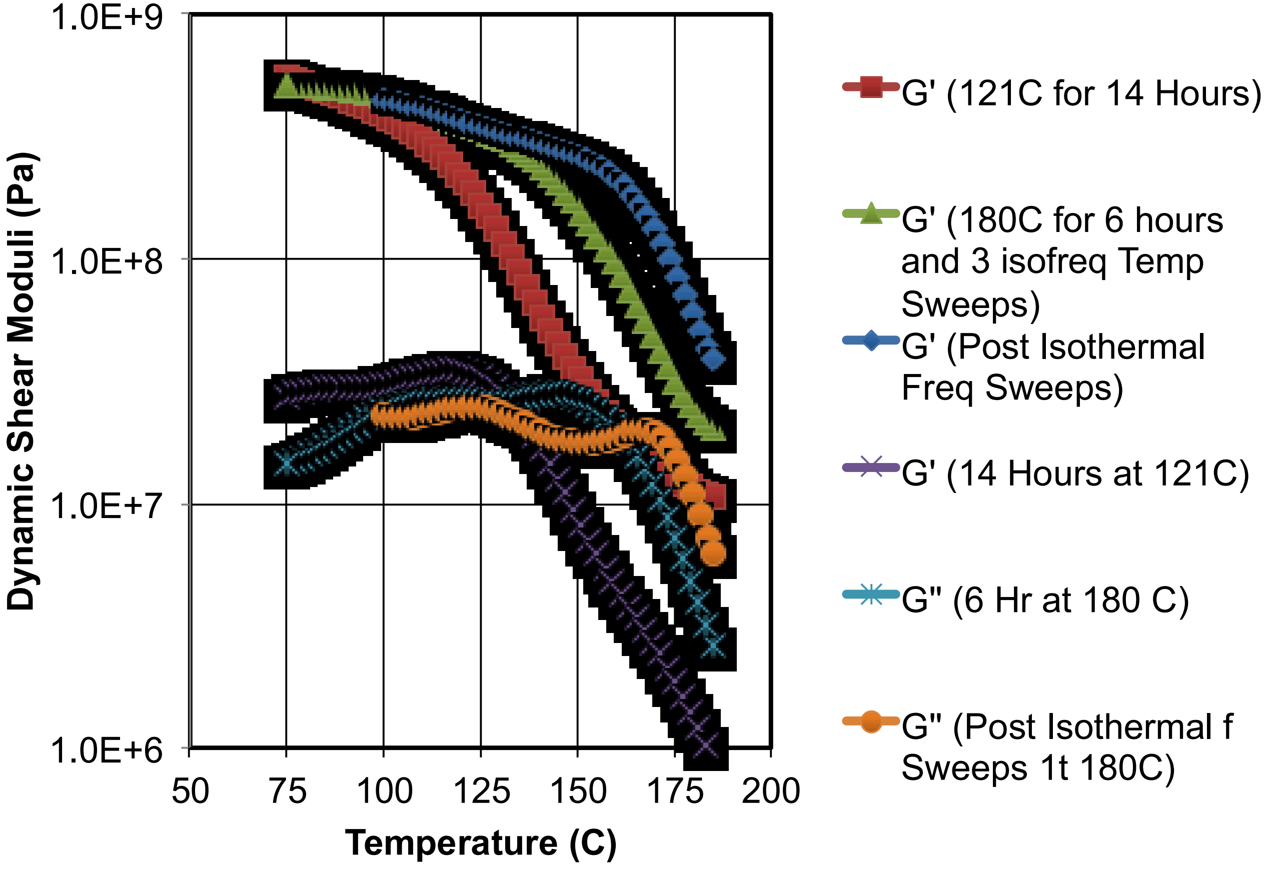
### III. Cure Effects on <u>Neat Polymer Specimens and Foams</u>

- 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

# 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

- 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

# Viscoelastic Model Fitting Approach

- Define Tg as the peak of the G''/G' (tan δ)
- 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 C1, C2, 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

# 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:**
  - T0, C1, C2 = 283 K, 8.86, and 101.6 K
  - T0, C1, C2 = 231K, 16.7, and 68.0 K for a PU material cross-linked with toluene diisocyanate and trimethylol propane

- **Our Fit**
  - T0, C1, C2 = 388 K, 11.9, and 98.6 K

# Two Possible Viscoelastic Model Fitting Approach

- Define Tg as the peak of the G’’/G’ (tan δ)
- 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 C1, C2, 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 $\tau$, $\beta$ directly associated with the volumetric/thermal relaxation function and the glassy and rubbery thermal expansion coefficients