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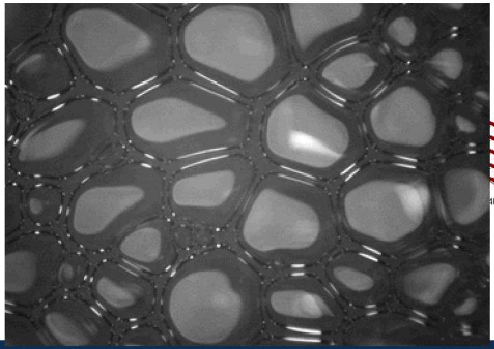

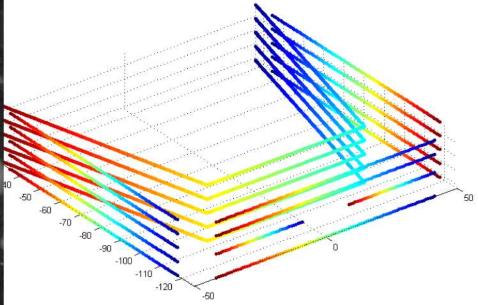

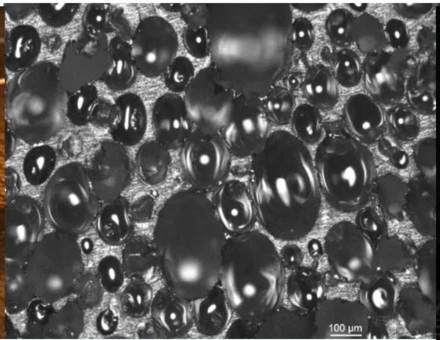

Material Models for Polyurethane Foam Encapsulation and Aging

Christine Roberts, Kevin Long, Lisa Mondy, Rekha Rao, Melissa Soehnel

DuraMAT Workshop

Albuquerque, NM

November 7, 2017

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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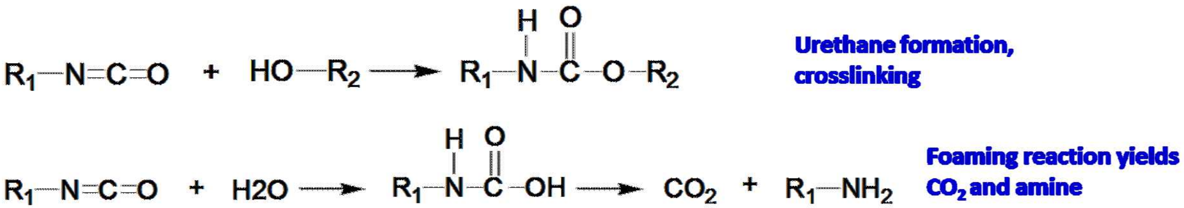
Polyurethane (PMDI) Foam: Introduction

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 structural and encapsulation PMDI foams BKC44306, BKC44307



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

Urethane formation, crosslinking

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

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
(0-10^3 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.

Must be true for both models and experiments.

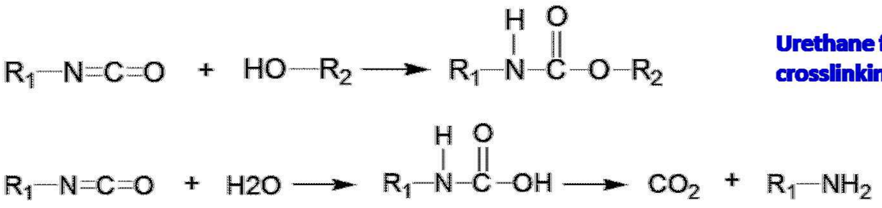
Competing Chemistry and Physics

Isocyanate reacts with water to create CO_2 and with polyol to polymerize

Five species to track:
Water, polyol, polymer, CO_2, isocyanate

Use experiments to determine rate coefficients vs temperature.

Two key reactions: Isocyanate reaction with polyols and water



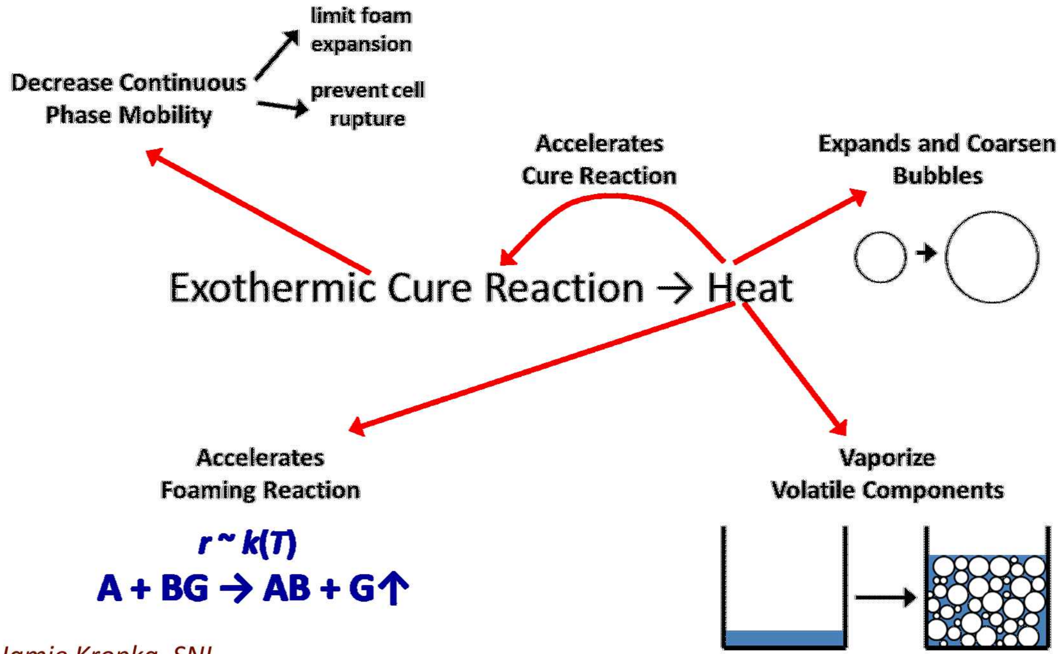
$$R_1-N=C=O + HO-R_2 \rightarrow R_1-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-O-R_2$$

Urethane formation, crosslinking

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

Foaming reaction yields CO_2 and amine

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



Decrease Continuous Phase Mobility

limit foam expansion

prevent cell rupture

Accelerates Cure Reaction

Expands and Coarsen Bubbles

Exothermic Cure Reaction → Heat

Accelerates Foaming Reaction

$r \sim k(T)$

$A + BG \rightarrow AB + G\uparrow$

Vaporize Volatile Components

Heat accelerates reactions and grows bubbles, but also accelerates polymerization.

Viscosity of the continuous phase evolves with time, limiting foam expansion. Viscosity of the foam also a function of CO_2 content.

Jamie Kropka, SNL

Polymer reaction rate constants

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

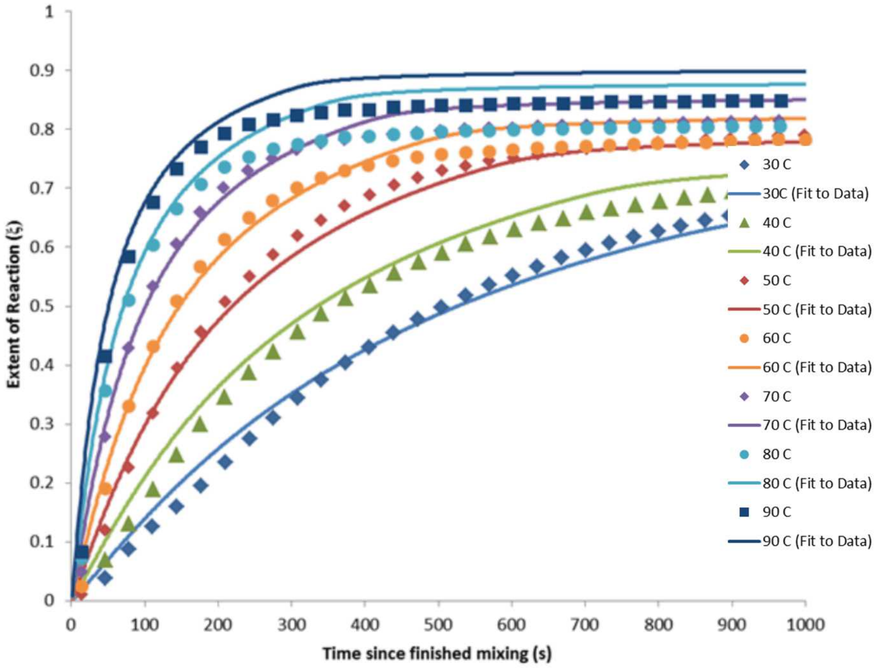
Urethane ester linkage (1218 cm^{-1}) used to measure extent of reaction with time.

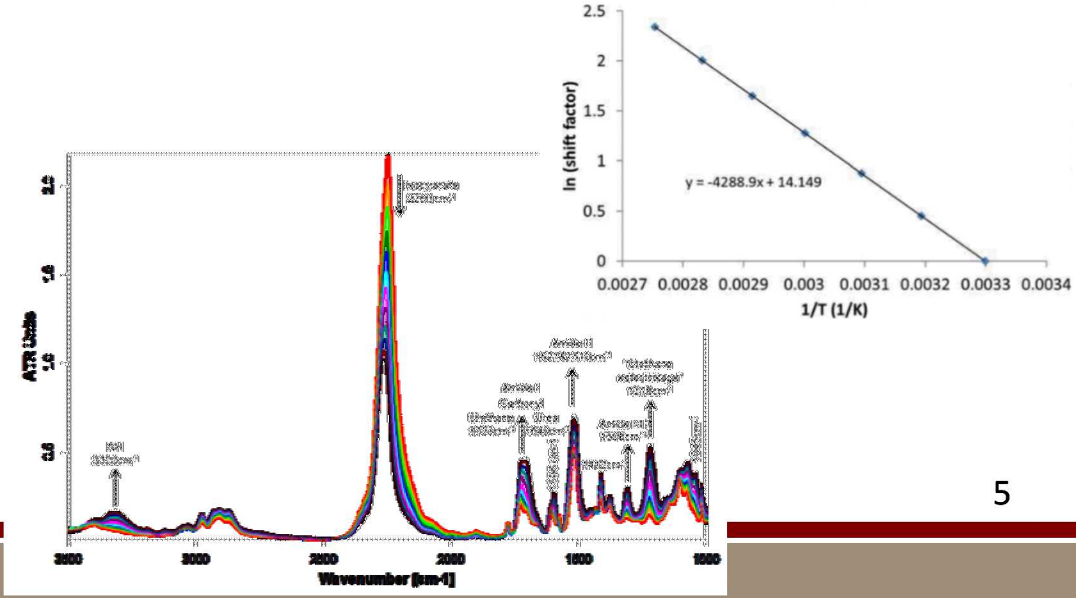
Model using Kamal cure kinetics approach. Vitrification slows curing reaction. T_g evolves with the extent of reaction.

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

$$\log_{10} a = \frac{-C_1\left(T - T_g[\xi]\right)}{C_2 + T - T_g[\xi]}$$

$$T_g[\xi] = \frac{T_{g0}(1-\xi) + \xi A T_{g\infty}}{1 - \xi + A\xi}$$





Sourer and Kamal, Thermochimica Acta, V 14, 1976

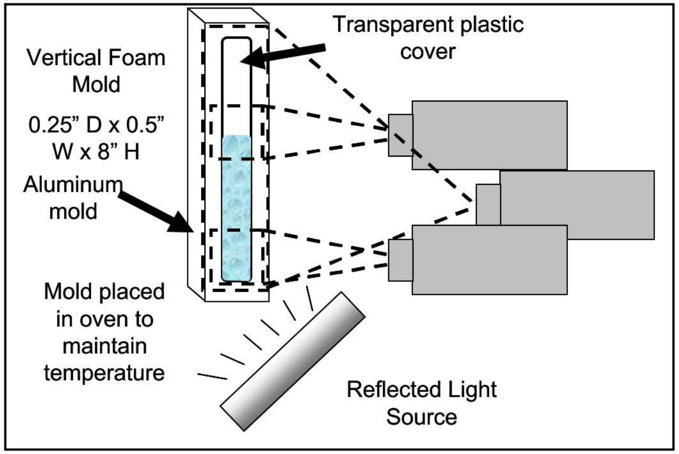
Gas Reaction Rate Constants

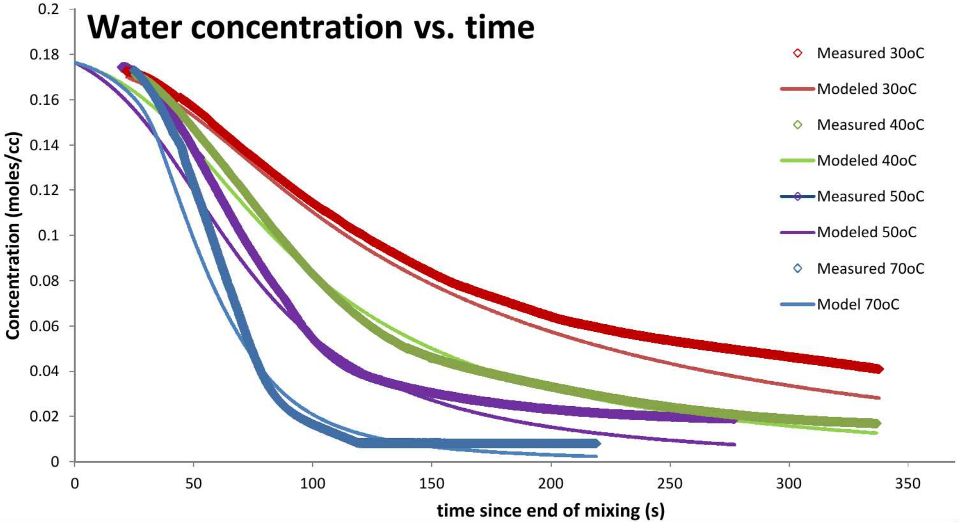
Measure height change in simple geometry to quantify foaming reaction

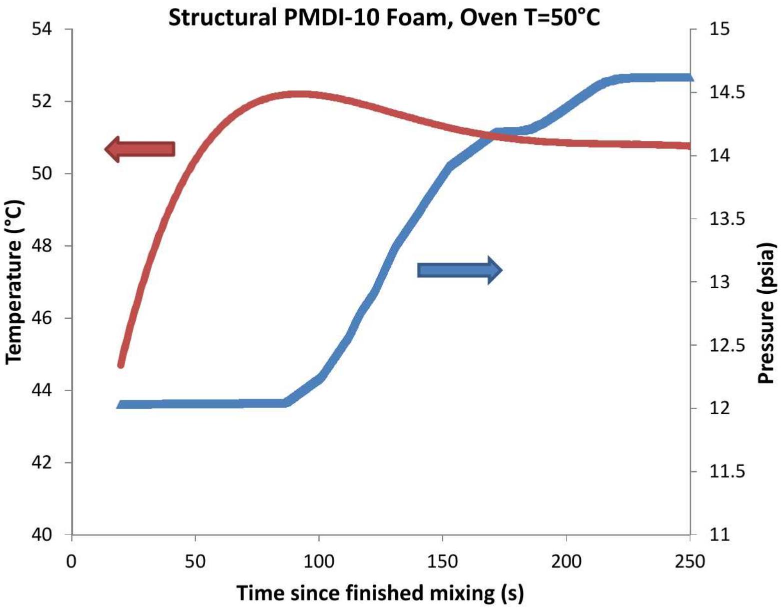
Measure pressure and temperature during foaming and use ideal gas law to calculate amount of CO_2.

Some uncertainty in initial condition… reaction is occurring during mixing and injections

Pressure continues to rise after foam has stopped expanding in volume. Implies CO_2 reaction progresses after foam viscosity restricts expansion.







Continuous Phase Viscosity Evolution

Viscosity is a function of extent of reaction and temperature

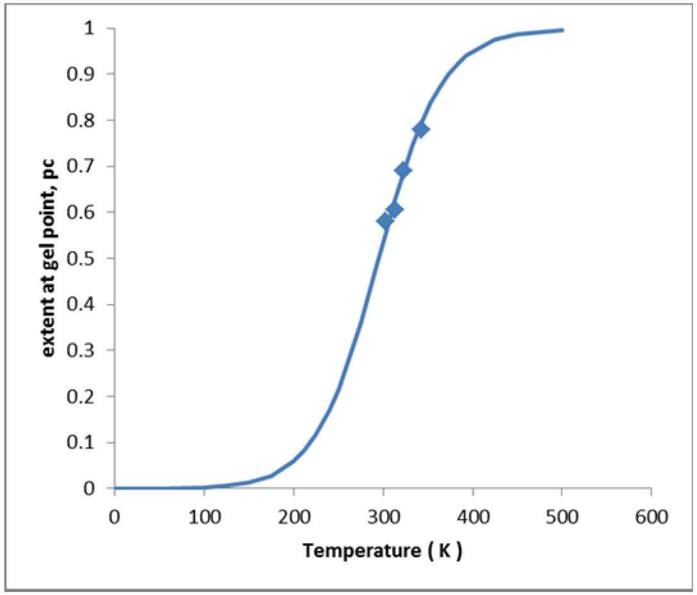
$$\eta_{foam} = \eta_{polymer}\,\eta_{\phi}$$

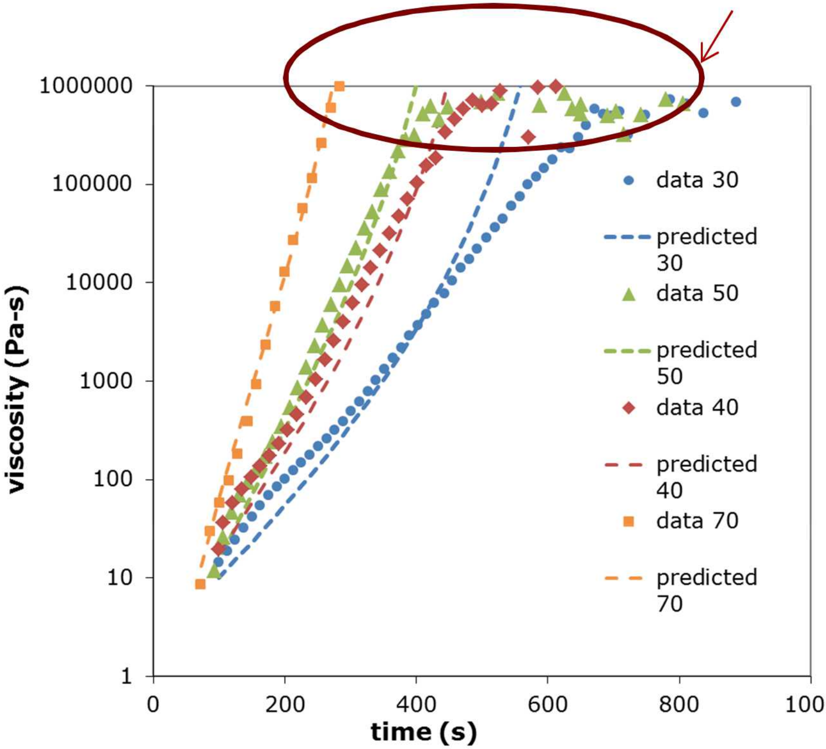
$$\mu_0 = \mu_0^0 \exp(\frac{E_\mu}{RT})(\frac{\xi_c{}^p - \xi^p}{\xi_c^p})^{-q}$$

$$\mu = \mu_0 \exp(\frac{\varphi_v}{1-\varphi_v})$$

Gas bubbles increase the viscosity of the foam compared to continuous phase at early stages of growth.

IR kinetics + dry formulation (non-foaming polymer) give an approximation of the curing continuous phase rheology.

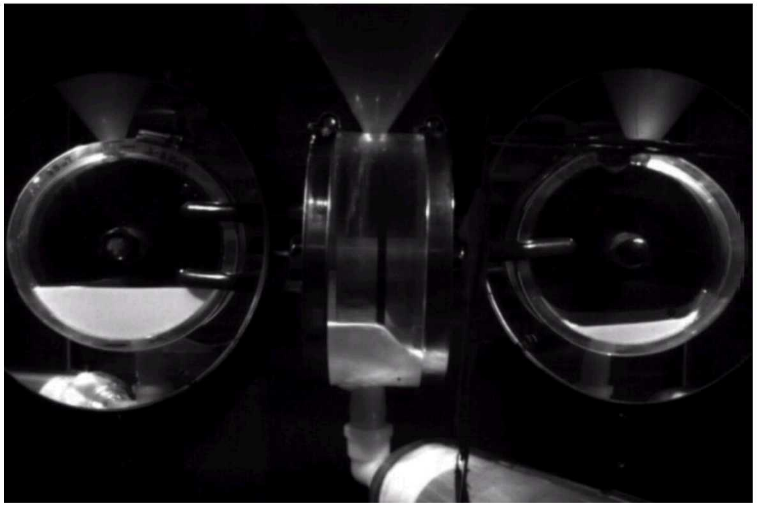


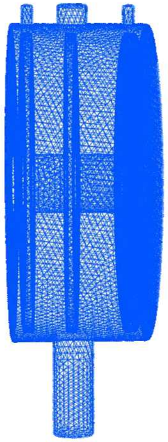

Data scatters when vitrifies

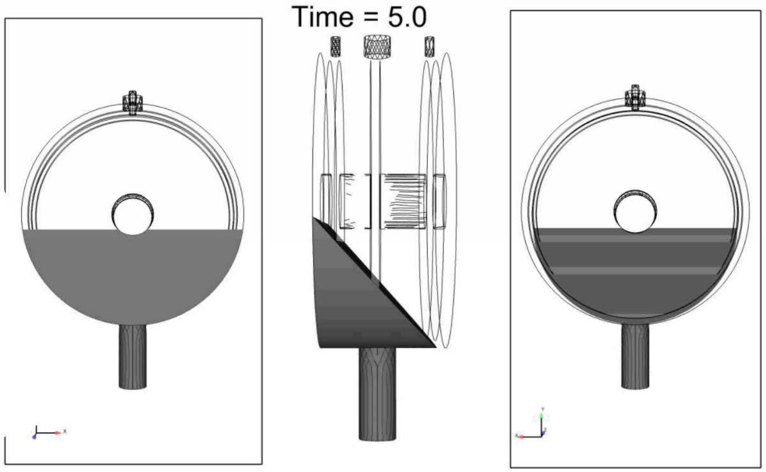
Martin, J. P.; *Phys. Rev. A* 1989, **39**,1325.

Validation

- **Idealized foam encapsulation part**
  - **Modeled after component that would have electronics**
  - **Volumes of different thicknesses set up a race to fill both sides**
- **Model now heavily being used for PMDI foam mold design**
  - **Void locations**
  - **Optimal vent locations**
  - **Filling temperatures**
  - **Final mold densities**
  - **Pressures, temperatures on components**
- **Model is input to aging predictions**



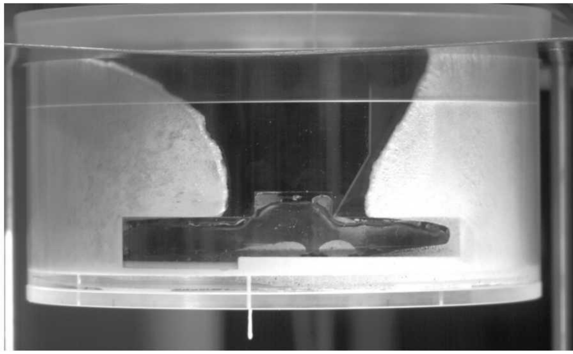




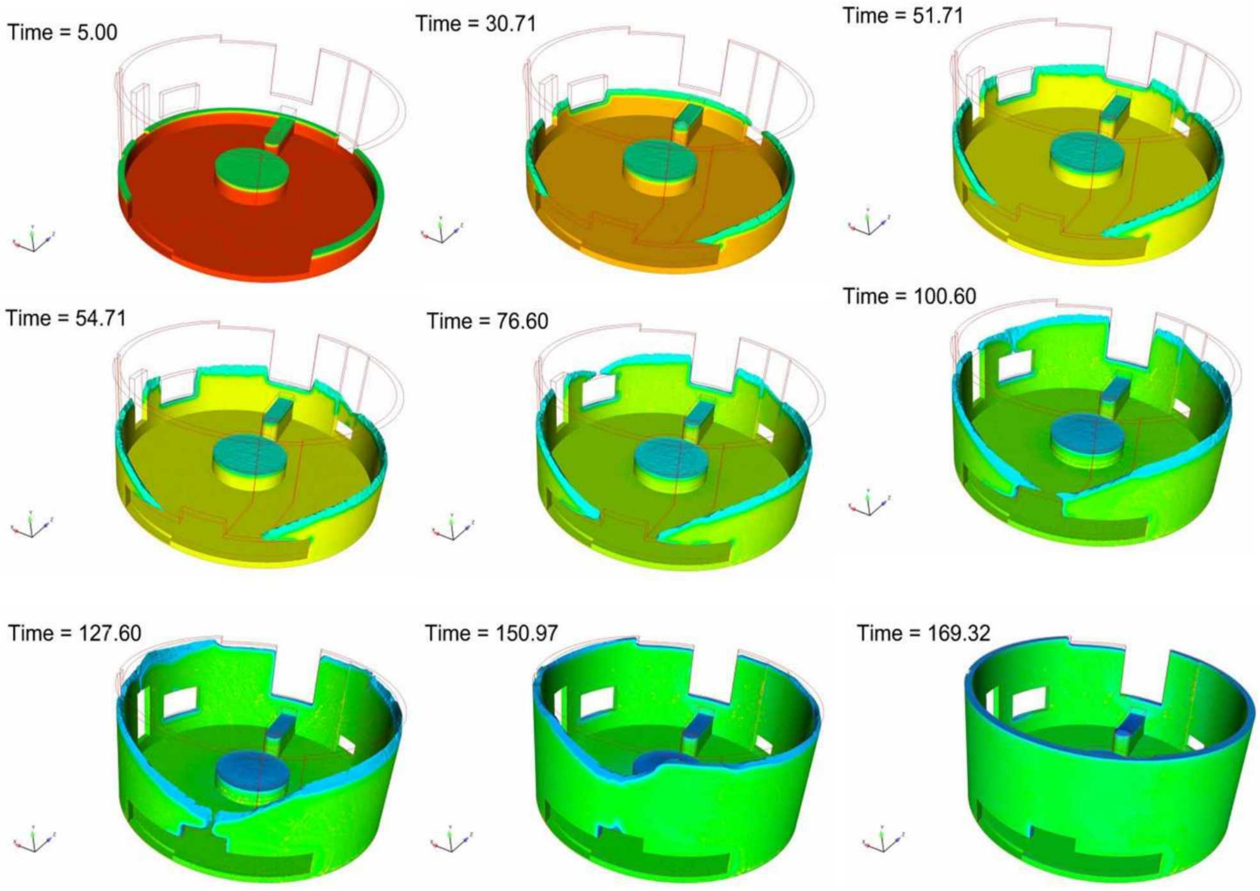
Rao et al., IJNMF, 2012

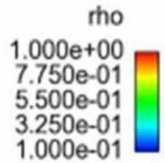
Modeling helps mold filling process design

Dummy mold created for validation experiments.
Vent locations, foam temperature on fill quality can be explored



Experiments also show knit lines over large feature



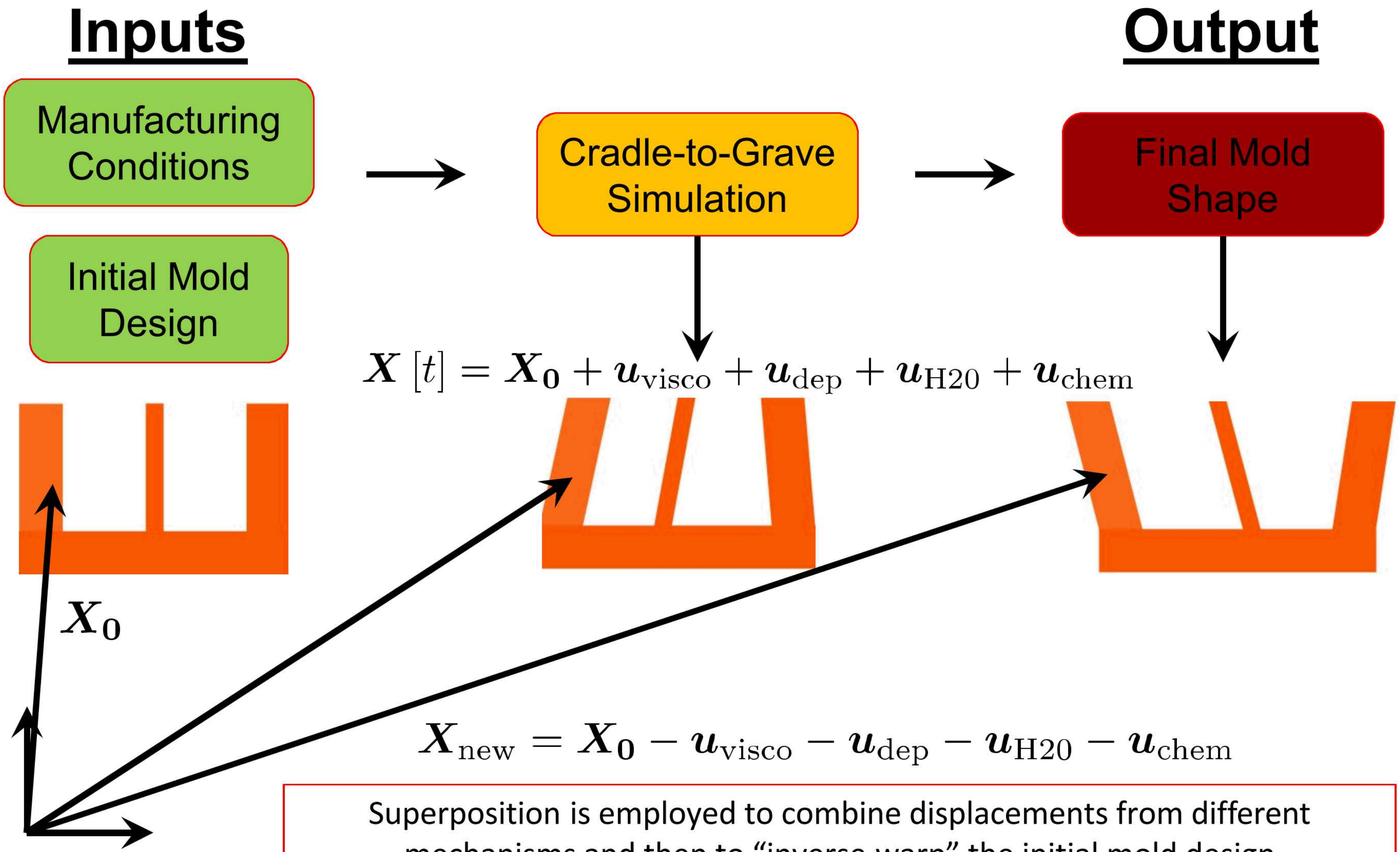


Aging of Polyurethane Foams

- **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.
  - When do you qualify a part?
- 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
  - Thermal cooldown from curing oven
  - Solid cure, viscoelastic relaxation of residual stress(physical aging)
  - Bubble pressure, loss of CO_2
  - Hydration/Dehydration (Swelling). Water uptake leads to subsequent reaction and CO_2 generation?

Mechanism: 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.

Aging of PMDI foams



Inputs

Manufacturing Conditions

Initial Mold Design

Cradle-to-Grave Simulation

Output

Final Mold Shape

$$\boldsymbol{X}[t] = \boldsymbol{X_0} + \boldsymbol{u}_{\text{visco}} + \boldsymbol{u}_{\text{dep}} + \boldsymbol{u}_{\text{H20}} + \boldsymbol{u}_{\text{chem}}$$

$$\boldsymbol{X}_{\text{new}} = \boldsymbol{X_0} - \boldsymbol{u}_{\text{visco}} - \boldsymbol{u}_{\text{dep}} - \boldsymbol{u}_{\text{H20}} - \boldsymbol{u}_{\text{chem}}$$

Superposition is employed to combine displacements from different mechanisms and then to “inverse warp” the initial mold design

NLVE Material Model

Balance Laws and Solution Fields:

- Mass + Momentum (*Displacements*) ← Lagrangian FEM
- Species Balance (*Chemical Reaction Extent*) ← ALE FEM
- Energy (*Temperature*) ← 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

NLVE Material Model, ctd

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

Material Time Dependencies

Thermal

Pressure

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

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

Shear Deformation

Matrix Cure

Glass Transition Evolution

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

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

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

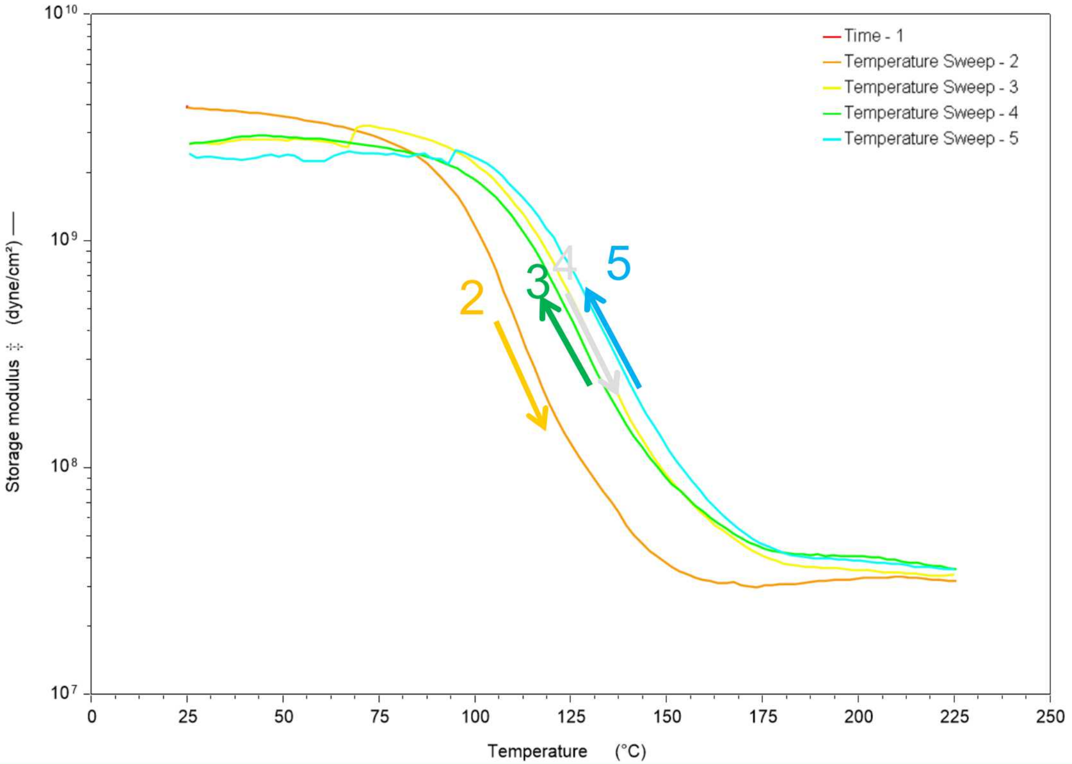
6) Uniaxial Compression
Isothermal and Cyclic Temperature Sweeps of "Dry Foam"

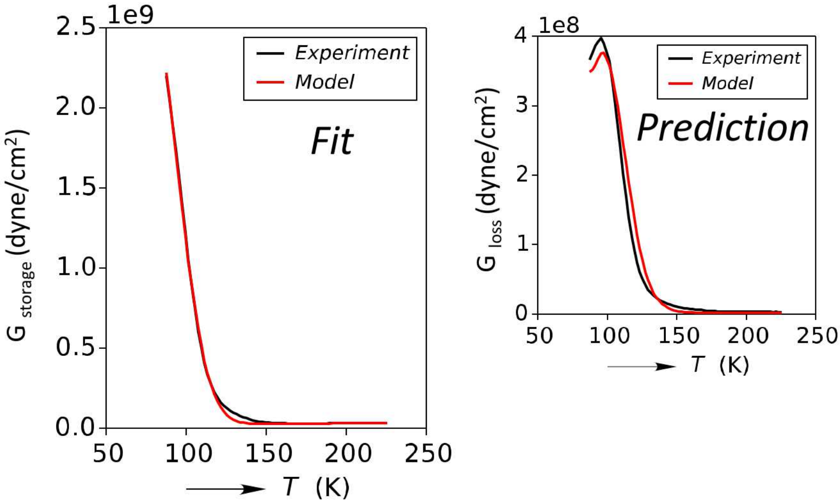
- Yield phenomena (Shear Deformation Induced Mobility)

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

Modulus Determination Vitrified Foam

- Oscillatory shear of a “cured” foam bar
  - Cured using normal production cure schedule (121 °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



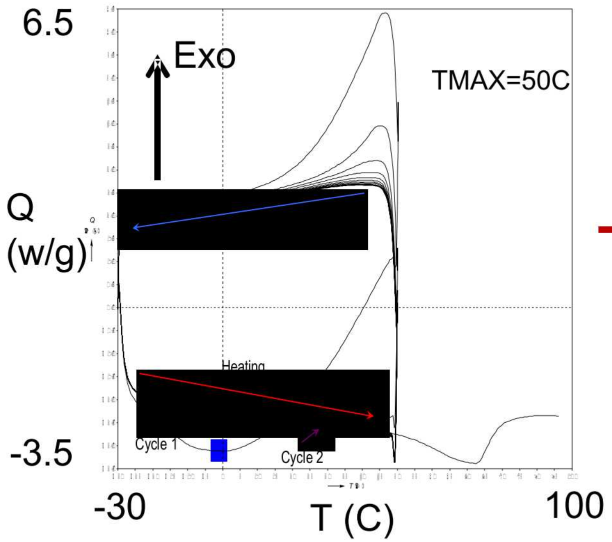


Near T_g, fit the Time-Temperature WLF Shift Factors and Williams-Watts Shear Relaxation Function via Optimization to the Storage Modulus Behavior

Relate Extent of Reaction to T_g

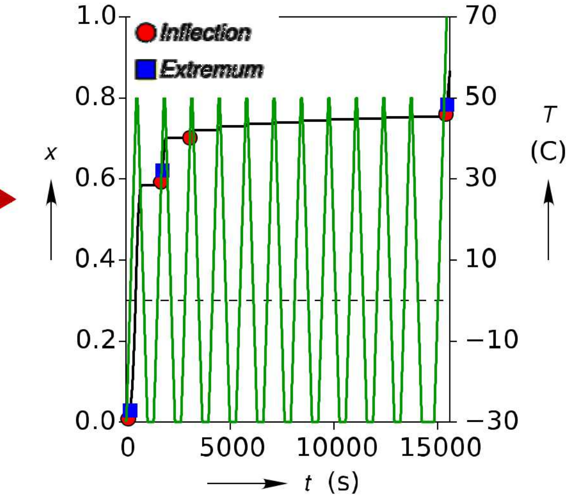
We require T_g as a function of the extent of reaction (Di Benedetto form)
Problem: Measuring T_g involves heating the material, which provokes more cure.
Solution: Model the curing of the sample during the measurement to find x at T_g.

Differential Scanning Calorimetry identifies T_g over a series of temperature ramps



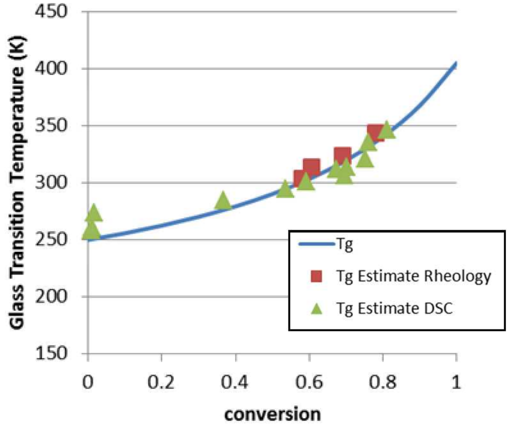
- ~10 mg samples
- Cycle the temperature between -30 C and T_{MAX}
- Ramp up to 100+C at end of test (10 cycles)

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

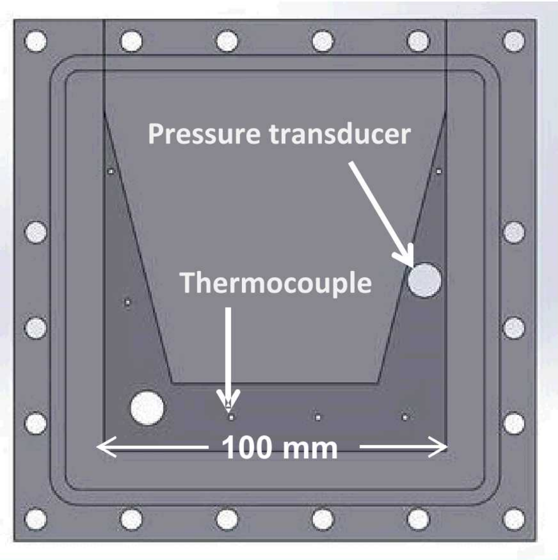


Cure Shrinkage Monitoring

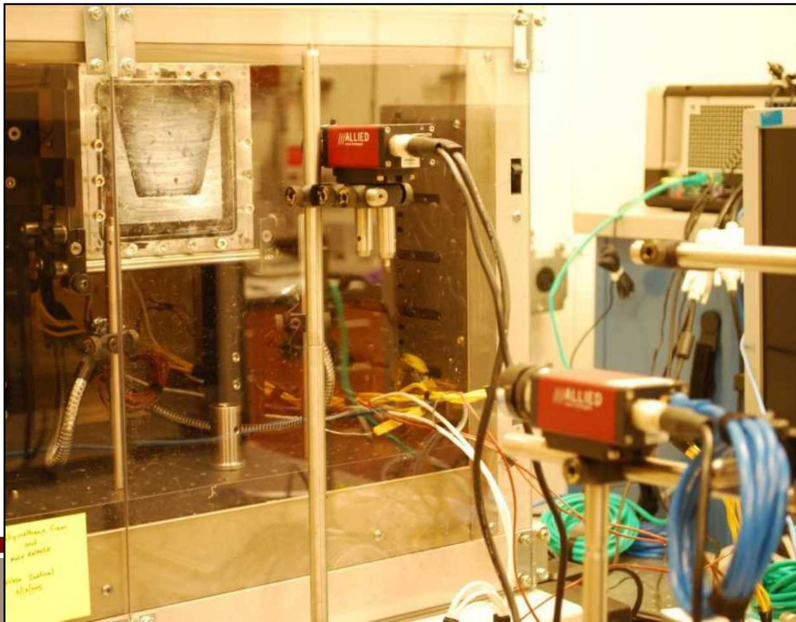
Observe cure shrinkage and warping over months to provide model validation data

- Geometry inspired by AWE previous work (Pockett + Warriner)
- Initially, filling conditions approximate those at KCP
  - PMDI S10 foam injected at 40 ^{o}C, overpacked to 12.5 lb/ft^3
  - After 15 mins, cured in oven at 120 ^{o}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



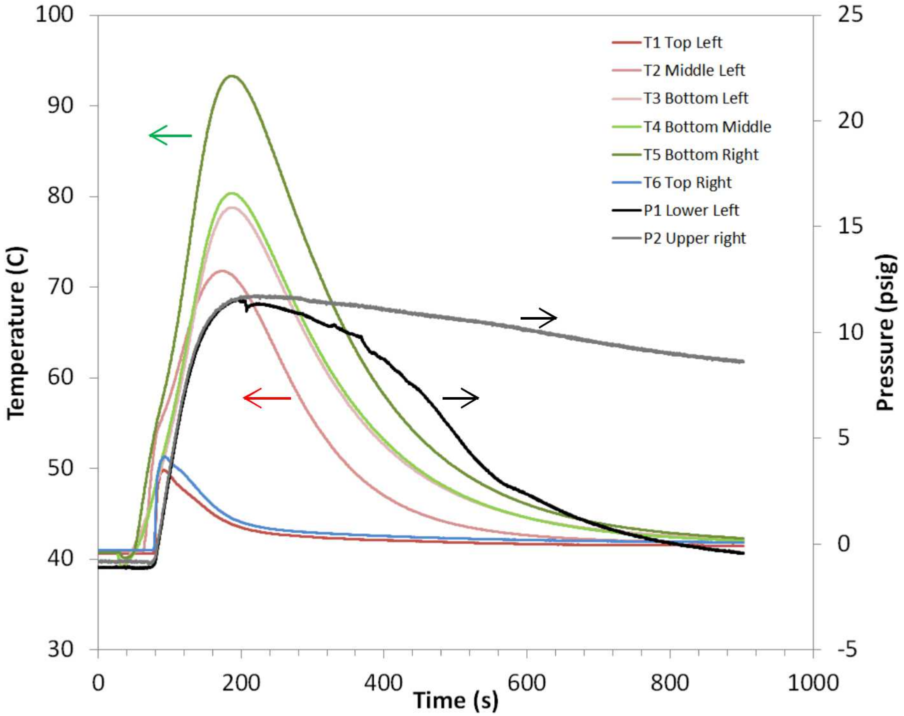
Ports for thermocouples and pressure transducers to record parameters during foaming.

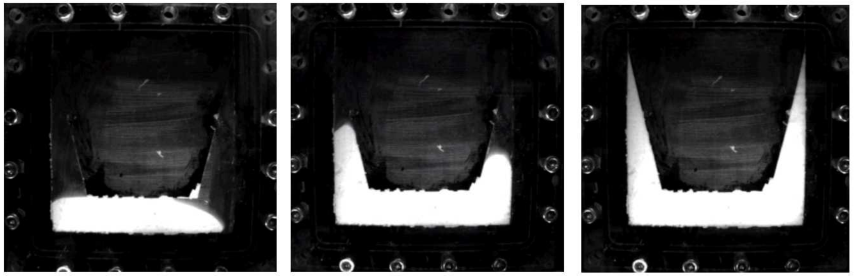


Fill filmed using cameras, transparent oven door

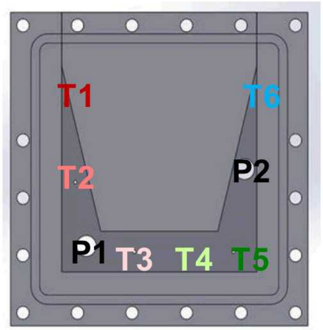
Foaming U-shaped Staple Mold

- 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.

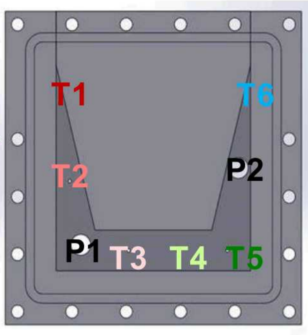




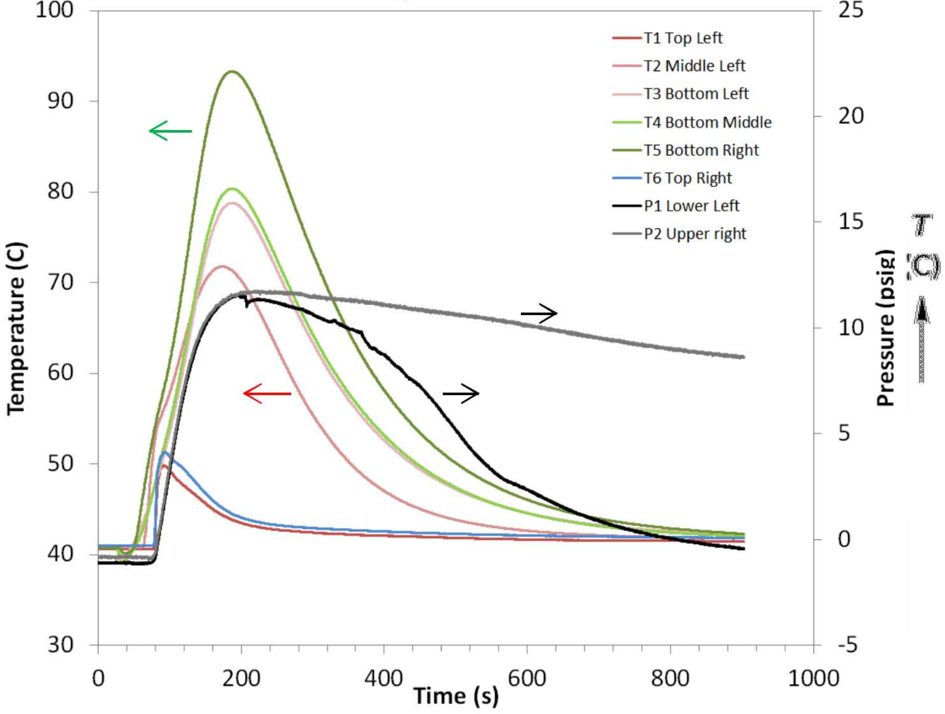
Some slight asymmetry due to bias of initial injection



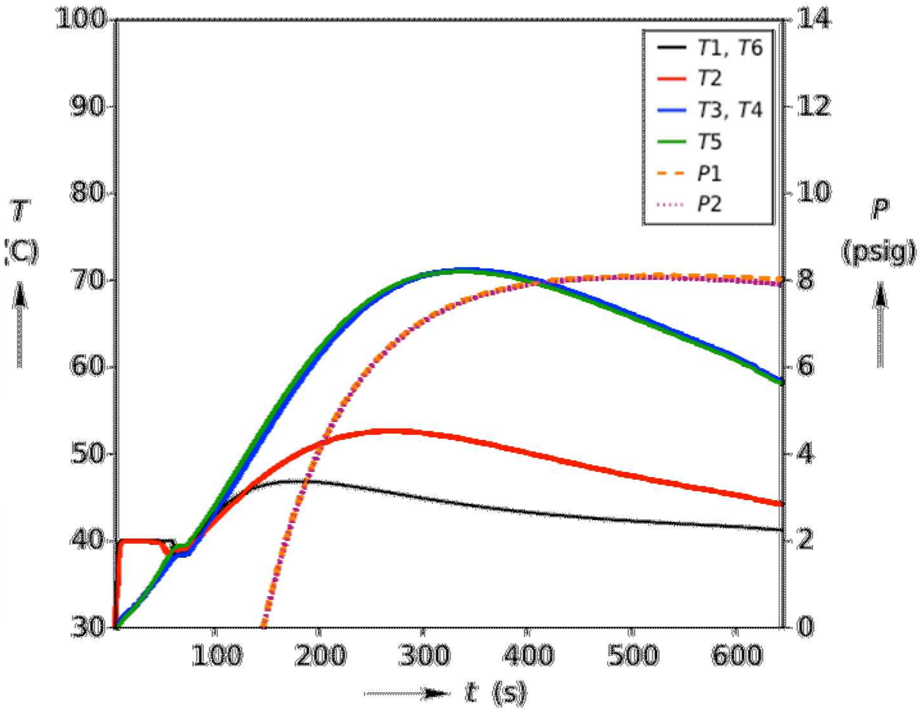
Foaming U-shaped Staple Mold



- Filling model captures general behavior well
  - Slightly cooler, slightly slower
- Filling model simulation is initial conditions for aging model

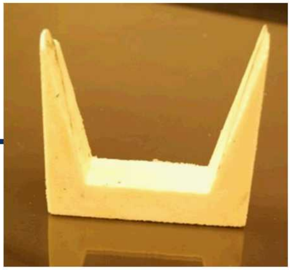


Experiment



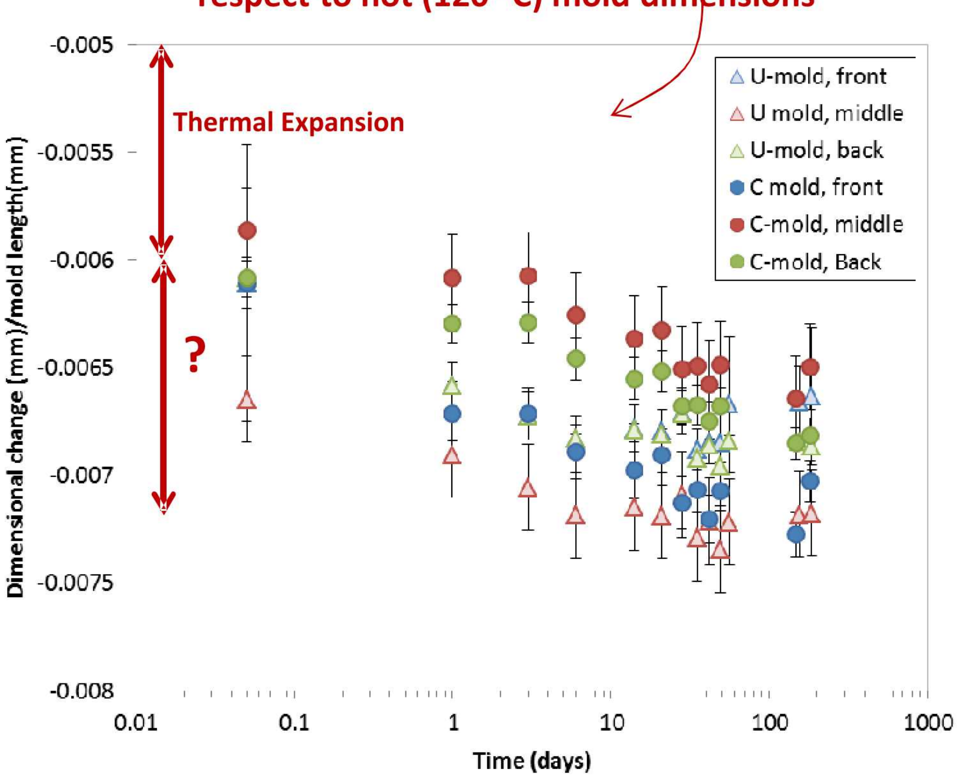
Model Predictions

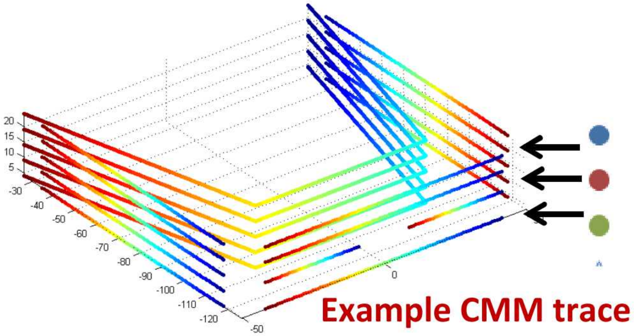
Cure Shrinkage Experimental Results



- C- and U- shaped staple foam pieces cured 120 ^{o}C, 4 hours in mold
- Mounted upright, measured using CMM weekly (100 mN probe force)
- Non-monotonic and complex warpage observed on thin staple arms

Shrinkage measured at the waist with respect to hot (120 ^{o}C) mold dimensions



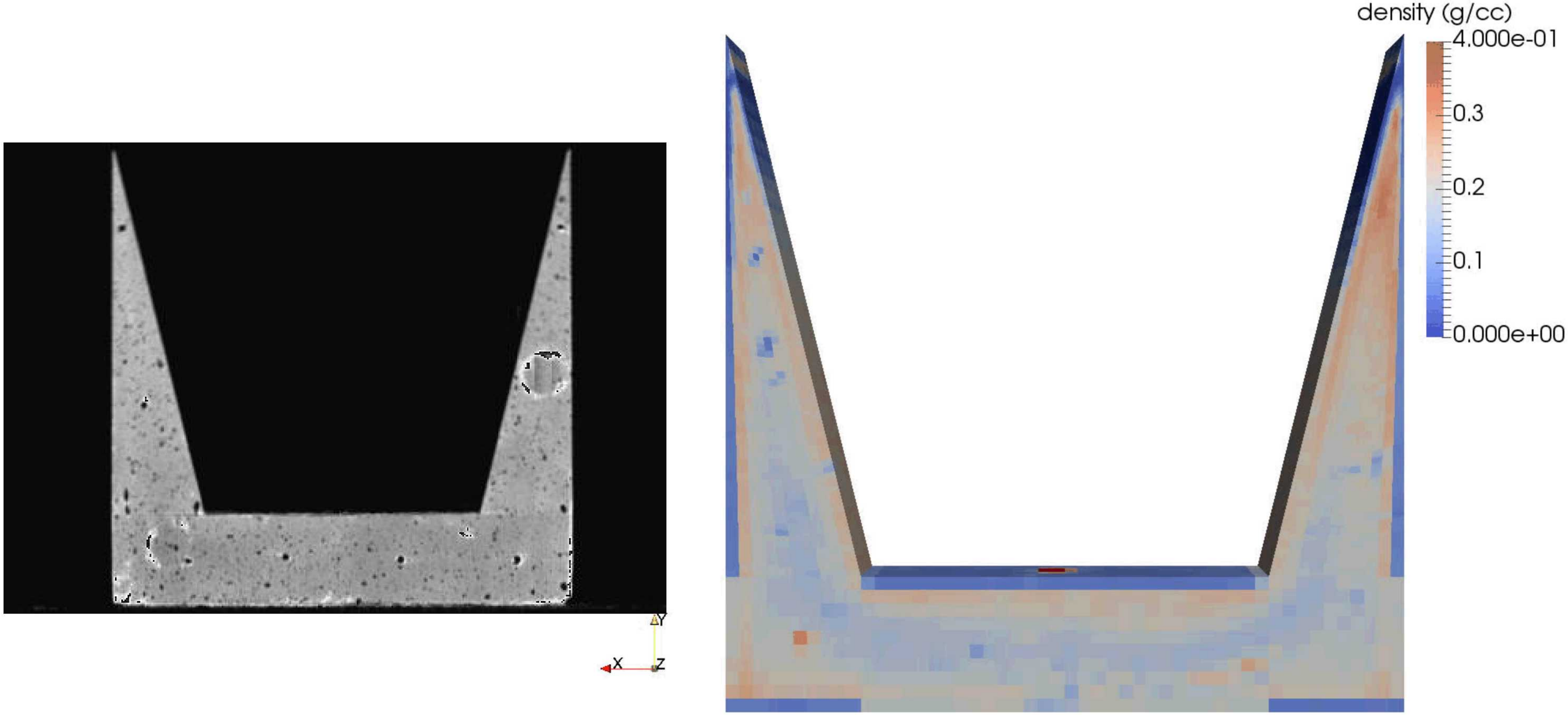


Example CMM trace

Thermal contraction after molding predicted by model to be (L-Lo)/Lo = -0.006 Good agreement with experiment.

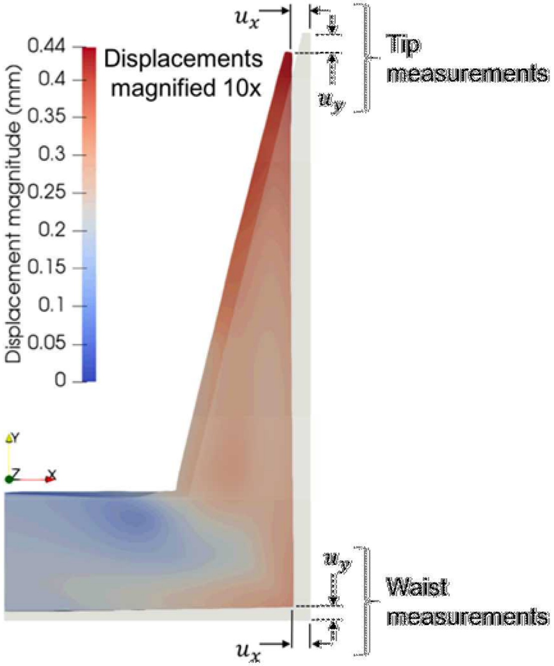
Initial calculations of the U-staple

- Uniform Gauge Pressure (12 psig), Density from the X-ray CT
- **1000 X Displacement for Visualization**

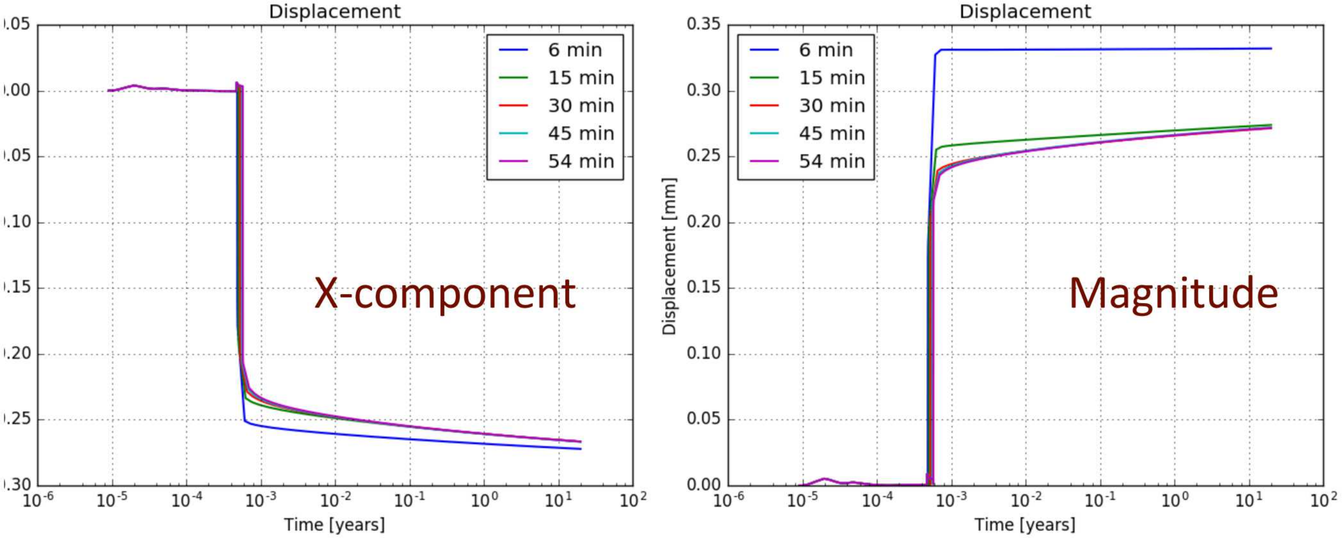


Depressurization consistently produces 1/10 or less the deformation compared with viscoelastic residual stress relaxation

Displacement predictions due to aging



Model Predictions: Waist



- Majority of warpage occurs immediately after release
  - Time of release from mold makes a difference to the amount of warpage observed
- After initial release, 5-20% additional warpage is observed over 20 or more years
- Complicated density gradients in experimental part affect shrinkage
  - Can simulate shrinkage of true density found through x-ray CT
- Volume changes due to cure shrinkage are small

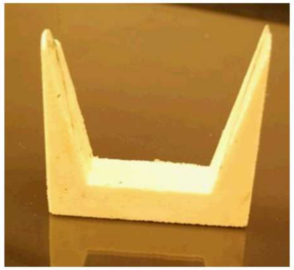
Conclusions

Cradle-to-grave model for PMDI foam growing out of a strong partnership between experimentation, modeling, and components groups

Validated foaming and filling model is now being used to design molds, vent locations and filling procedures for polyurethane parts

- Tracks density, extent of cure, viscosity development
- Overprediction of voids currently an issue
- Bubble scale model currently under development

A model framework was developed to predict stress relaxation and warpage during foam aging



- Manufacturing warpage immediately after demolding encompasses most of the shrinkage
- Continued viscoelastic stress relaxation and cure shrinkage can occur over decades
- Effects of low levels of humidity and continued CO_2 generation are unknown – future work will address these areas

Acknowledgements

Henry Lorenzo (SNL): CMM measurements

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

Parallels in photovoltaics

Failures in photovoltaic modules have been attributed to thermomechanical stresses in encapsulant materials

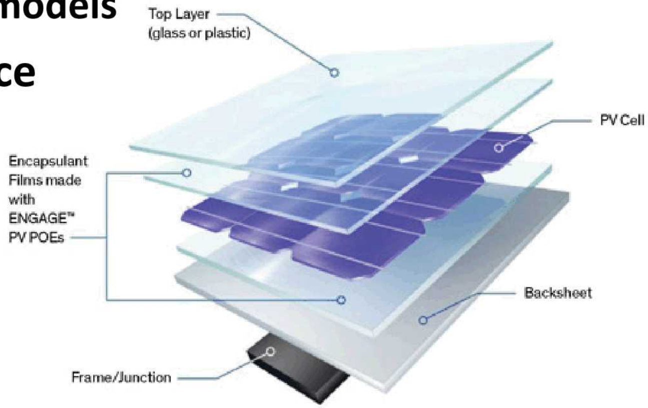
- Delamination, fracture, bond fatigue
- Aging of encapsulants also an issue

Module and cell scale models for stresses in PV modules being developed at Sandia

- Strong collaboration culture between experiments/modeling
- Poster/Presentation: James Hartley

Need for improved material models for encapsulation materials

- Materials of interest include polyolefin and ethylene vinyl acetate polymers
- Properties: thermal expansion coefficient, modulus, Tg, extent of cure, adhesion
    - Experience collecting data in the right form for stress models
- Links between processing conditions and performance
- Aging and its effects on viscoelastic properties



Credit: Dow polyolefin elastomers

Backup slides

Project Scope

- Simulate the manufacturing process
- Develop the residual stress state
- Predict the component warpage over time