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On The Effects of Manufacturing on the Dimensional Stability of Chemically Blown Polyurethane Foams

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Polyurethane (PMDI) Foams

Application Space

- **PMDI (poly-Methylene diphenyl diisocyanate) is used as an encapsulant and as a structural material to mitigate against shock and vibration**

The Problem

- **Manufacturing processes can produce a residual stress state in components that can cause them to warp over time**
- **Short Term: Challenges adhering to tight dimensional tolerances on parts**
- **Long Term: Parts may continue to change shape. What is the time scale, and when will it be a problem**

Objective

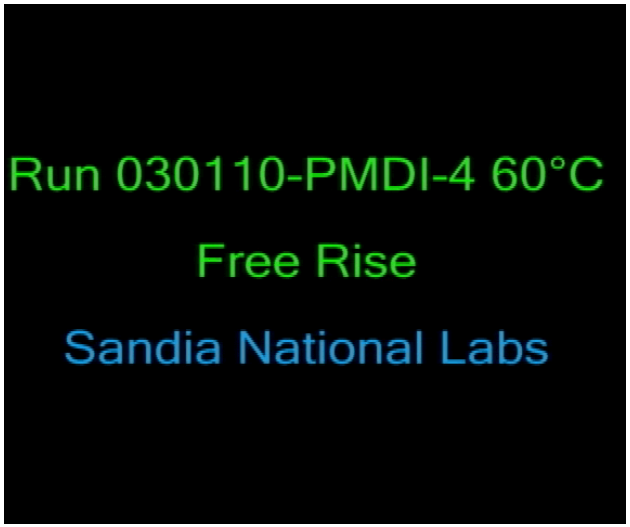
- **Determine how manufacturing induced variations and residual stresses with dimensional stability during aging of structural foams.**

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

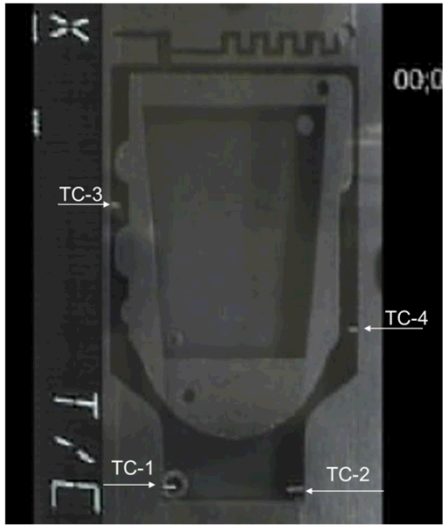
Cradle-to-Grave Modeling of Foam

Mixing

Injection, foaming and initial curing at lower T



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

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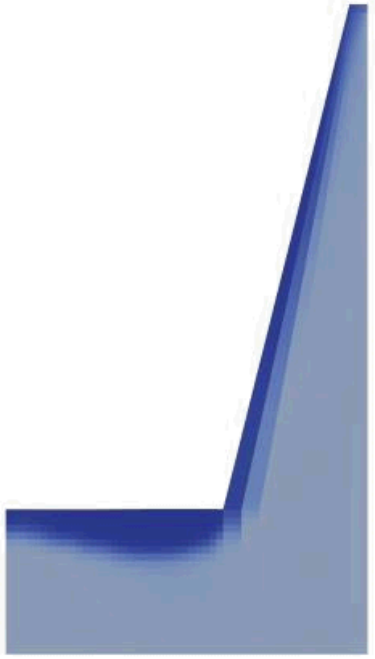
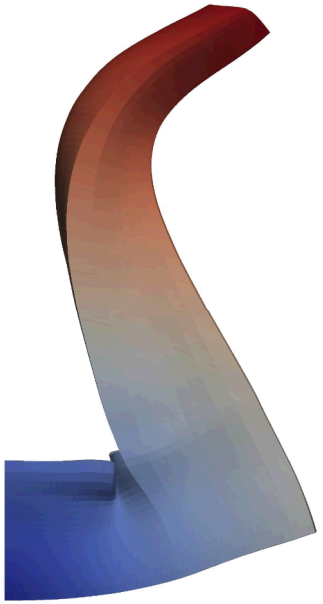
Outline

1. Aging Mechanism Hypothesis
2. Model Development
3. Preliminary Calculations
4. Discussion





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Hypothesis: Manufacturing Conditions Determine a Complex Physical Aging Scenario

Chemically Blown Foams Involve:

- **Foaming, Filling, Matrix Curing, Gelation, Solid-State Cure History, and Post-Cure Thermal-Mechanical Conditions**
- **Matrix curing beyond gelation causes the stress-free volume of the matrix material to shrink**
  - **When coupled with boundary constraints, residual stresses build**
  - **When not coupled with boundary constraints, the volume of the component may shrink**
- **Density variations give rise to different local stress-strain relationships**
- **Extent of curve variations may cause different glassy relaxation time scales**

Hypothesis

- **In the absence of additional chemistry, component warpage is mitigated by density, extent of cure, and residual stress variations that arise from manufacturing conditions**

Three Stage Modeling Approach

Stage I	Stage II	Stage III
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	**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	**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

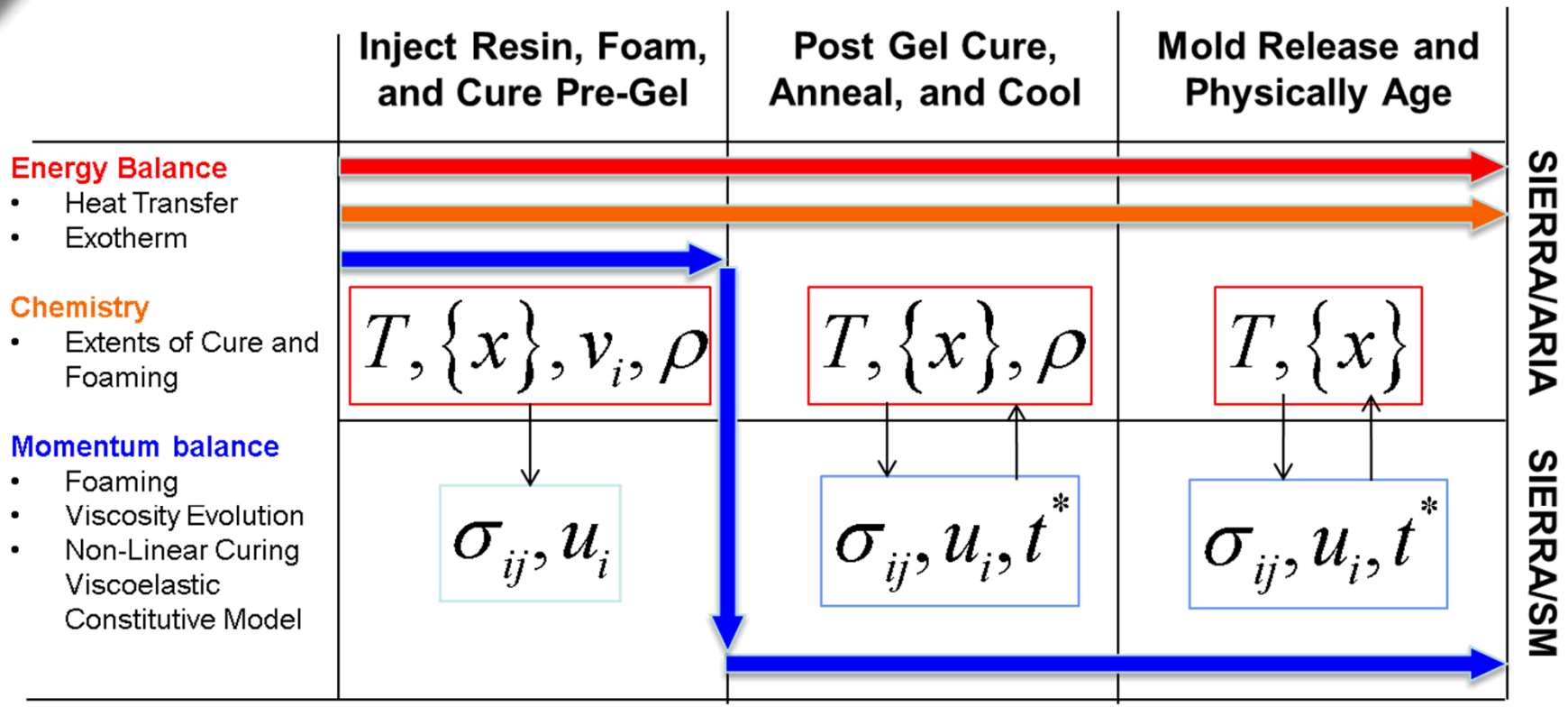
Matrix Gelation

Matrix Vitrification

An Overview of the Model

- **Foaming, Filling, and Polymerization** are simulated on an **Eulerian** mesh until the foam (solid phase) gels (solidifies)
  - Current foaming model over-predicts gas void size and is a source of error
- A **Lagrangian** description of the balance laws ensues in which the solid phase is represented by a curing, **non-linear viscoelastic model**.
  - The solid phase continues to cure
  - The cure schedule is completed
  - The component is released from the mold and allowed to age
- **Density gradients** are locked in during the Eulerian step
- **Extent of cure** gradients are locked in if the solid phase vitrifies during cure
- **Residual stresses** form and relax as the thermal and mechanical boundary conditions change

Three Stage Modeling Approach



$$T, \{x\}, v_i, \rho, u_i, \sigma_{ij}, t^*$$

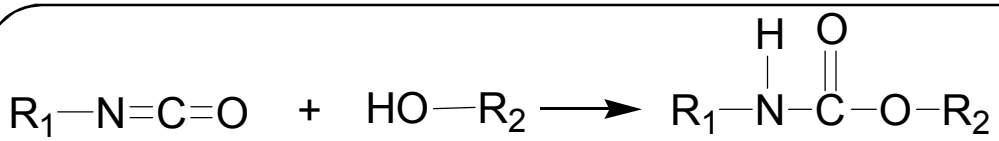
Variables: Temperature, Extent of Reaction, Liquid Foam Velocity, Density, Solid Foam Displacement, Cauchy Stress, Solid Material Time Scale

Multiphysics Coupling in Sierra Mechanics

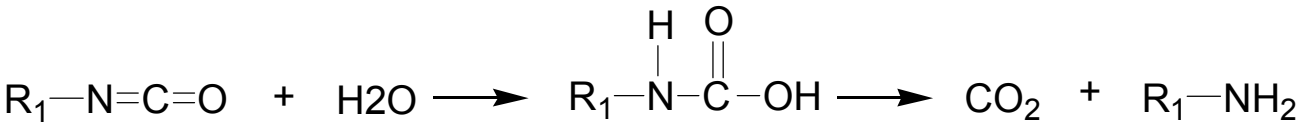
Polyurethane Resin Cure and Foaming Reactions

Two key reactions: **Isocyanate reaction with polyols and water**

→ **Represent Chemical Kinetics with Two Competing Extents of Reaction: ξ , α**

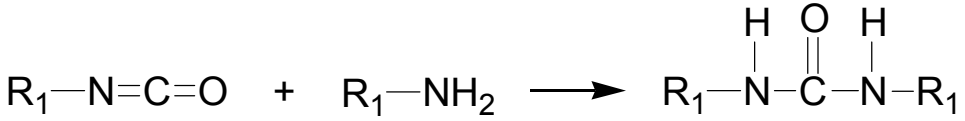


POLYMERIZATION: Urethane formation, crosslinking

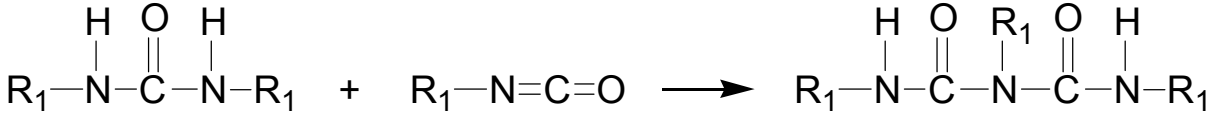


FOAMING: CO_2 and amine

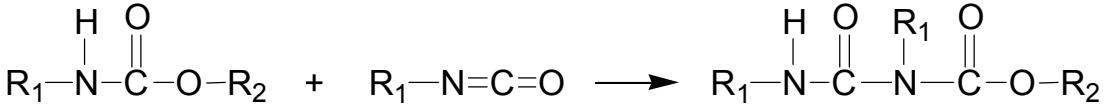
Various follow up reactions: **Isocyanate reaction with amine, urea and urethane**



Urea formation



Biuret formation



Allophanate formation

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Equations of Motion During Stage I: Eulerian Fluid Description

Variable density, shear viscosity, and bulk viscosity

$$\rho\frac{\partial \mathbf{v}}{\partial t} = -\rho\mathbf{v}\bullet\nabla\mathbf{v} - \nabla p + \nabla\bullet(\mu_f(\nabla\mathbf{v} + \nabla\mathbf{v}^t)) - \nabla\bullet\lambda(\nabla\bullet\mathbf{v})I + \rho\mathbf{g}$$

Momentum

$$\frac{D\rho_f}{Dt} + \rho_f\nabla\bullet\mathbf{v} = 0$$

Mass

Variable heat capacity and thermal conductivity
Energy source terms associated with the reaction exotherms

Energy

$$\rho C_{pf}\frac{\partial T}{\partial t} + \rho C_{pf} v\bullet\nabla T = \nabla\bullet(k\nabla T) + \rho\varphi_e\Delta H_{rxn}\frac{\partial \xi}{\partial t}$$

Condensation chemistry

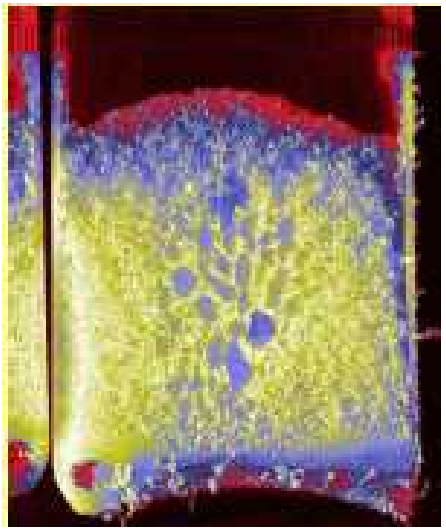
$$\frac{\partial \xi}{\partial t} + \nabla\bullet(\xi v) = k^i e^{\Delta E/RT}(1-\xi)^n$$

Extent of reaction equation for polymerization

Michaelis-Menten

$$\frac{d\alpha}{dt} = \frac{k(1-\alpha)^n}{(1-\alpha)^m + M}$$

Extent of reaction equation for the foaming reaction



NMR imaging shows coarse microstructure (Altobelli, 2006)

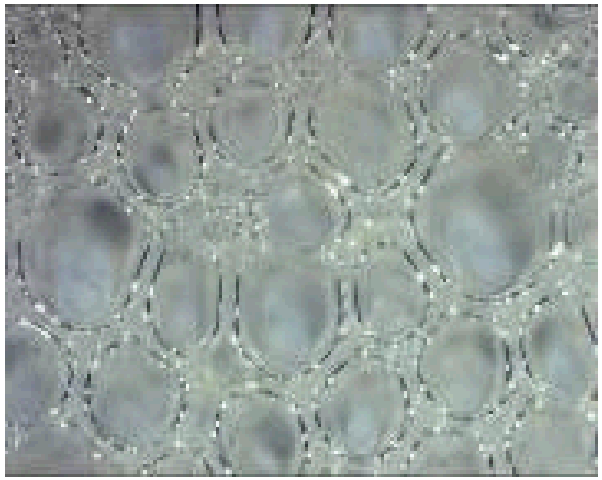
Complex Material Models Vary with Cure, Temperature, and Gas Fraction

Foaming reaction predicts moles of gas from which we can calculate density

$$n_{CO_2}(t) = n_{CO_2}^{init} + \alpha(t) n_{CO_2}^{\max}$$

$$\phi(t) = \frac{n_{CO_2} MW_{CO_2} / \rho_{CO_2}}{n_{CO_2} MW_{CO_2} / \rho_{CO_2} + V_{liquid}}$$

$$\rho_{foam} = (\rho_{CO_2} - \rho_{liquid})\phi(t) + \rho_{liquid}$$



Epoxy foam is a collection of bubbles in curing polymer

Thermal properties depend on gas volume fraction and polymer properties

$$k = \frac{2}{3}\left(\frac{\rho}{\rho_e}\right)k_e + \left(1 - \frac{\rho}{\rho_e}\right)k_v$$

$$C_{pf} = C_{pl}\phi_l + C_{pv}\phi_v + C_{pe}\phi_e$$

Shear and bulk viscosity depends on gas volume fraction, temperature and degree of cure

$$\mu = \mu_0 \exp\left(\frac{\varphi_v}{1-\varphi_v}\right) \quad \mu_0 = \mu_0^0 \exp\left(\frac{E_\mu}{RT}\right)\left(\frac{\xi_c^2 - \xi^2}{\xi_c^2}\right)^{-4/3}$$

$$\lambda = \frac{4}{3}\mu_0 \frac{(\phi_v - 1)}{\phi_v}$$

- Experiments to determine foaming and curing kinetics as well as parameters for model
- Equations solved with the finite element method using a level set to determine the location of the free surface (Rao et al., IJNMF, 2012)

Stage II and III: Post-Gelation Cure: Curing, Heat Transfer, and Viscoelasticity

- Energy balance and species balance continue to determine the temperature and advancements in the extent of matrix and gas release extents of cure
- Momentum balance now determines the deformation of the solidified foam
- Spatial variations in density and extent of matrix cure give rise to residual stresses and disparate viscoelastic responses
- Non-linear viscoelastic curing model fit to curing data

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

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

Logarithmic Strain — Temperature — Extent of Matrix Cure from ARIA

Material Clock

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

Density Scaling

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

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

Stage II and III: Post-Gelation Cure: Curing, Heat Transfer, and Viscoelasticity

- Mechanical properties depend on the temperature, extent of cure, and histories of deformation, temperature and extent of cure

Material Clock Dependencies

Thermal

Pressure

$$N=\left\{\left[T(t)-T_{ref}\right]-\int_0^t ds\ \mathrm{f}_1\left(t^*-s^*\right)\frac{dT}{ds}(s)\right\}+C_3\left\{I_1(t)_{ref}-\int_0^t ds\ \mathrm{f}_1\left(t^*-s^*\right)\frac{d\mathrm{I}_1}{ds}(s)\right\}$$

$$+C_4\left\{\int_0^t\int_0^t ds\,du\,f(t^*-s^*,t^*-u^*)\frac{d\underline{\underline{\varepsilon}}_{dev}(s)}{ds}:\frac{d\underline{\underline{\varepsilon}}_{dev}(u)}{du}\right\}+C_5\left(x(t)\right)\left\{\left[x(t)-x_{ref}\right]-\int_0^t ds\ \mathrm{f}_1\left(t^*-s^*\right)\frac{dx}{ds}(s)\right\}$$

Shear Deformation

Matrix Cure

Glass Transition Evolution

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

$$C_5\left(x(t)\right)\equiv C_{5a}+C_{5b}\,x+C_{5c}\,e^{\left(x/C_{5d}\right)^{C_{5e}}}$$

Shear Modulus

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

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

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

Why is a Viscoelastic Constitutive Equation Needed?

These PMDI foams vitrify during cure

- Glassy materials are often described with a non-linear viscoelastic model or a rate dependent plasticity model

The residual stress state from manufacturing arises from:

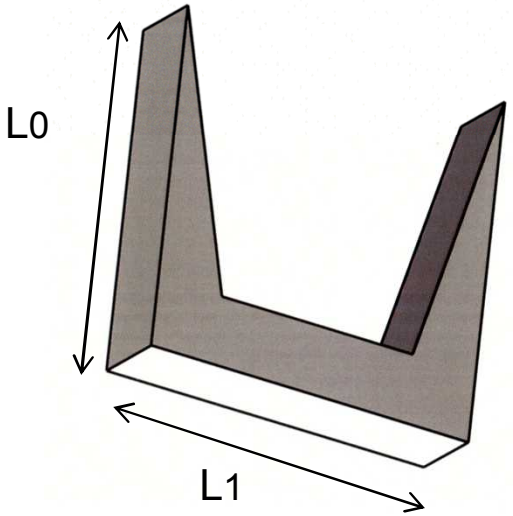
- Volume change during polymerization
- Thermal Expansion
- Thermal-mechanical history and boundary conditions

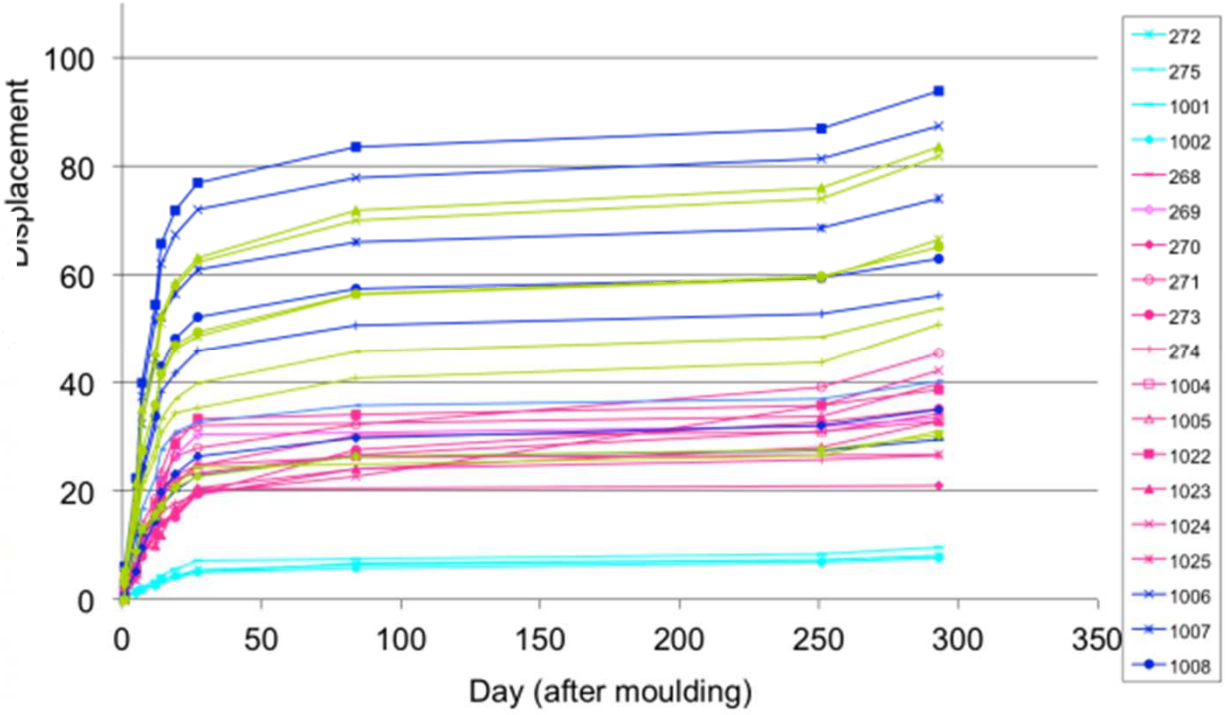
This residual stress state relaxes as determined by the spatially varying material time scale (Key Feature of a Viscoelastic Approach)

- Curing thermal-elastic model could not account for relaxation
- Perhaps a curing visco-plastic model could?

A Simple Test Problem: A Foam Staple

- Part is similar to components we seek to support
- Features long, slender regions susceptible to warpage
- Parametric study was undertaken to obtain physical intuition and reduce experimental matrix





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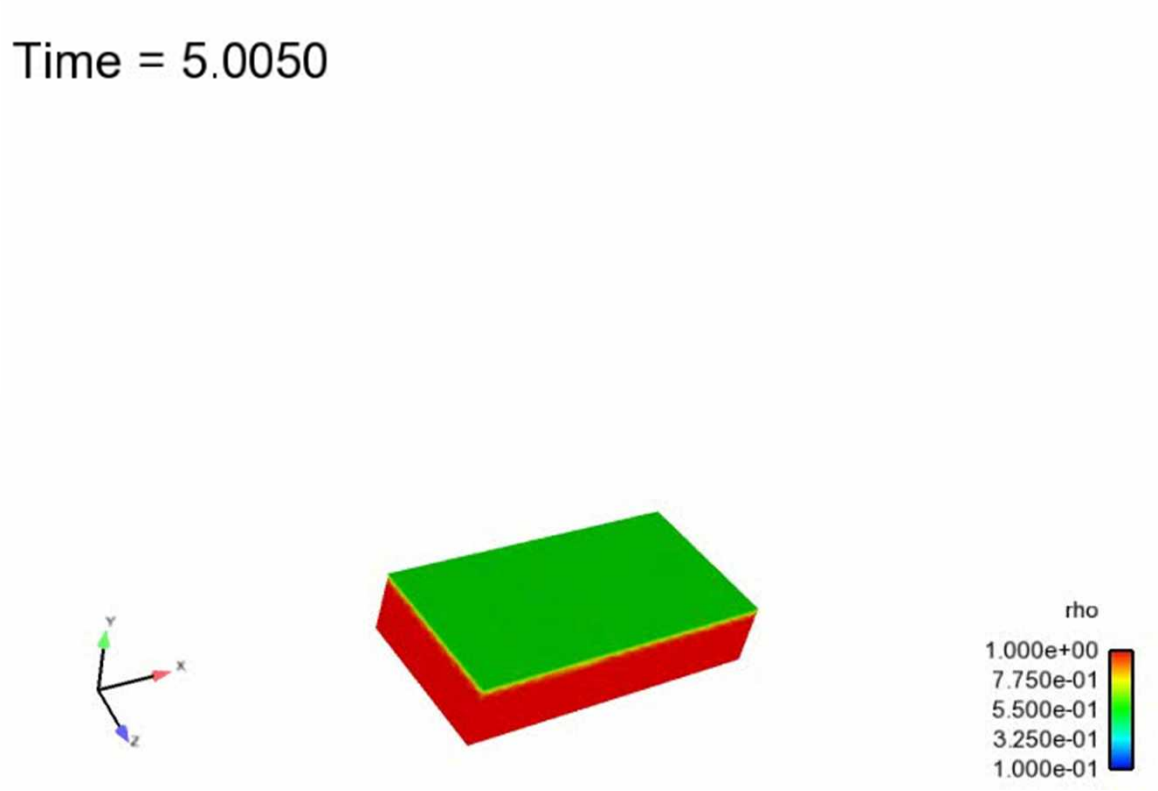
Pre-Gel Foaming and Filling

- The resin foams and quickly fills the mold (within 100 seconds)
- Density continues to decrease as gas evolves and the matrix cures
- Foam is close to the gel point at 121 seconds (0.35)
- Residual air is still in issue for the simulation

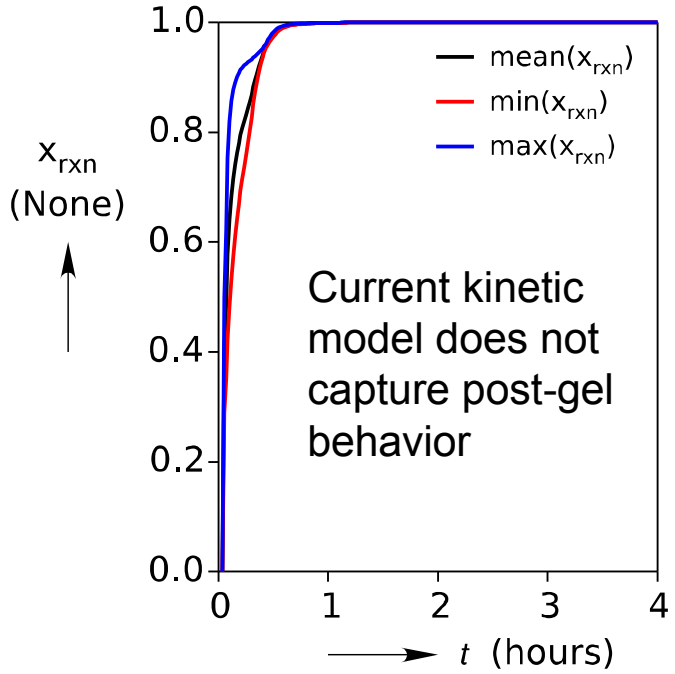


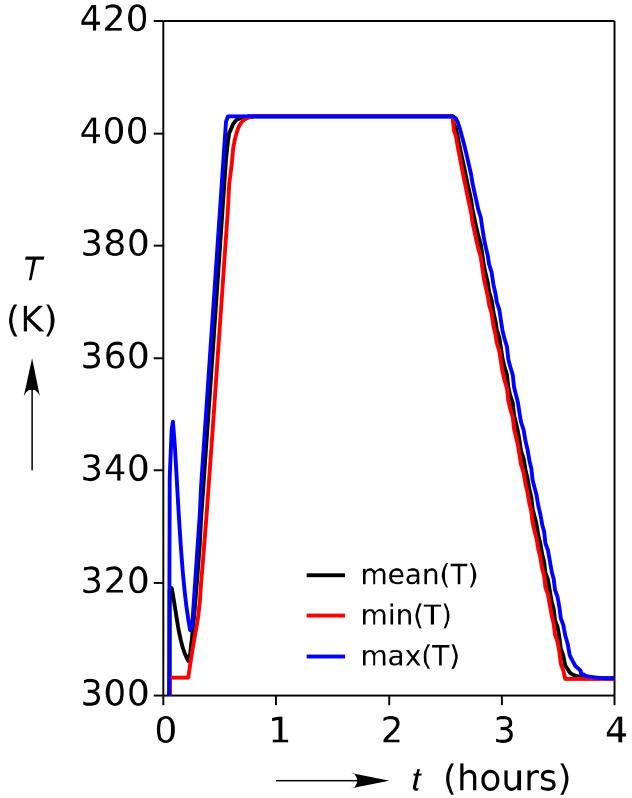
Parametric Study Description

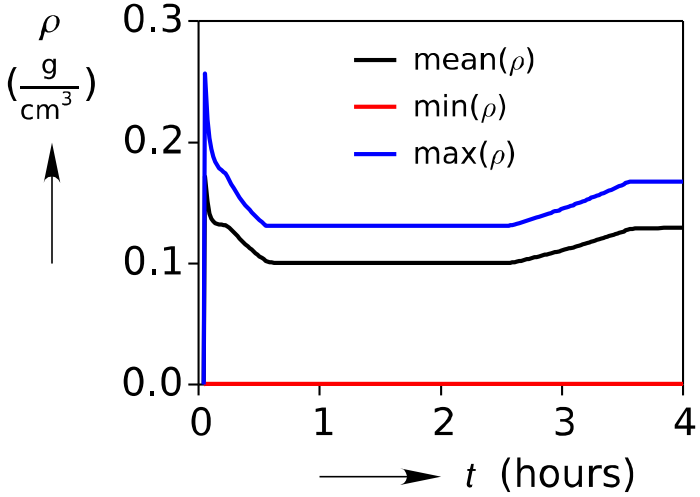
- Ultimately, we want to understand which material and environmental parameters exacerbate the loss of dimensional stability
- We are also challenged to fully populate the fluid, thermal, chemical, and mechanical models
  - Experiments are difficult
- Therefore, we perform parametric studies both to improve our intuition and to narrow our experimental investigations

Temperature, Density, and Reaction Extent During the Manufacturing

1. Mold filling occurs until the viscosity diverges (near 140 seconds for this mold)
2. The staple is brought to 130 C for 2 hours, held, and then cooled to room temperature
3. At room temperature, the staple is released from the mold and allowed to relax free of external constraints







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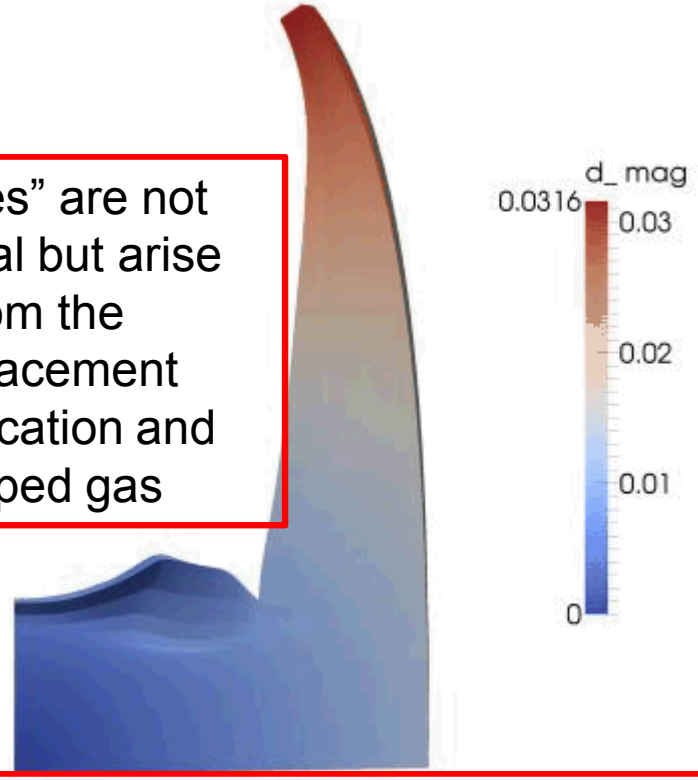
The "Nominal" Simulation

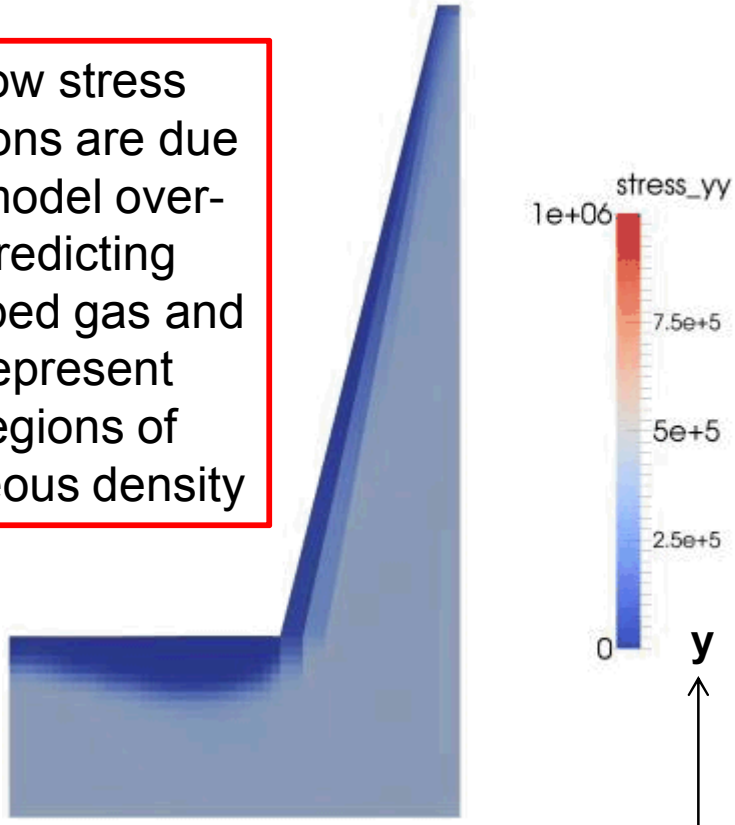
Displacements (cm) amplified by 100

- 10% Volume Strain on 100% Cure
- Final T_g = 130°C at 100% Cure
- Cure chemistry is *not* arrested due to vitrification

"Ruffles" are not physical but arise from the displacement amplification and trapped gas



Low stress regions are due to model over-predicting trapped gas and represent regions of gaseous density



Long, slender regions experience the most deformation both because of spatial variations in stress but also due to their large initial length

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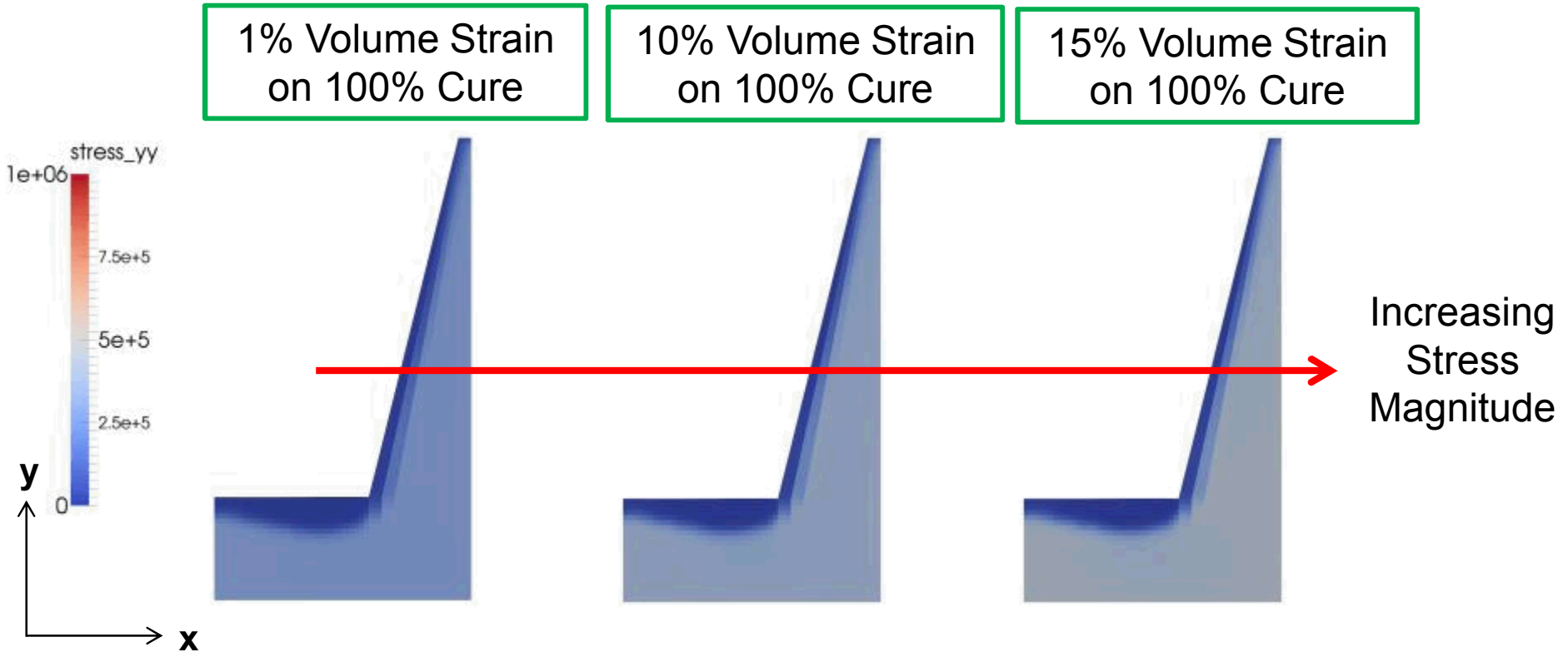
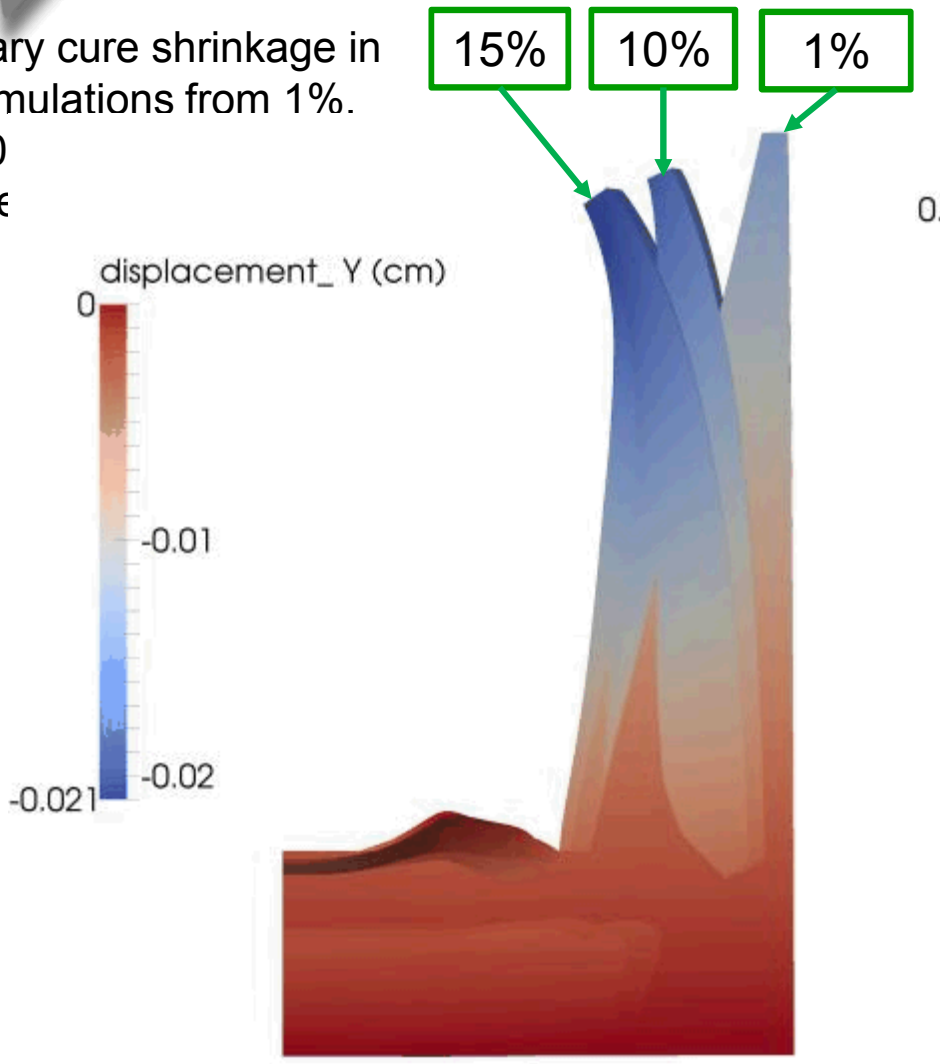
Cure Shrinkage Exacerbates the Residual Stress State Prior to Mold Release

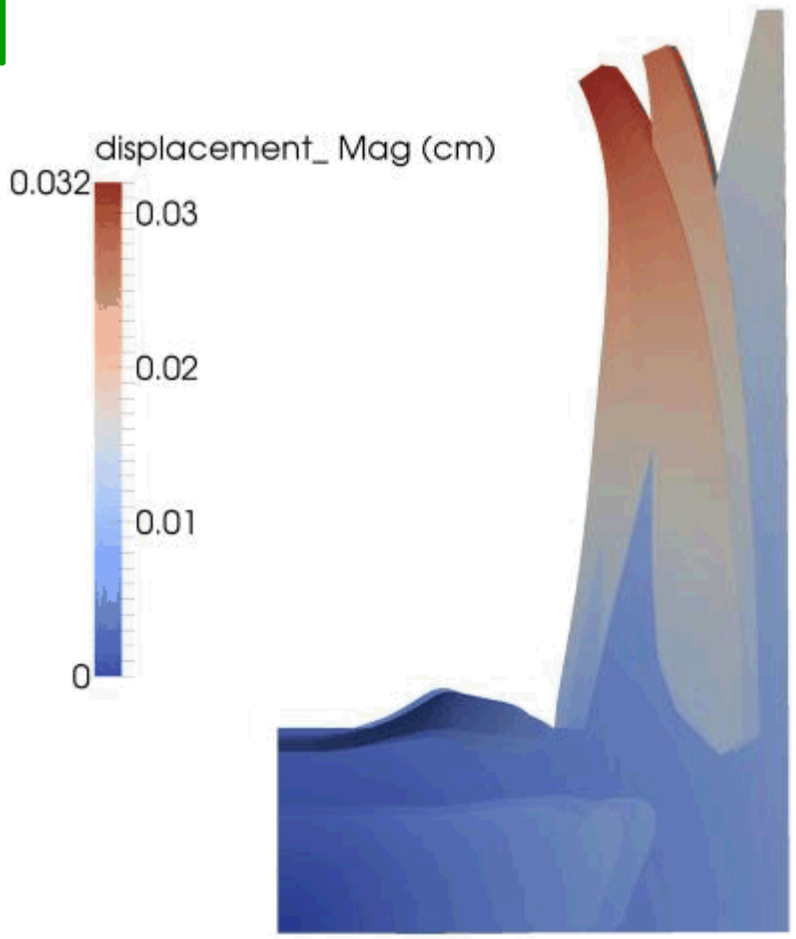


- Volume change on cure (Cure Shrinkage) is an input parameter to the nonlinear viscoelastic model.
- Increasing its value heightens the stress state just prior to component release at room temperature

Cure Shrinkage Exacerbates the Loss of Dimensional Stability

Vary cure shrinkage in simulations from 1%. 10 the





Displacements of 0.03 cm (300 microns) correspond to about 0.3% of the initial long side of the staple

Displacements (cm) amplified by 100

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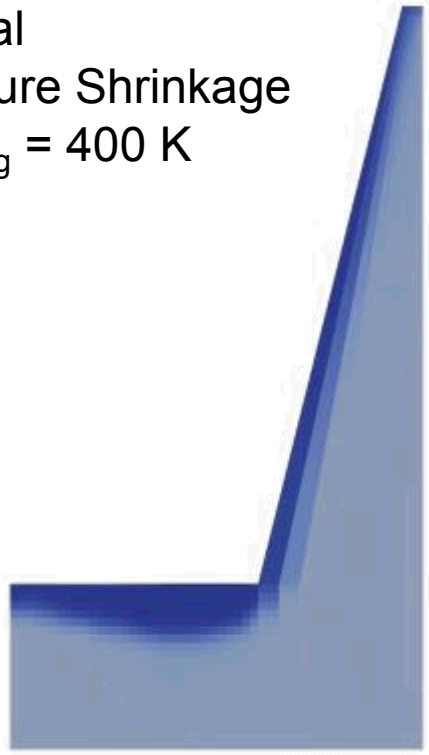
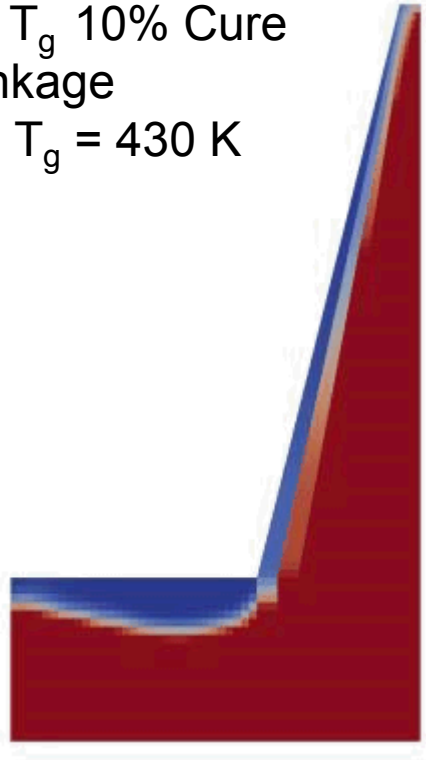
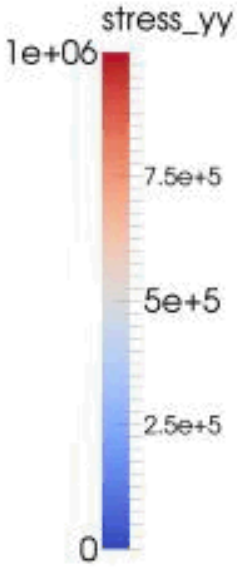
The Role of the Final Glass Transition and Cure History on Dimensional Stability

Nominal
10% Cure Shrinkage
Final T_g = 400 K



High T_g 10% Cure
Shrinkage
Final T_g = 430 K





- Prior to mold release, the stress state is *significantly* higher (by a factor of three) in the simulation with the higher T_g than with the nominal simulation.
- This residual stress state drives more deformation upon mold release as well as a more significant stress relaxation during component aging.

The Role of the Final Glass Transition and Cure History on Dimensional Stability

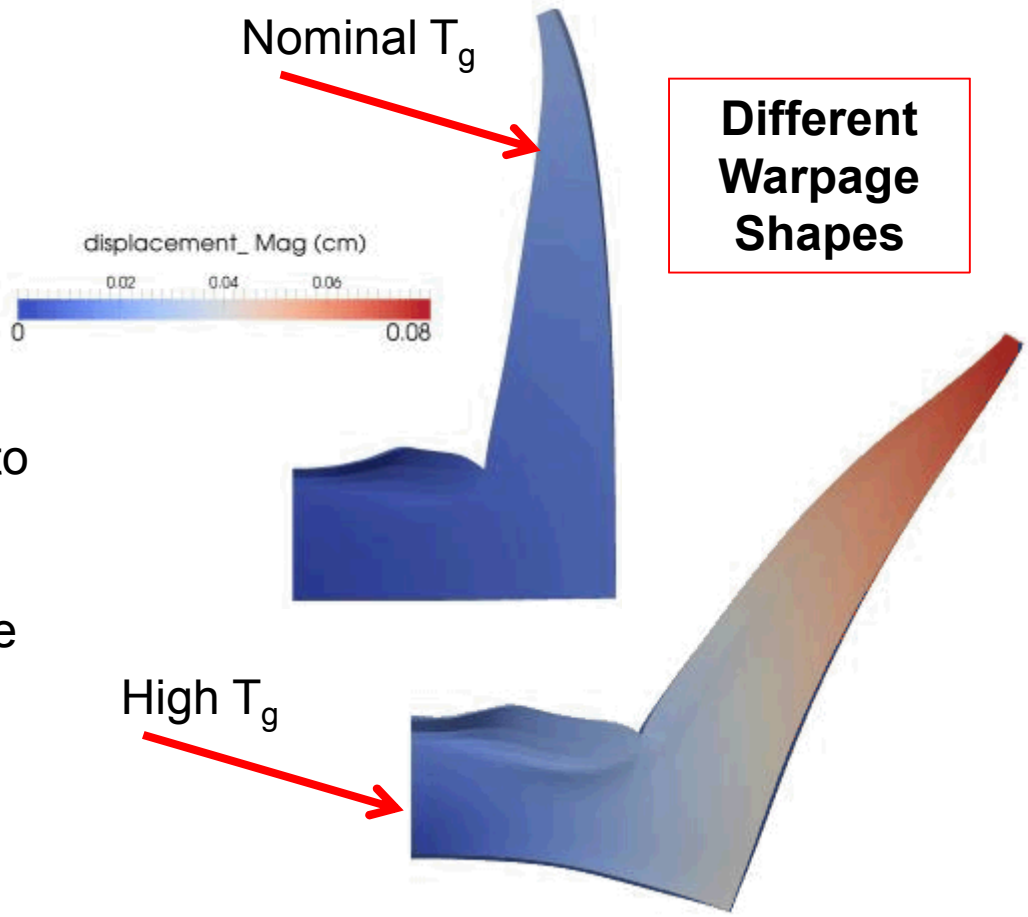
10% Volume Strain on 100% Cure

- Final T_g = 130 C at 100% Cure (Nominal)
- Final T_g = 160 C at 100% Cure (High T_g)
- Without displacement amplification, these two structure are very close in dimensions.

Why is the stress state higher prior to release?

- With a higher T_g, the component vitrifies earlier, and so more of the cure occurs in the glass state.
- In reality, we expect that vitrification arrests cure. But if it can continue, possibly by other mechanisms, the shape is less stable

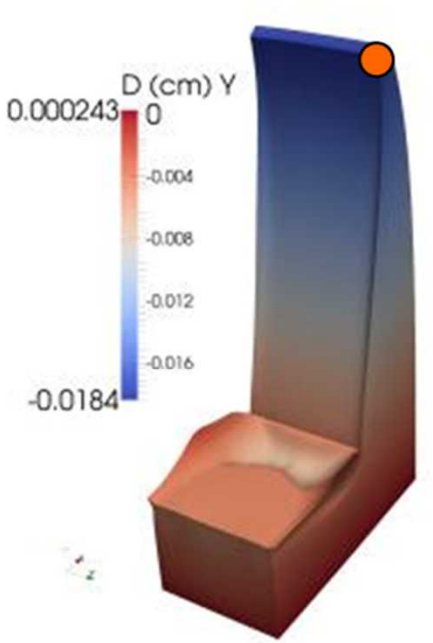
Displacements (cm) amplified by 100

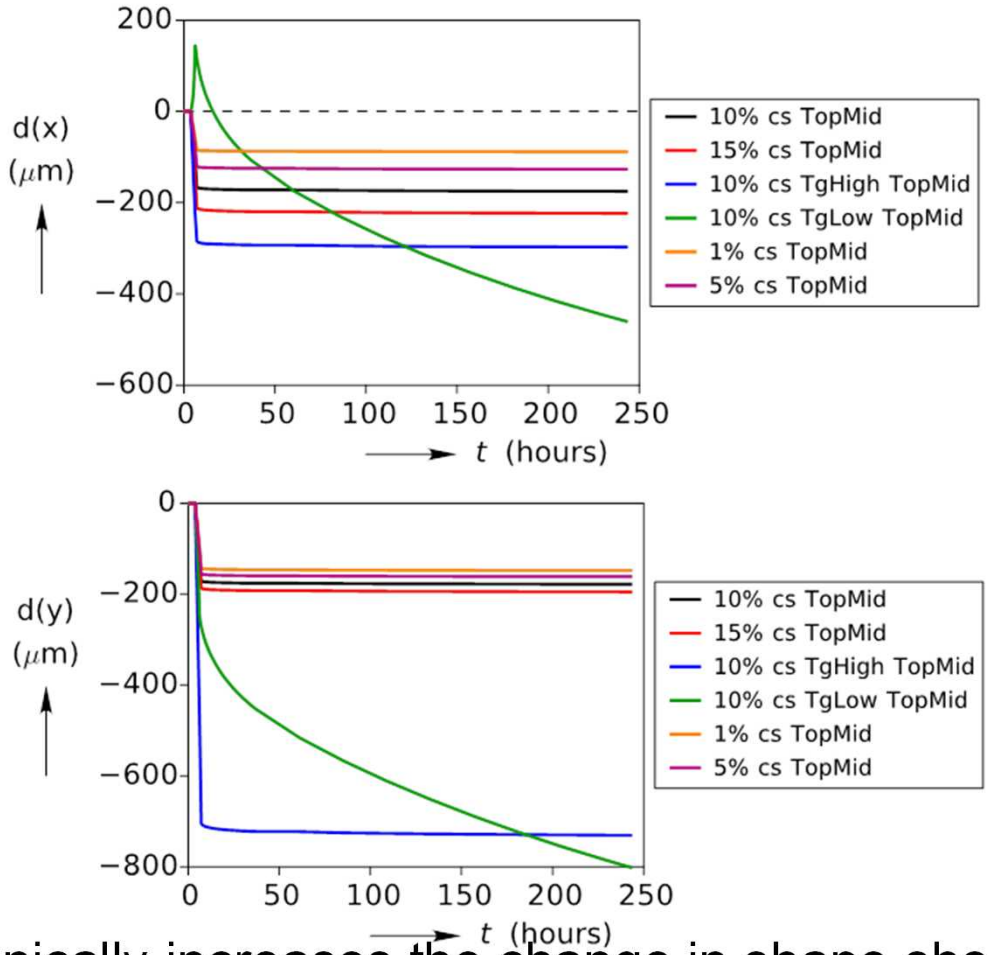


Different Warpage Shapes

At 800 micron deformation, the displacement is nearly 1% of the structure's initial length

Warpage of the Staple-Tip Under Different Cure Shrinkage and State-of-Cure Conditions





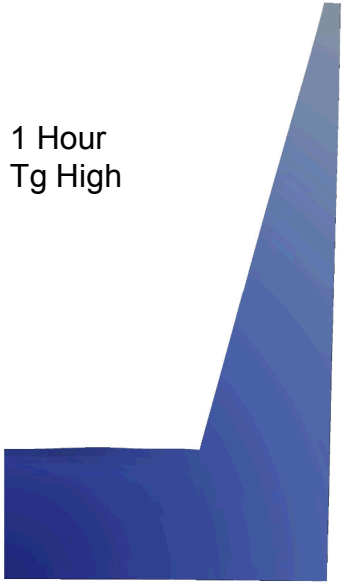
- Cure shrinkage monotonically increases the change in shape shortly after release, but little further shape change is observed
- Rubbery cure results in significant cure shrinkage, a faster material clock, and much more warpage

Conclusions and Future Work

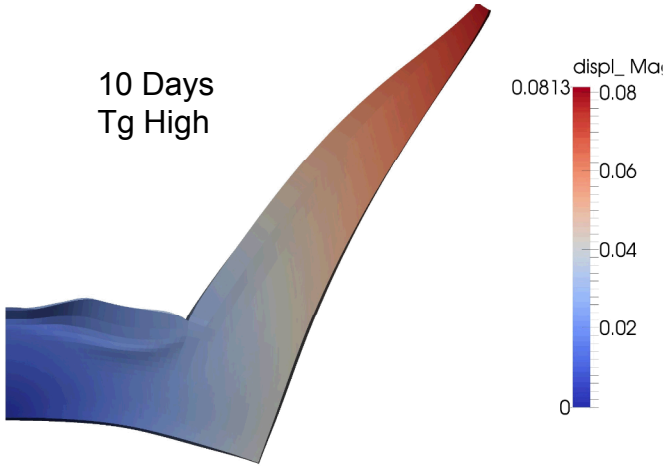
- Initial parametric studies show deformations between 0.1% and 1% of the original specimen dimensions
- More cure shrinkage monotonically produces more change of shape
- The effect of thermal history, here represented by the ultimate T_g, is complicated. The stress state just prior to release is higher for a higher T_g, causing more short-time scale warpage. This is counter-intuitive, since the relaxation time scale is longer with a higher T_g.
- Once we implement vitrification induced arrested kinetics, we will better understand the precise role of thermal history on the residual stress state and deformation. Current model not fully predictive, because of this missing physics.
- With vitrification included in kinetics, we will have gradient in T_g, which could lead to more complexity and heterogeneous response
- Work next FY will make will fill in the missing physics with experimental data and improved kinetics and gas transport models.

TgHigh and TgLow

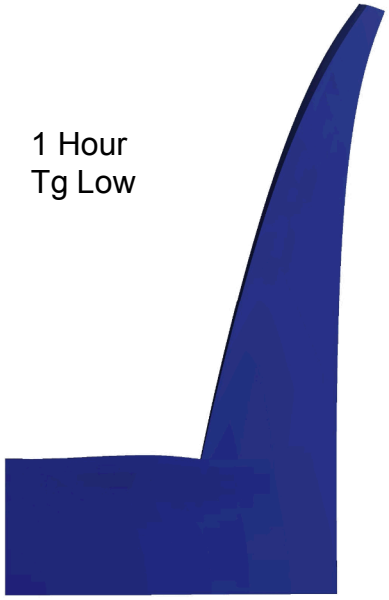
1 Hour
Tg High



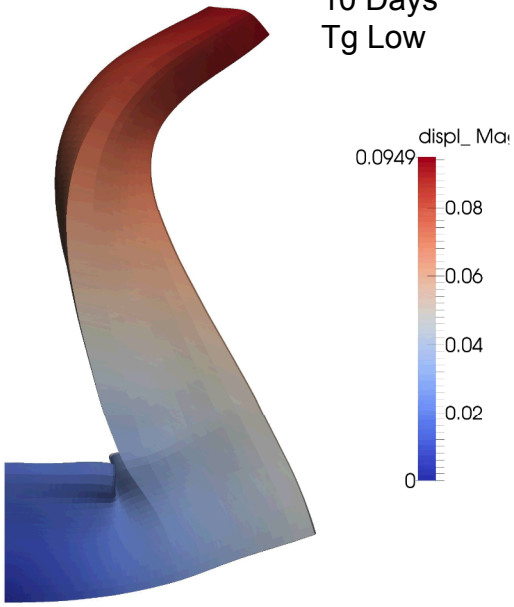
10 Days
Tg High



1 Hour
Tg Low



10 Days
Tg Low



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QUESTIONS?

Kinetic Model Must Include CO_2 Generation and Polymerization Reaction

$$rate_1 = k_1 e^{-\Delta E_1 / RT} [isocyanate]^a [polyol]^b$$ **Polymerization**

$$rate_2 = k_2 e^{-\Delta E_2 / RT} [isocyanate]^c [H_2O]^d$$ **CO_2 generation**

- Must track five species: water, polyol, polymer, carbon dioxide, and isocyanate , since we have competing primary reaction
- Use experiments to determine Arrhenius rate coefficients

$$\frac{D[CO_2]}{Dt} = +rate_2$$

$$\frac{D[H_2O]}{Dt} = -rate_2$$

$$\frac{D[isocyanate]}{Dt} = -rate_1 - rate_2$$

$$\frac{D[polyol]}{Dt} = -rate_1$$

$$\frac{D[polymer]}{Dt} = +rate_1$$

- Must provide initial conditions for all species
- Integrate rate equations as part of the simulation
- Density predicted from gas generation

$$\phi(t) = \frac{n_{CO_2} / MW_{CO_2} \rho_{CO_2}}{n_{CO_2} / MW_{CO_2} \rho_{CO_2} + n_{liquid} / MW_{liquid} \rho_{liquid}}$$

$$\rho_{foam} = (\rho_{CO_2} - \rho_{liquid})\phi(t) + \rho_{liquid}$$

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Post-Gelation and Post Cure: Curing, Heat Transfer, and Viscoelasticity

- Energy balance and species balance continue to determine the temperature and advancements in the extent of matrix and gas release extents of cure
- Momentum balance now determines the deformation of the solidified foam
- Spatial variations in density and extent of matrix cure give rise to residual stresses and disparate viscoelastic responses
- Non-linear viscoelastic curing model fit to curing data

Cauchy Stress: From the Universal Curing Model Developed at SNL (Adolf & Chambers)

$$\underline{\underline{\sigma}} = \left\{K_g(T(t)) - K_\infty(T(t))\right\}\int_0^t ds\ f_1(t^*-s^*)\frac{dI_1}{ds}(s)\ \underline{\underline{I}} - \left\{K_g(T(t))\ \beta_g - K_\infty(T(t))\ \beta_\infty\right\}\int_0^t ds\ f_1(t^*-s^*)\frac{dx}{ds}(s)\ \underline{\underline{I}}$$

$$-\left\{K_g(T(t))\delta_g(T(t)) - K_\infty(T(t))\delta_\infty(T(t))\right\}\int_0^t ds\ f_1(t^*-s^*)\frac{dT}{ds}(s)\ \underline{\underline{I}}$$

$$+\ 2\left\{G_g(T(t),x(t)) - G_\infty(T(t),x(t))\right\}\int_0^t ds\ f_2(t^*-s^*)\ \frac{d\underline{\underline{\varepsilon}}_{dev}}{ds}(s)$$

$$+\left\{K_\infty(T(t))I_1 - K_\infty(T(t))\delta_\infty(T(t))\left[T(t)-T_{sf}\right] - K_\infty(T(t))\ \beta_\infty\left[x(t)-x_{sf}\right]\right\}\underline{\underline{I}} + 2\int_0^t G_\infty(s)\ \frac{d\underline{\underline{\varepsilon}}_{dev}}{ds}ds$$

Material Clock

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

Density Scaling

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

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

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Post-Gelation and Post Cure: Curing, Heat Transfer, and Viscoelasticity

- Mechanical properties depend on the temperature, extent of cure, and histories of deformation, temperature and extent of cure

Material Clock Dependencies

$$N = \left\{ \left[T(t) - T_{ref} \right] - \int_0^t ds\ \mathrm{f}_1\left(t^* - s^*\right) \frac{dT}{ds}(s) \right\} + C_3 \left\{ I_1(t)_{ref} - \int_0^t ds\ \mathrm{f}_1\left(t^* - s^*\right) \frac{d\mathrm{I}_1}{ds}(s) \right\}$$

$$+C_4 \left\{ \int_0^t \int_0^t ds\, du\, f(t^* - s^*, t^* - u^*) \frac{d\underline{\underline{\varepsilon}}_{dev}(s)}{ds} : \frac{d\underline{\underline{\varepsilon}}_{dev}(u)}{du} \right\} + C_5\left(x(t)\right) \left\{ \left[x(t) - x_{ref} \right] - \int_0^t ds\ \mathrm{f}_1\left(t^* - s^*\right) \frac{dx}{ds}(s) \right\}$$

Glass Transition Evolution

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

$$C_5\left(x(t)\right) \equiv C_{5a} + C_{5b}\, x + C_{5c}\, e^{\left(x / C_{5d}\right)^{C_{5e}}}$$

Shear Modulus

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

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

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

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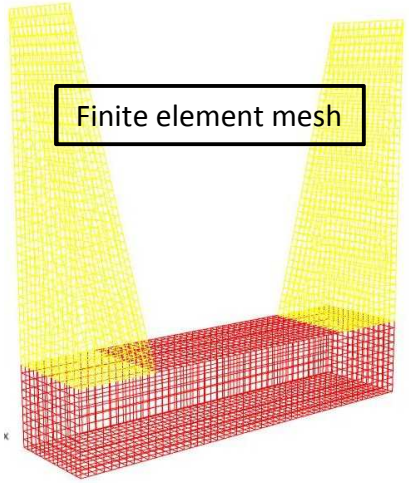
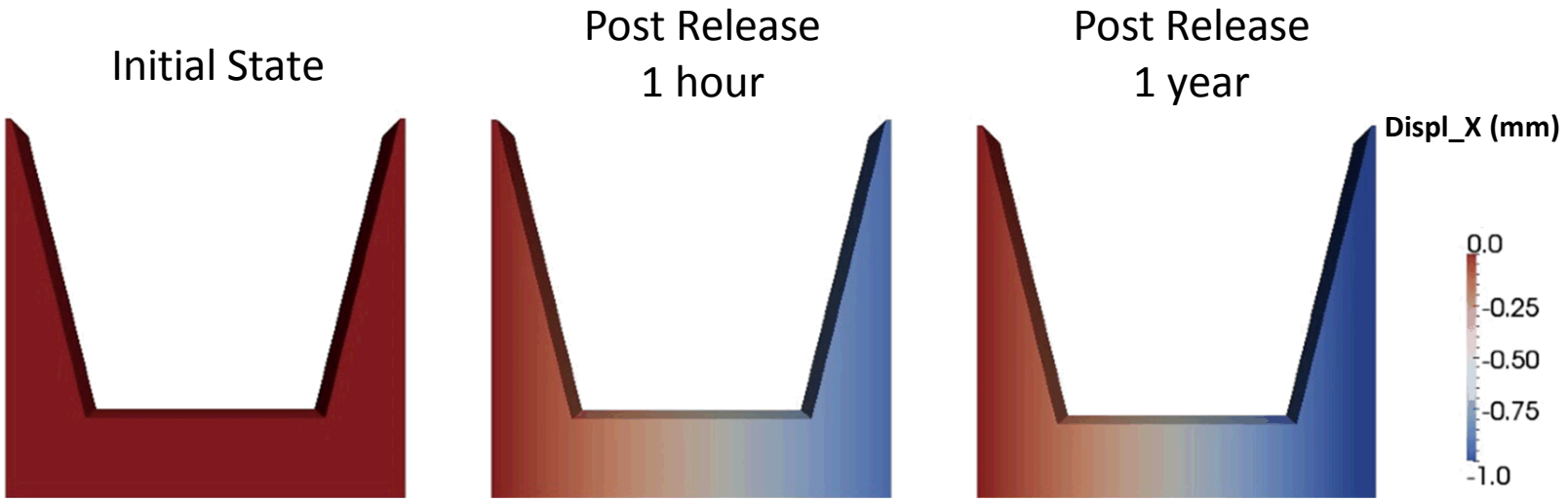
Uniform Motion Under Homogenous Fill Without Boundary Condition Constraint

- **The foam is cooled without constraint**
- **It is then aged for 1 year under traction free conditions.**
- **The foam deforms spherically due to viscoelasticity; the shape does not distort.**





Homogeneous Material Properties and Boundary Conditions Give Only an Isotropic Response

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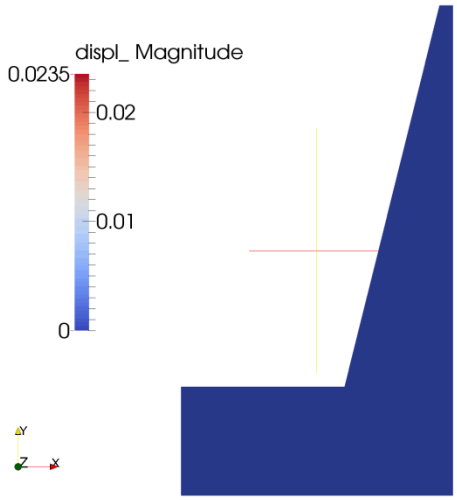
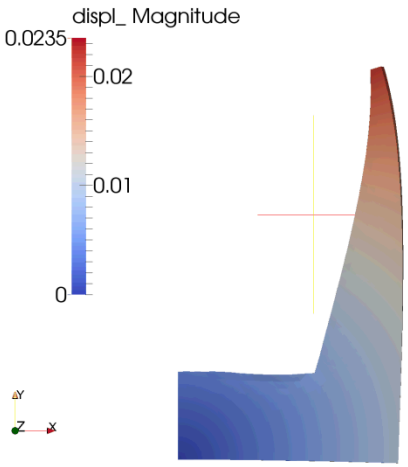
10% Cure Shrinkage Impacts the Final Shape (Mesh Displacements (cm) amplified by 100)

Time: 3.006589



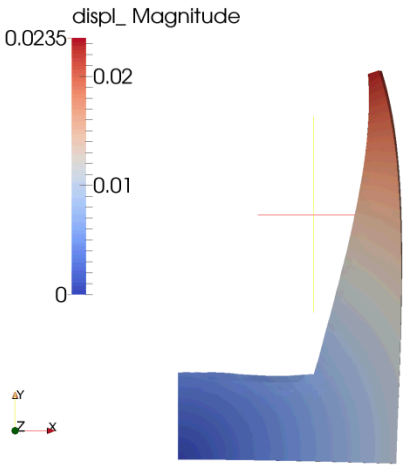
- 2 hours after resin injection
- Bonded to the mold sidewalls
- At the end of the 120 C Anneal

Time: 4.018443



- 10 minutes after mold release, 200 micron displacements are observed

Time: 27.705058

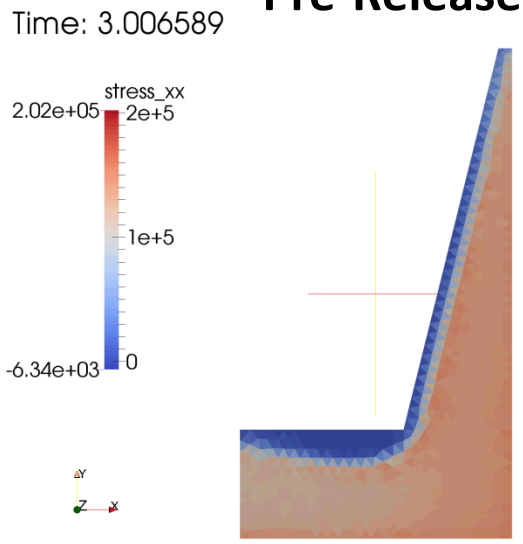


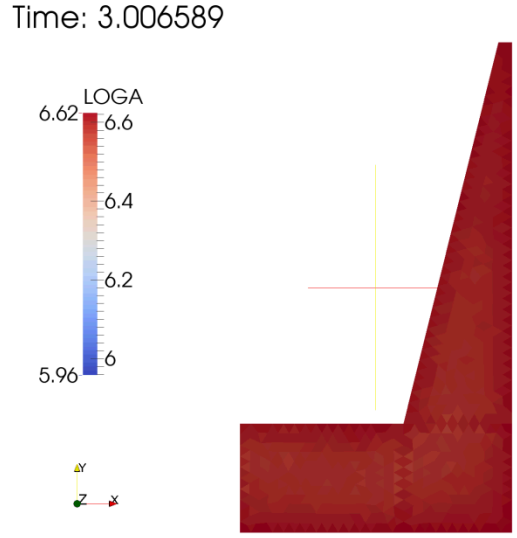
- 24 hours after mold release, little additional deformation is seen

Cure shrinkage, variations in density, and thermal contraction contribute to residual stresses that cause warpage

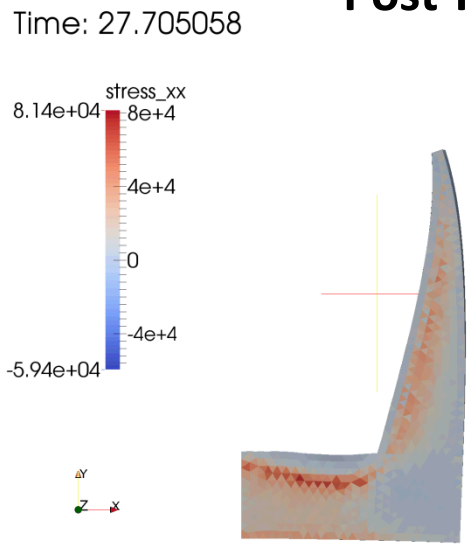
Residual Stresses Locked in Due to Vitrified State

Pre-Release





Post-Release



The peak stress state (in dyne / cm^2 or 0.1 Pa) is relieved by roughly an order of magnitude when the grips are released.

The material time scale is SLOW, which means that with this stripped-down viscoelastic response, it would take 10-100 million seconds for the structure to relax

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
- Hydrostatic compression in the glassy state
  - Bulk modulus measurements
- Thermal-Mechanical Analysis (TMA) through the glass transition
  - Coefficients of thermal expansion

II. Viscoelastic Characterization on Fully Cured <u>Neat Polymer (Dry Foam) Specimens</u>

- Iso-frequency temperature sweep in oscillatory shear
  - T_g
  - Isothermal frequency sweeps in oscillatory shear above T_g
  - Shear WLF characterization
  - Shear relaxation function in the time domain
- TMA sweeps across the glass transition
  - Fit the volumetric relaxation function

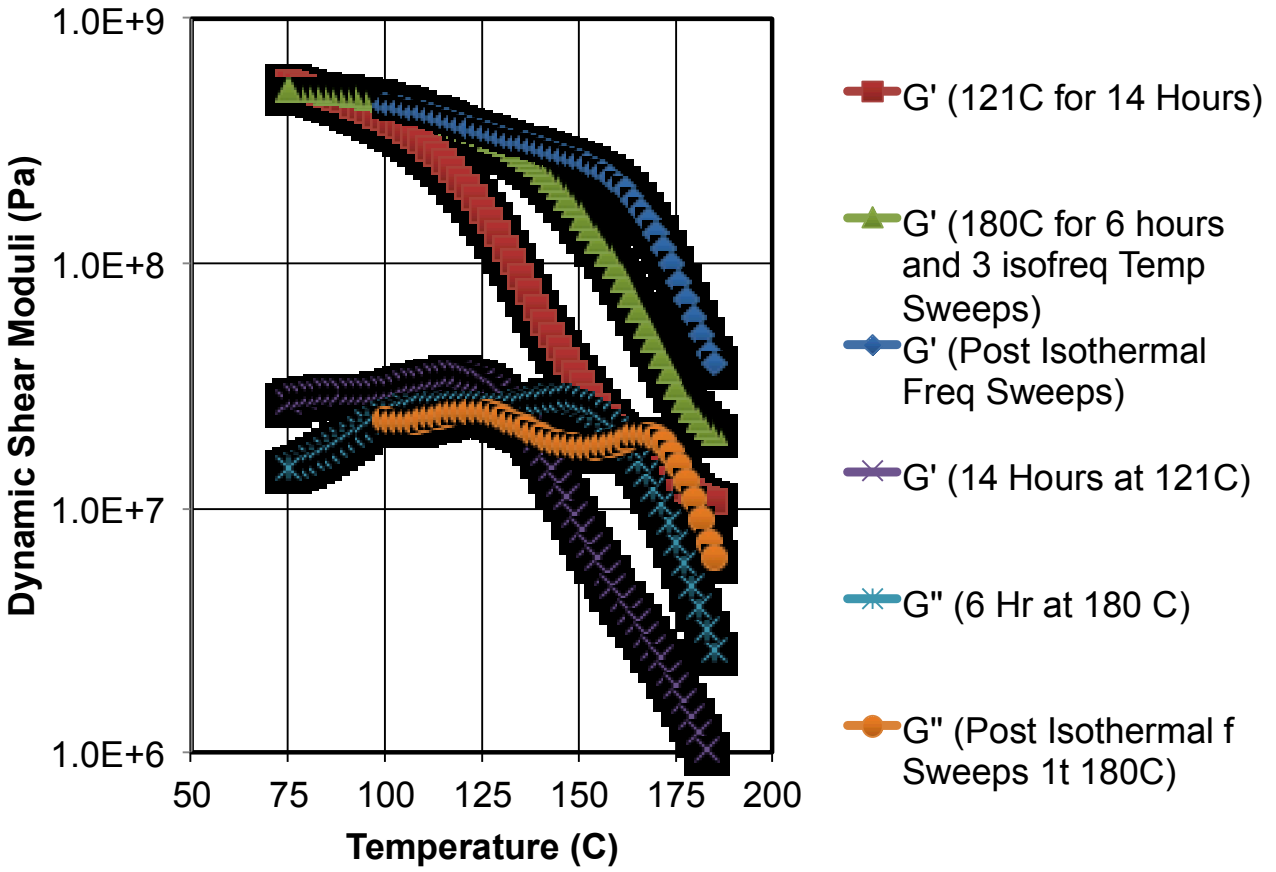
III. Cure Effects on <u>Neat Polymer Specimens</u>

- 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 possibly on rectangular bars analyzed in the TMA or kovar tube
  - Volume change vs. extent of reaction

Then We Face Reality!

- **We cannot reach a stable (no further curing) rubbery state without incurring decomposition and/or other side reactions**

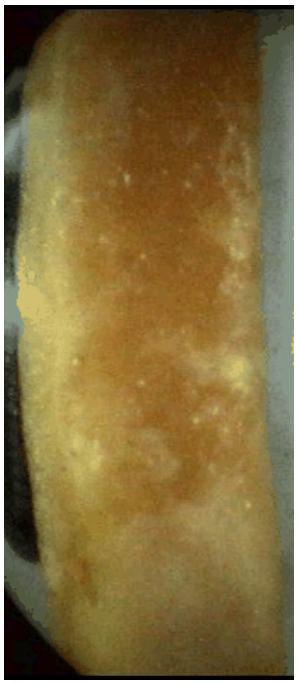
- **Instead of fully cured dry foam specimens, we characterize above the cure schedule (between 120 and 180 C)**
  - **Viscoelastic measurements are convoluted by additional cure**



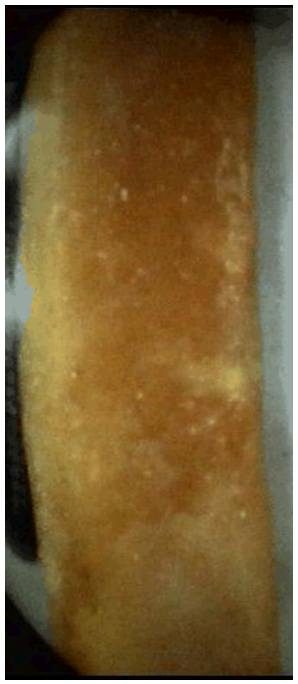
Curing continues up to 225 C, where we observe decomposition. No stable rubbery state

Experimental characterization of the structural foam

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

Summary and Future Work

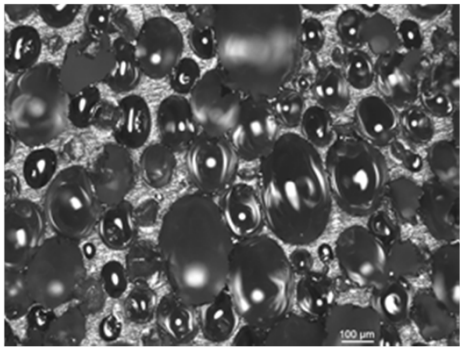
Summary

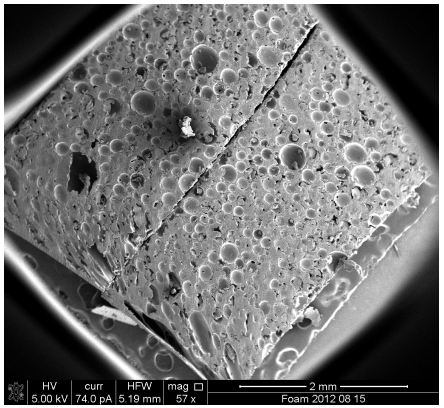
- Multi-physics framework developed to simulate foam filling, curing, gelation, vitrification, and physical aging
- Cure shrinkage, thermal contraction, and spatial variations in density and extent of cure are all important in the development of residual stresses

Future Work

- Fluid and gas compressibility and behavior at walls
- Arrest cure kinetics with vitrification
- Experimental characterization of “fully cured” foam
- Anisotropic bubble formation and constitutive response

SEM of foam showing polydispersity





Bubble at walls are elongated and show coarsening

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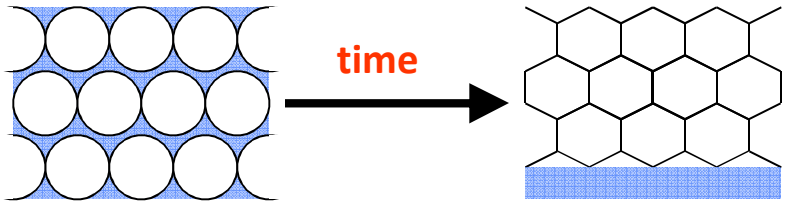
Foam characterization is challenging

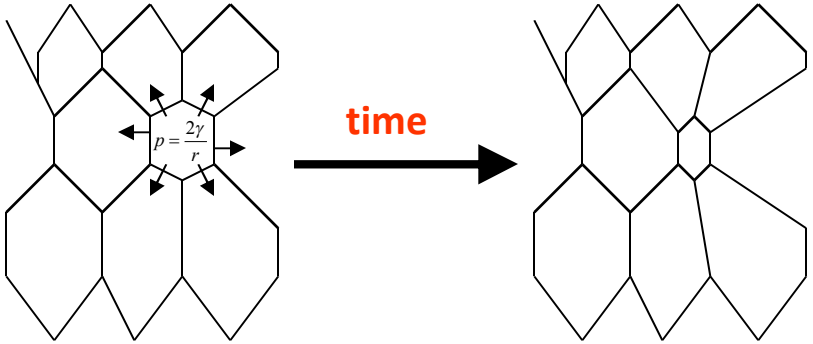
Structure is continuously evolving

- Foams are multiphase materials with a compressible gas dispersed as bubbles in a continuous phase
- Bubble microstructure affects macroscopic properties
- Microstructure can evolve in reversible and irreversible manner
- Property measurements can alter foam
- Evolving volume is an additional issue
- Evolving crosslinks reduce free volume resulting in cure shrinkage and stress evolution
- Glassy versus rubbery behavior
- Above T_g we can also experience degradation

Liquid Drainage



Cell Coarsening

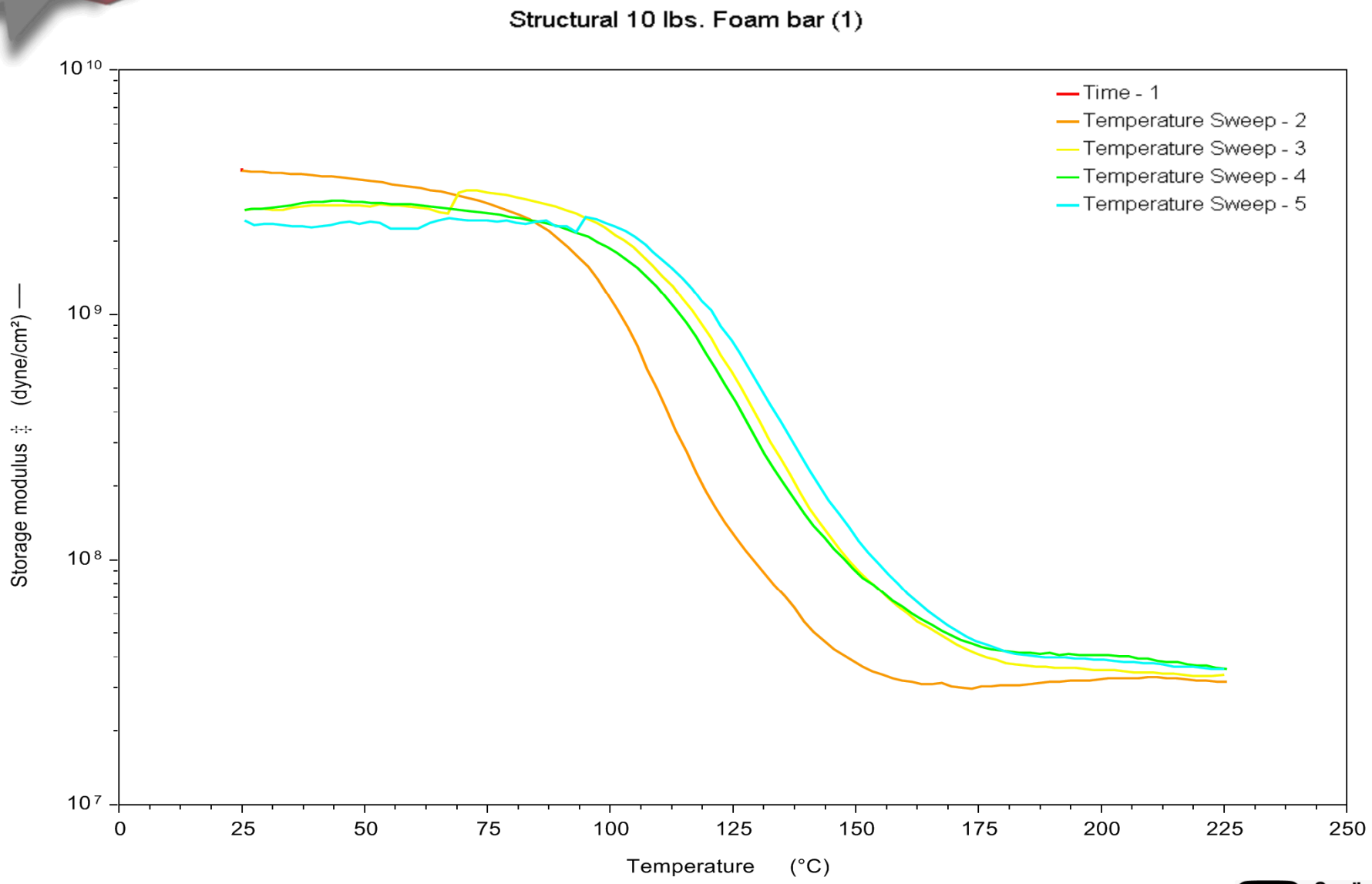


Coalescence and rupture also occur

New Oscillatory Shear Data From September 2014 from Melissa Soehnel

- 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

Raw Data from the ARES 2 Rheometer



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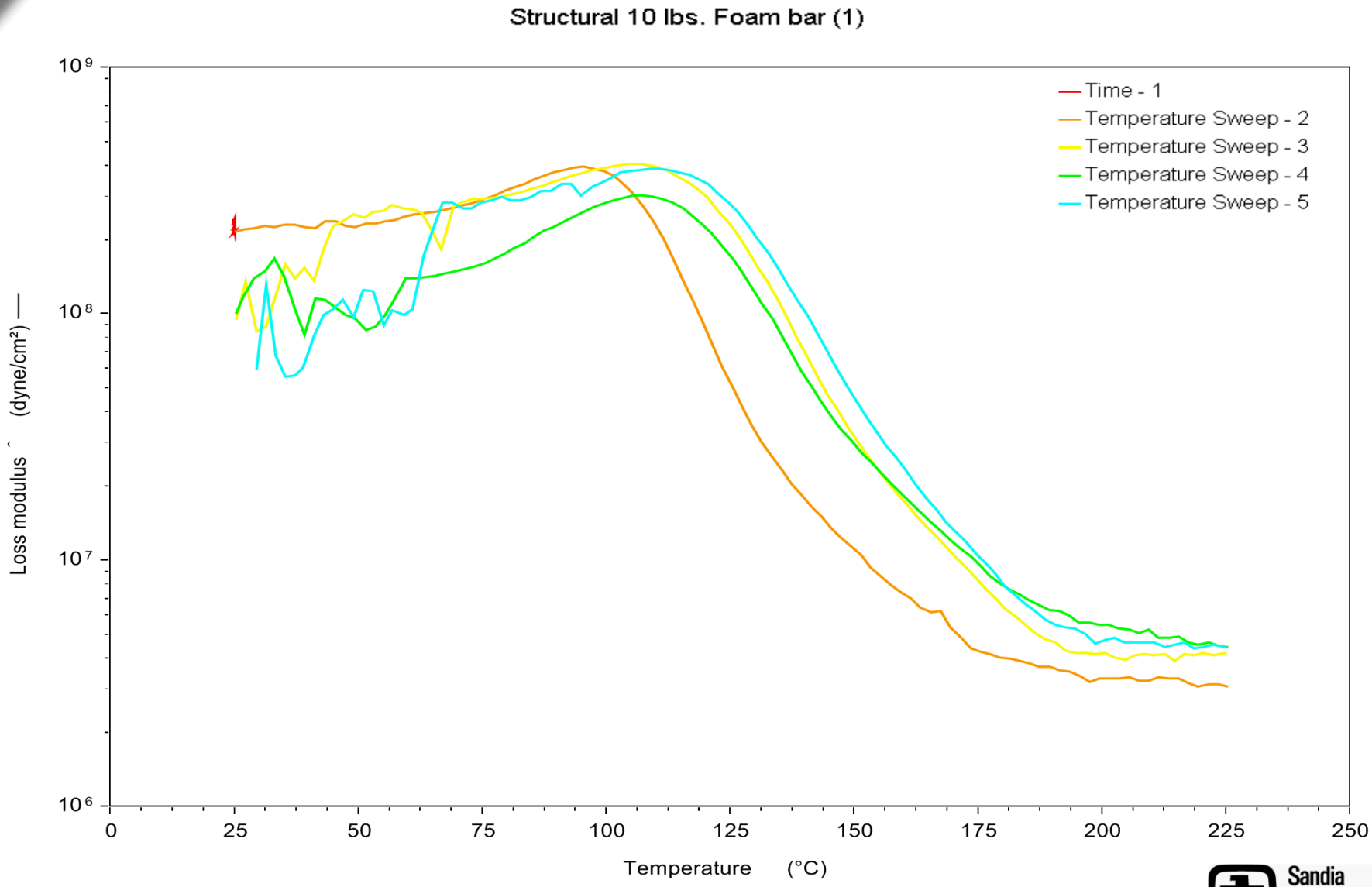
Raw Data from the ARES 2 Rheometer



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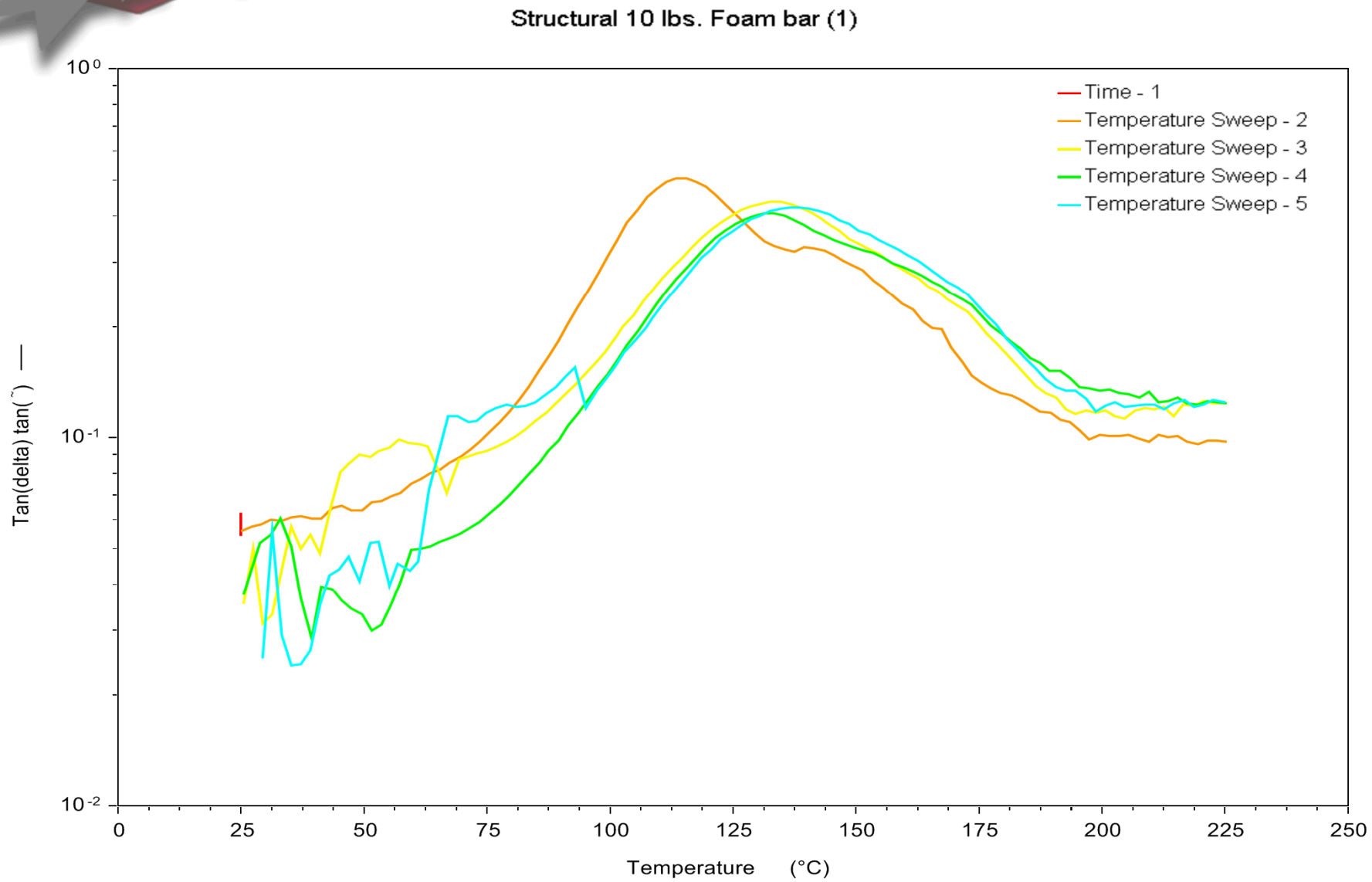
Raw Data from the ARES 2 Rheometer



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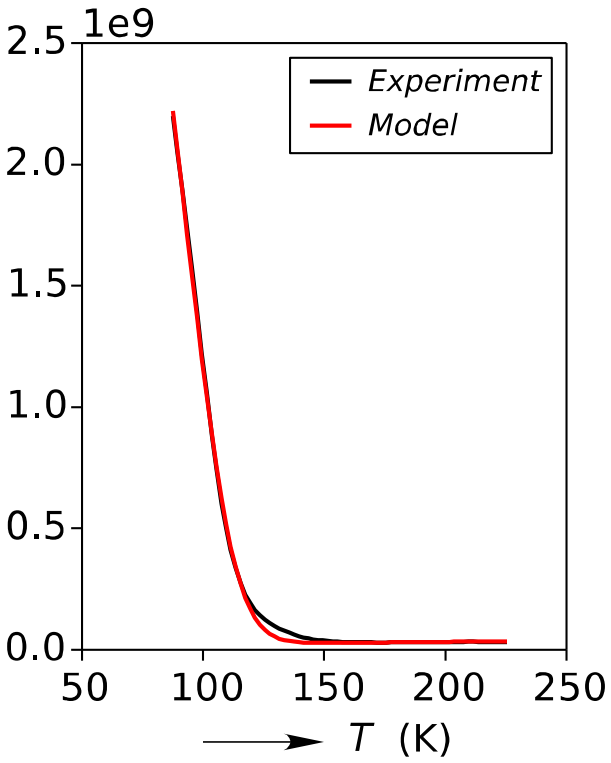
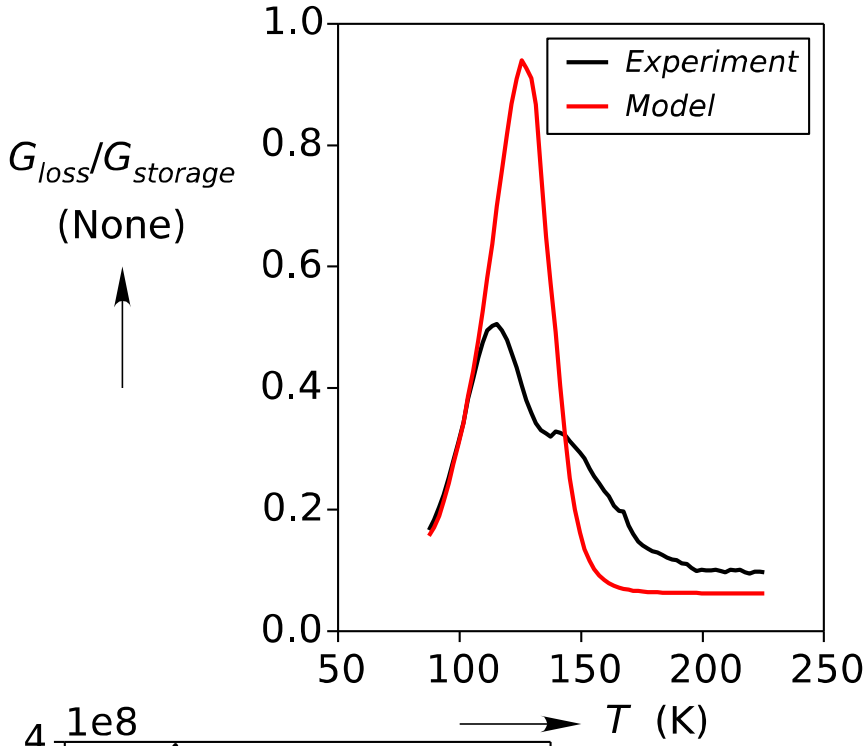
Possible Viscoelastic Model Fitting Approach

- **Assume:**
  - **Linear Viscoelastic Behavior**
  - **Time-Temperature Superposition (TTS)**
  - **Rheological Simplicity**
  - **WLF Form of the TTS**
  - **No Temperature dependence of Geq or Gglassy**
- **Fitting Procedure 1:**
  - **Assume C1, C2 from the Ferry's Book on page 278**
  - **Use a reference temperature that corresponds to the peak of the tan delta experimental curve from the first temperature sweep**
  - **Fit the (tau, beta) parameters from the Williams-Watts Stretched exponential shear relaxation function (instead of a direct proney series) as well as Geq and Gglassy to try to generate the G' vs. T curve using Sierra or a semi-analytical code**
- **Fitting Procedure 2:**
  - **Fit WLF Geq, Gglassy, C1, C2, tau, and beta directly to the G' vs. T curve using sierra or a semi-analytic code**

Fitting Results





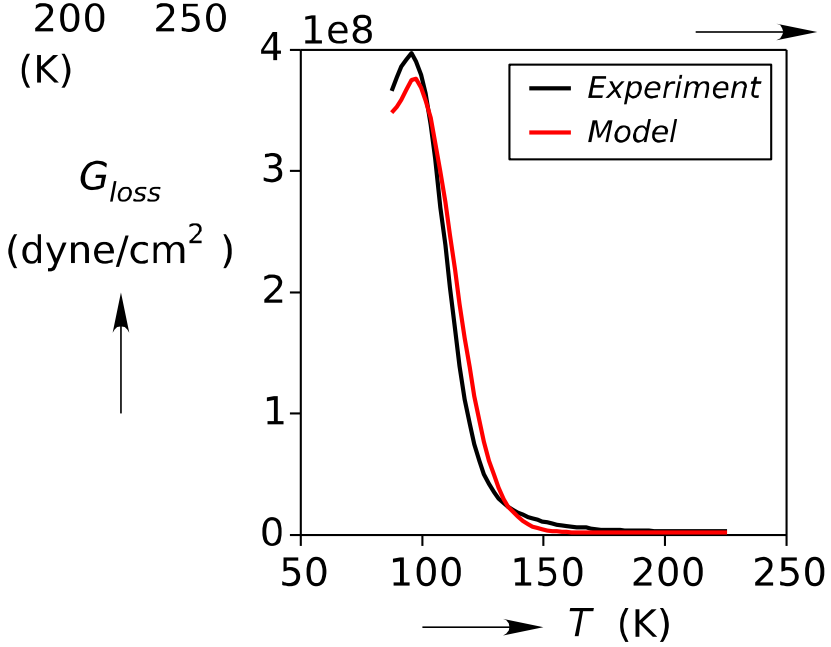
$$C_1 = 11.9499$$

$$C_2 = 98.591 \quad K$$

$$T_{ref\,0} = 115.47 \quad K$$

$$WW_\tau = 0.9216E-3 \quad s$$

$$WW_\beta = 0.181$$



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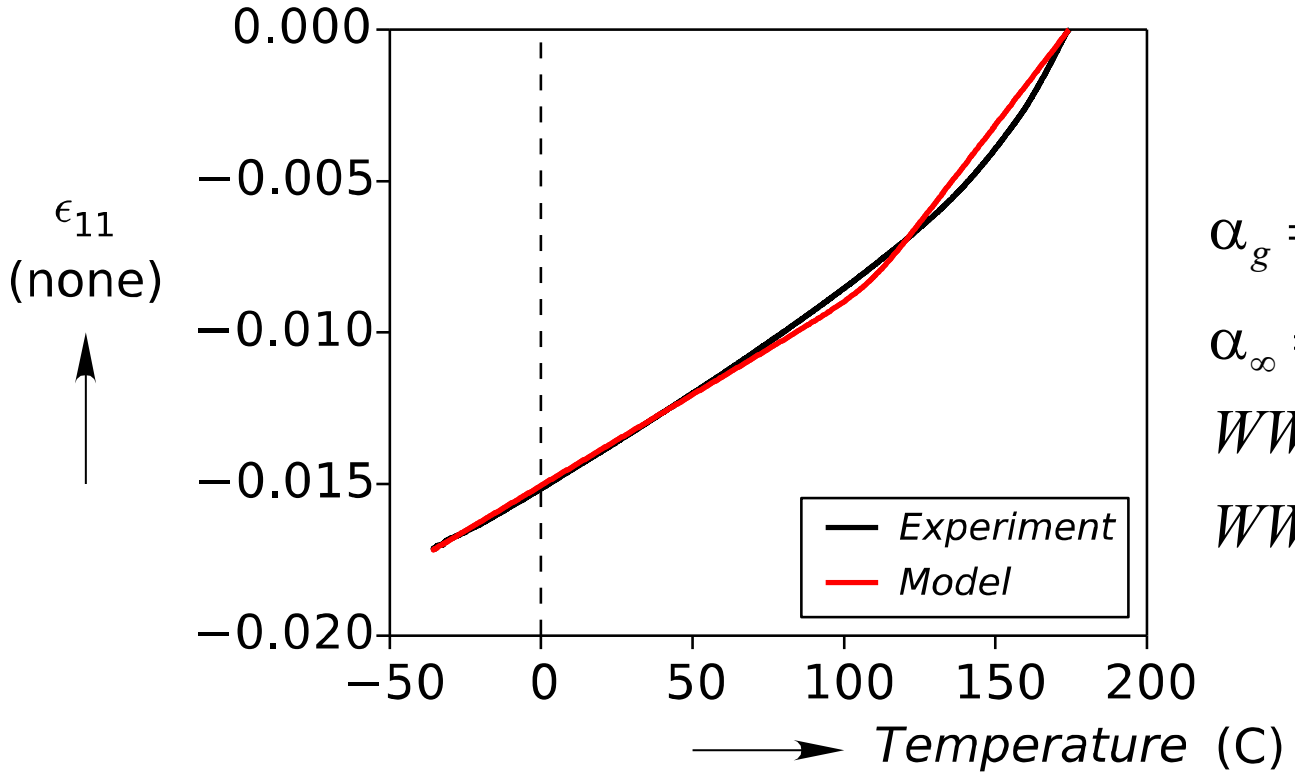
Concerns

- **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**

TMA Fitting



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

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

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

$$WW_\beta = 0.176101$$

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Fitting Cure Kinetics, Tg vs. Extent of Cure, and Vitrification Parameters on the kinetics
Ideal Case

- **Fit the initial cure kinetics prior to vitrification**
- **Fit Tg vs. extent of cure from the final (unchanging) long time scale isothermal cure data**
- **Fit the vitrification parameters to give the full cure kinetics**

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

Fit to early times with w, a, beta=0

$$k = k_o e^{-\frac{E_a}{RT}}$$

Simplify this by assuming:
C3 = 0
C5b

$$C_5 = C_{5a} + C_{5b}x + C_{5c}\exp\left(\left(\frac{x}{C_{5d}}\right)^{C_{5e}}\right)$$

Simplify this by assuming:
C5c = 0

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Summary of the Material Shift Factor and the Evolving Glass Transition

$$\log_{10} a = -\frac{C_1 N}{C_2 + N}$$

Material Time Scale Shift Factor

$$C_1 = WLFC_1$$

$$C_2 = WLFC_2\left(1 + C_3\alpha_\infty\right)$$

Williams-Landel-Ferry "like" Coefficients

$$N \approx T - T_{ref}\left(x\right)$$

Shifting Term

$$C_5 = C_{5a} + C_{5b}x + C_{5c}\exp\left(\left(\frac{x}{C_{5d}}\right)^{C_{5e}}\right)$$

Coefficient Controlling the Tg Evolution

$$T_{ref}\left(x\right) = T_{ref\,0} - \left(C_3\beta_\infty + C_5\right)\left(x - x_{ref\,0}\right)\left(1 + C_3\alpha_\infty\right)^{-1}$$

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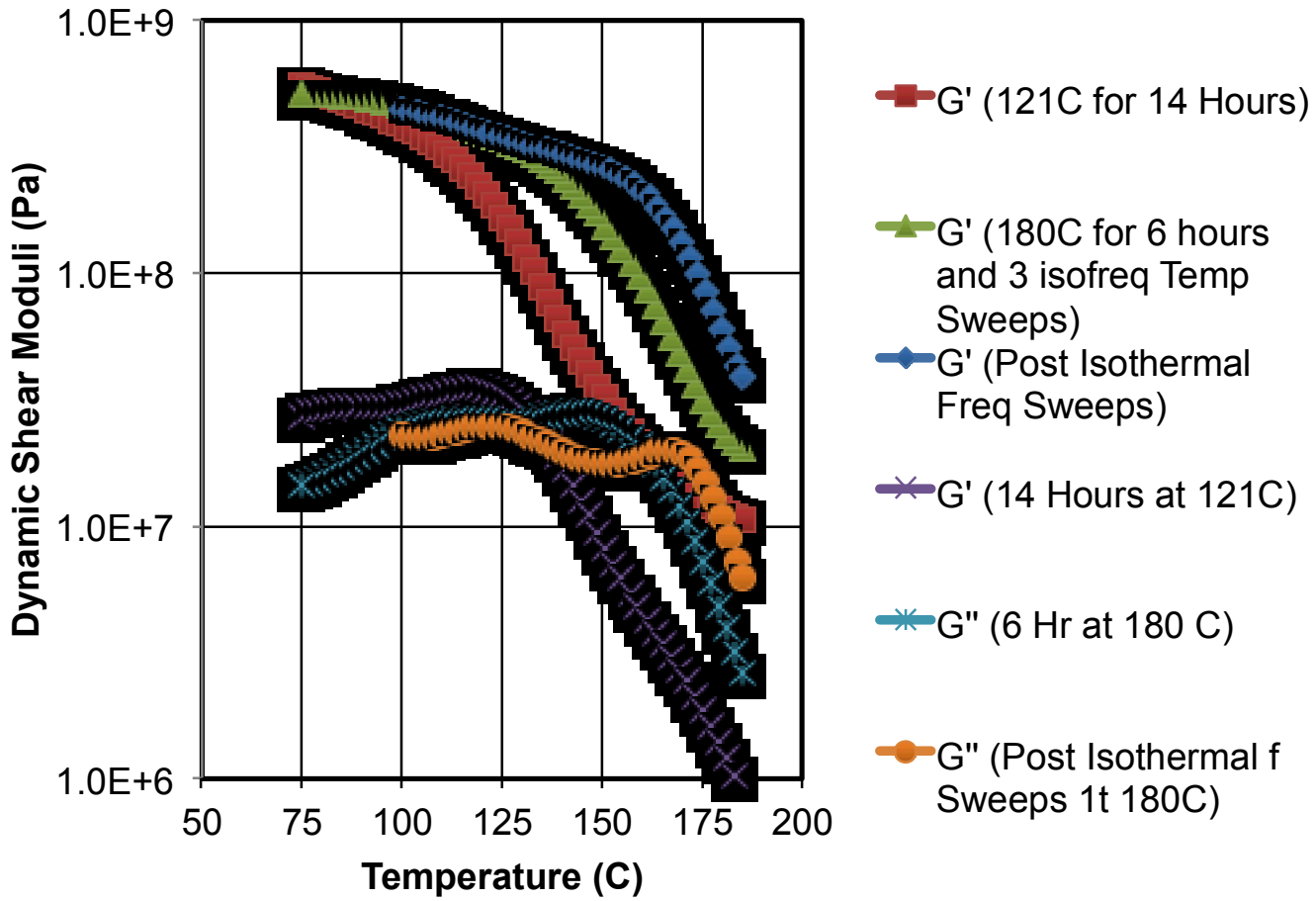
A look at the March 2014 Data



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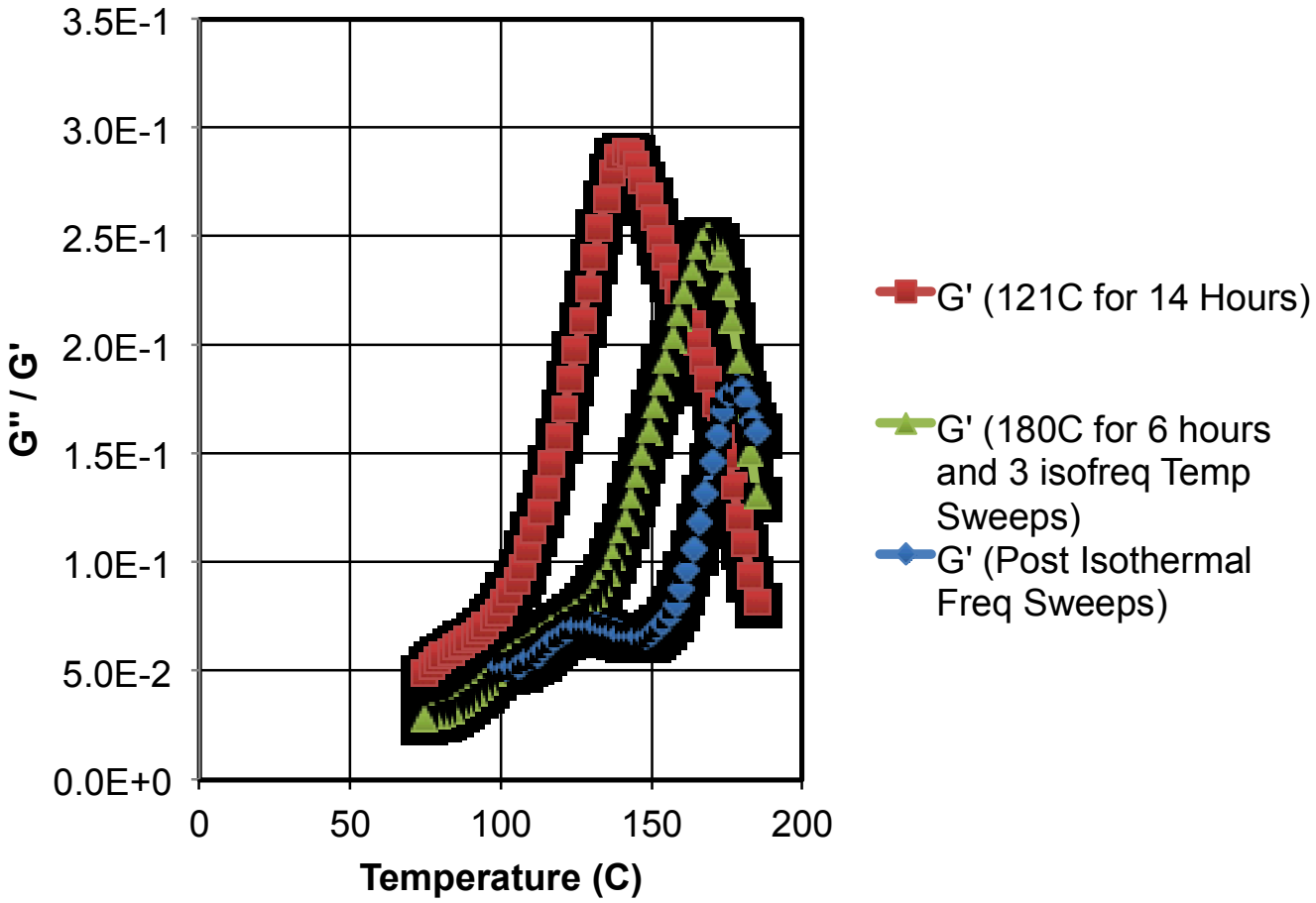
A look at the March 2014 Data



Attempt to Use The March 2014 Data

- Assume that the relaxation behavior of the network does not substantially change with the cure that takes place at higher temperatures
- Assume that the Time Temperature Superposition Principal (TTS) applies
  - WLF temperature dependence of the shift factor
- Assume that the network structure characterized is representative of the structure
- Assume that the “neat” (dry) foam network structure has the same relaxation behavior as the structural PMDI foam

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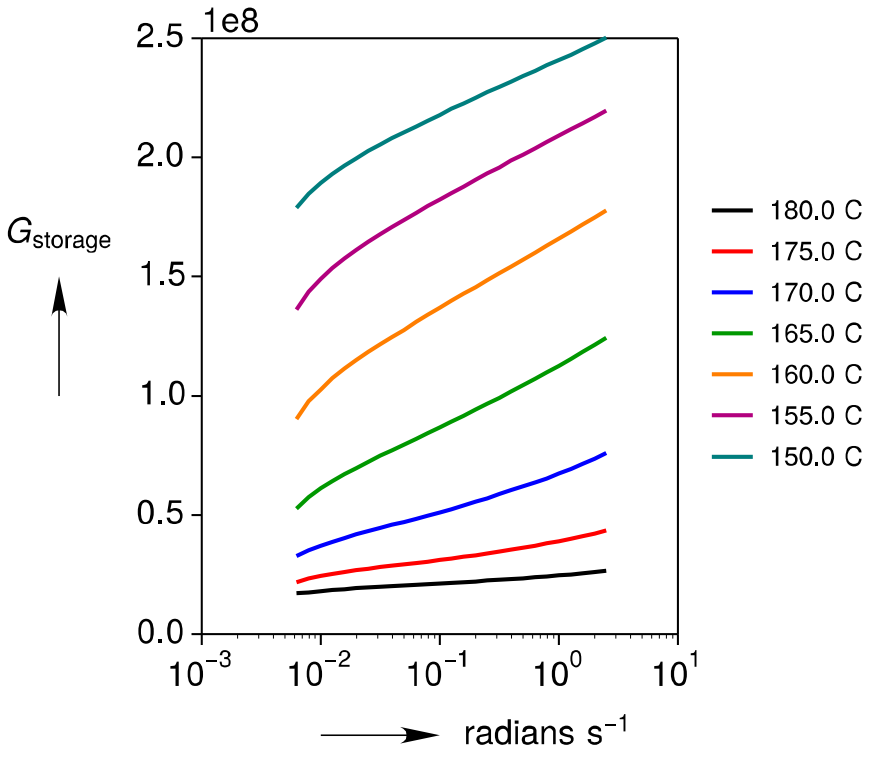
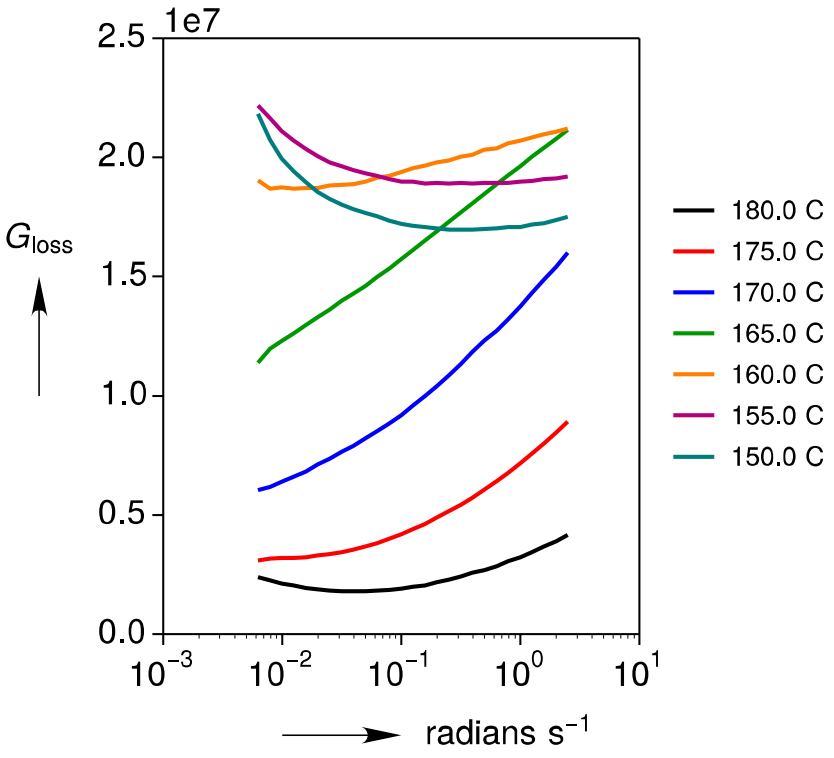
- Assume that the network structure characterized is representative of the structure
- Assume that the “neat” (dry) foam network structure has the same relaxation behavior as the structural PMDI foam

Raw Oscillatory Shear Isothermal Frequency Sweeps: 180, 175, 170, … 150 C
Data Post 120C for 4 hours and then 180C for 6 hours.





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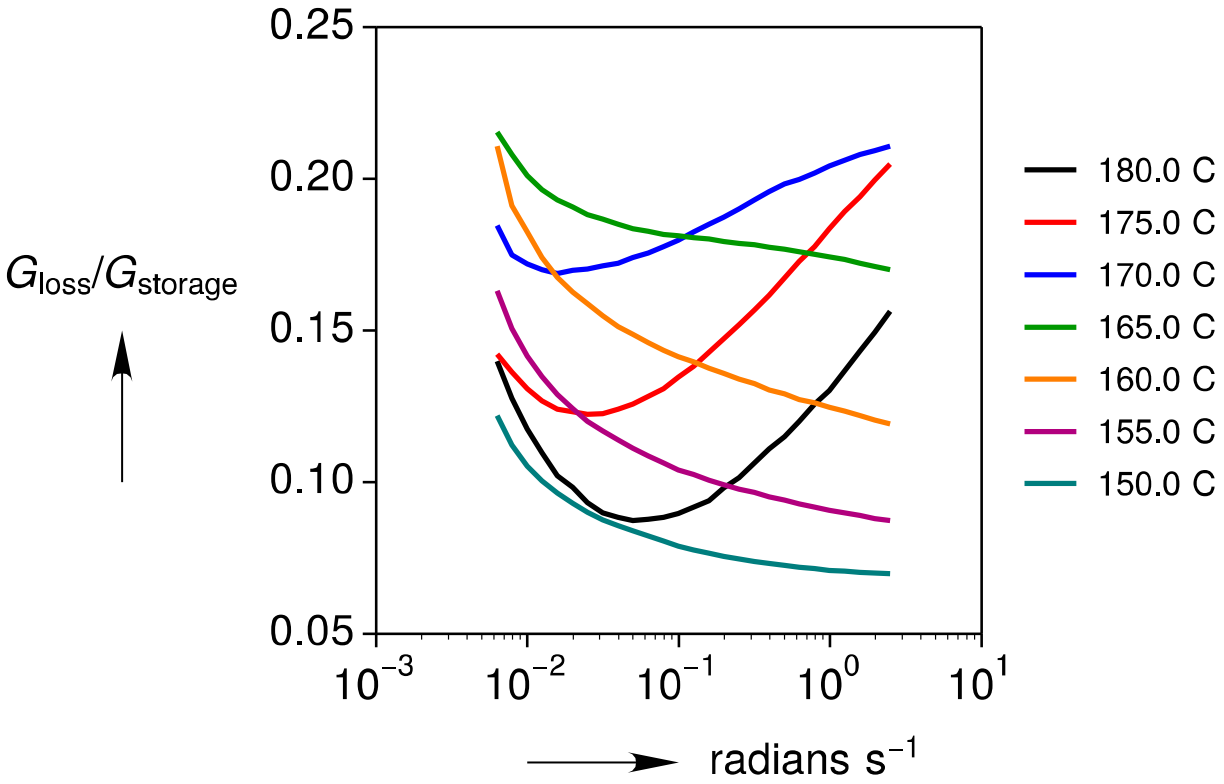
Raw Oscillatory Shear Isothermal Frequency Sweeps: 180, 175, 170, … 150 C
Data Post 120C for 4 hours and then 180C for 6 hours.



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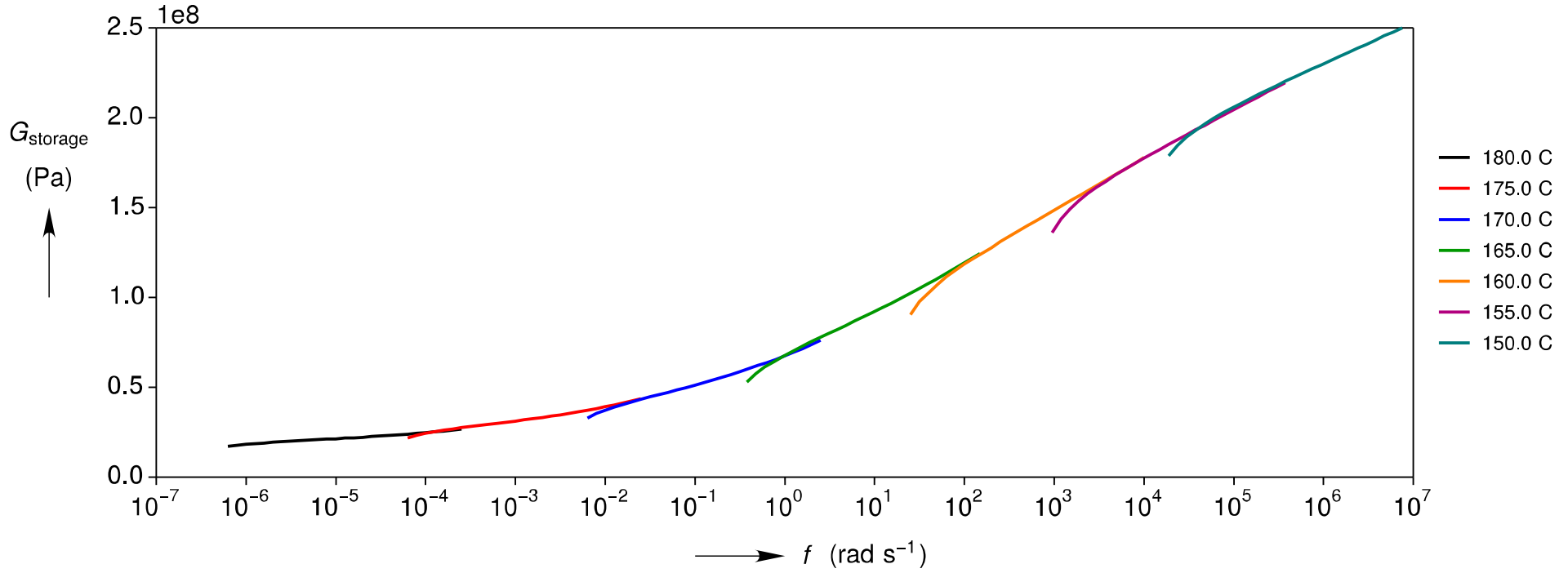
Raw Data



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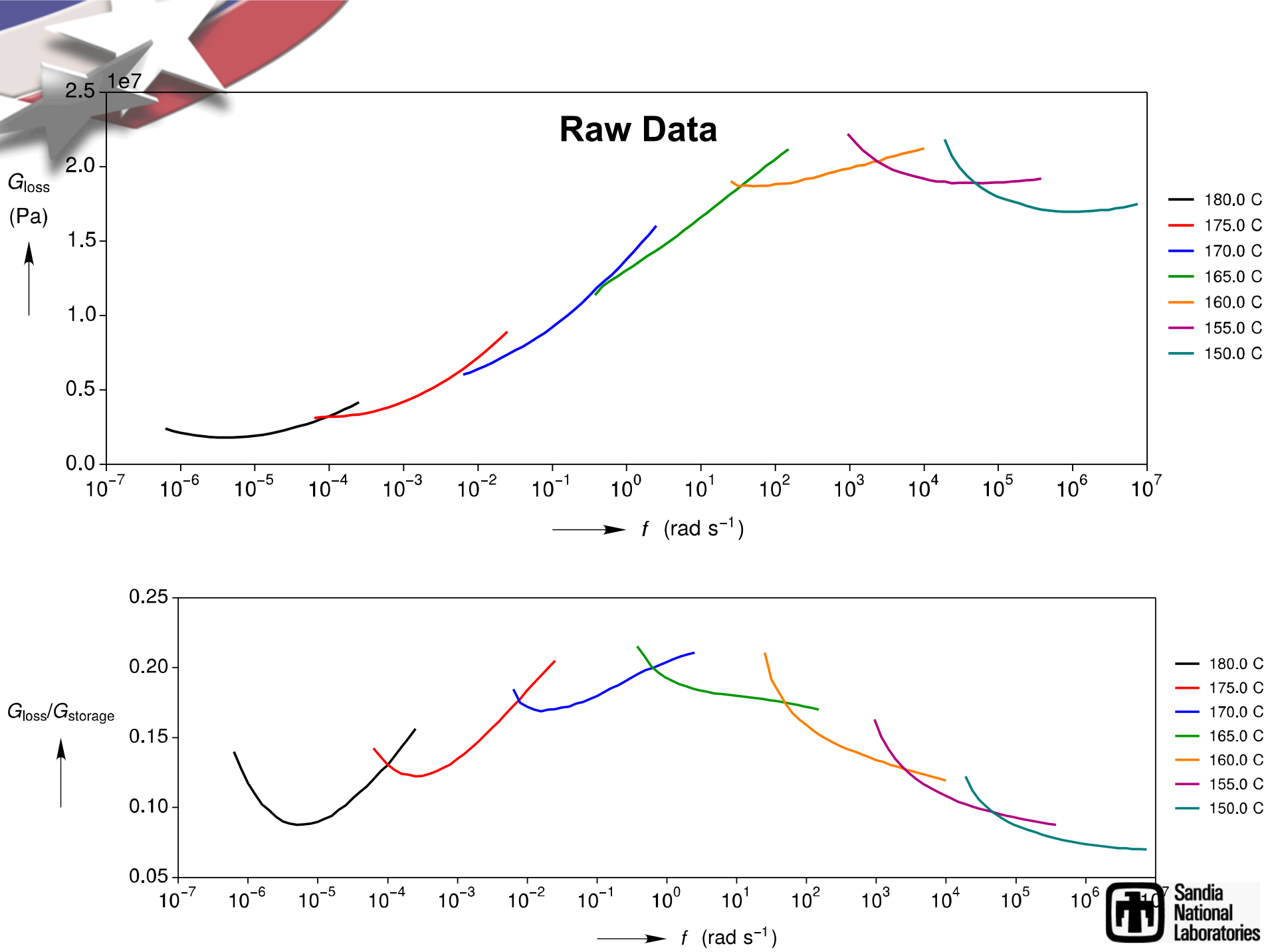
Raw Data
1e7
2.5
2.0
1.5
1.0
0.5
0.0
G_{loss} (Pa)
10^{-7} 10^{-6} 10^{-5} 10^{-4} 10^{-3} 10^{-2} 10^{-1} 10^{0} 10^{1} 10^{2} 10^{3} 10^{4} 10^{5} 10^{6} 10^{7}
f (rad s^{-1})
180.0 C
175.0 C
170.0 C
165.0 C
160.0 C
155.0 C
150.0 C
0.25
0.20
0.15
0.10
0.05
$G_{loss}/G_{storage}$
10^{-7} 10^{-6} 10^{-5} 10^{-4} 10^{-3} 10^{-2} 10^{-1} 10^{0} 10^{1} 10^{2} 10^{3} 10^{4} 10^{5} 10^{6} 10^{7}
f (rad s^{-1})
180.0 C
175.0 C
170.0 C
165.0 C
160.0 C
155.0 C
150.0 C
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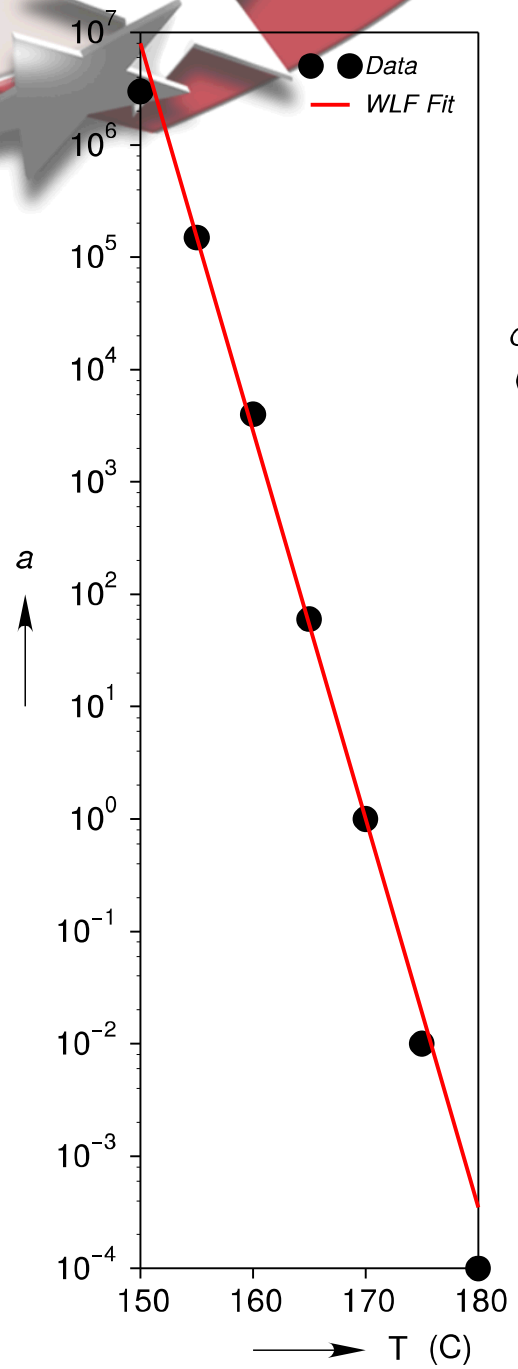
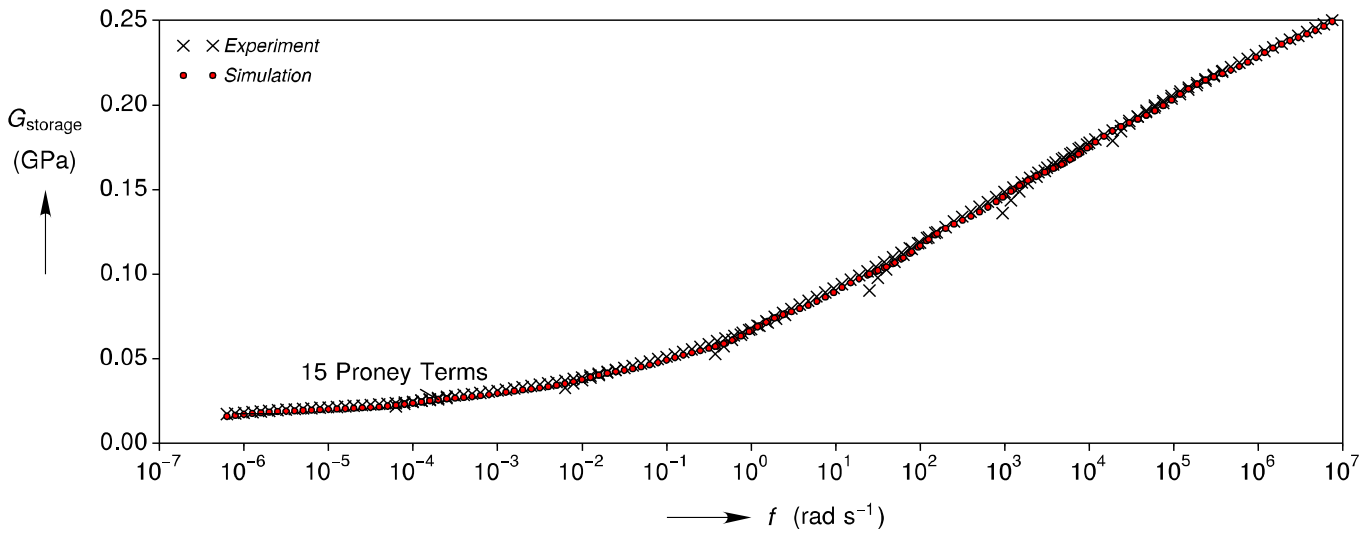
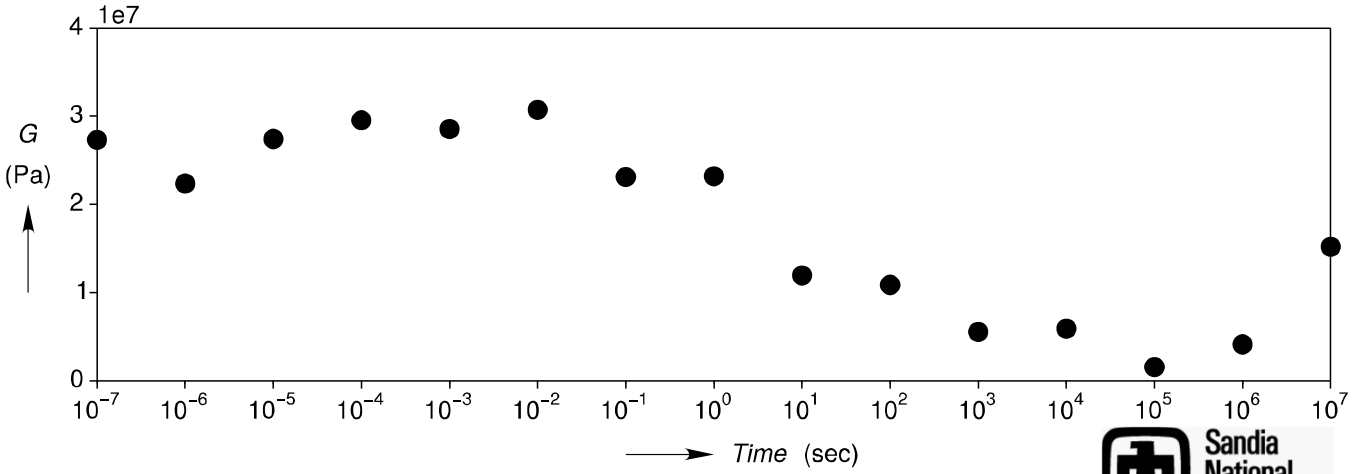
C_1 = 1.791e+05, C_2 = 5.186e+05 (K)

WLF Fitting







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