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Foam Property Prediction from Process Modeling

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Material Science Seminar

Sandia National Laboratories
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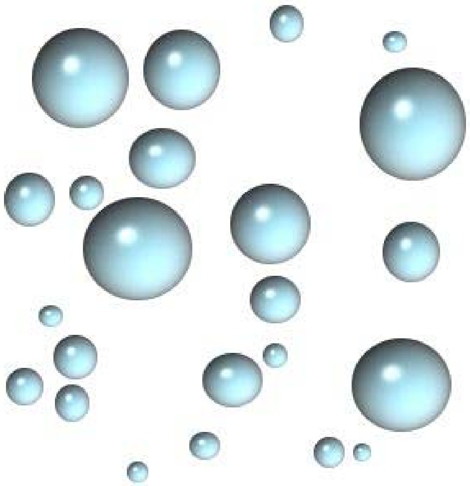
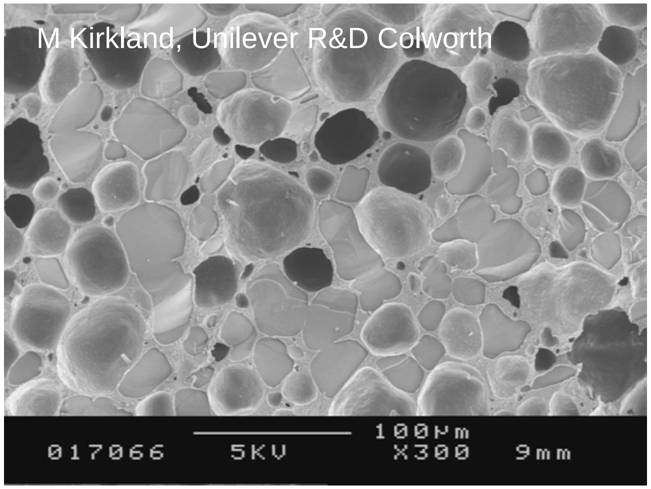
What is a Foam?

- A multiphase material of gas bubbles in a liquid or solid matrix
- How do you make a foam?
  - Generate bubbles in a liquid
  - Stabilize them with particles, fat globules, or surfactant
  - Solidify liquid -freezing, polymerization, or phase change – if desired



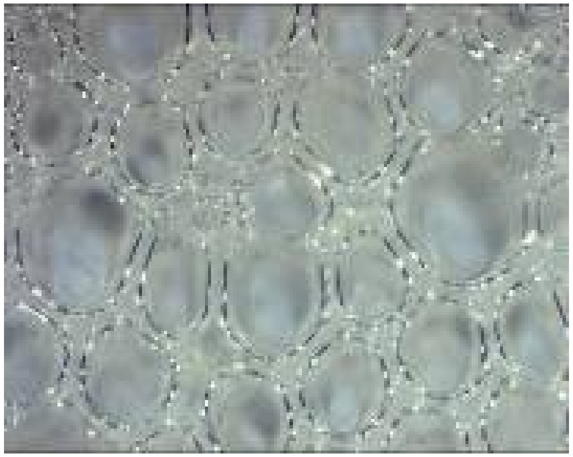
Bubbles

Whipped cream



M Kirkland, Unilever R&D Colworth

Ice cream is a foam – that’s why it is so much work to make



Epoxy foam is a collection of bubbles in polymer

Foams need enough bubbles to jam, *e.g.* bubbles are touching or it is just a bubbly liquid

Sandia's interest in foam

Explosion Suppression

no foam

foam

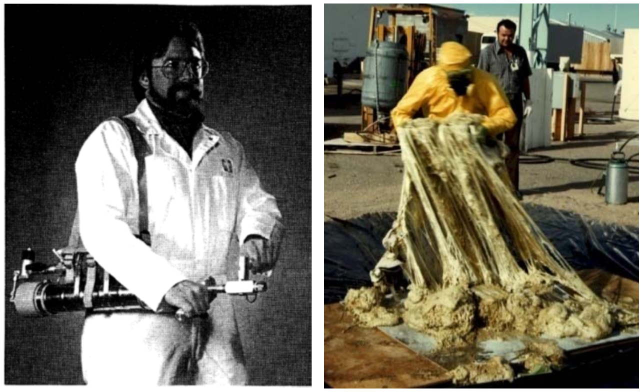
Aubert et al. *Scientific American* 254 74 (1986)
Courtesy of P.B. Rand

Decontamination

Courtesy of J.B. Kelley

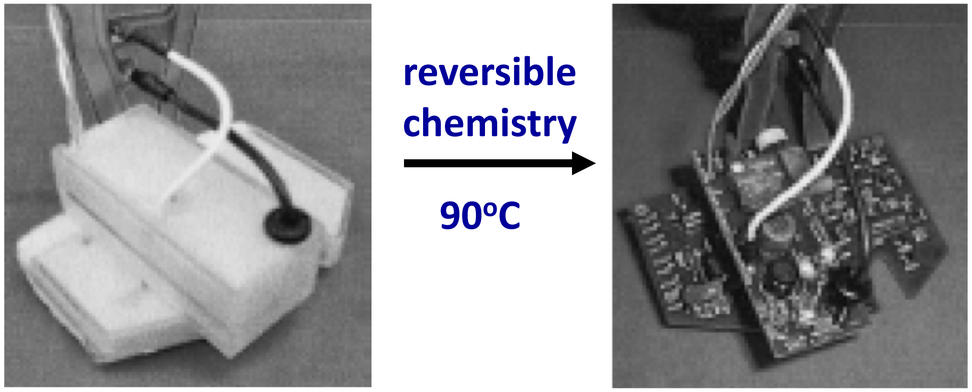
Encapsulation

Intruders/Unruly Crowds



Scott *SAND096-2495C*; Russick *SAND2002-1103P*

Electronics—removable foam



reversible chemistry

90°C

McElhanon et al. *J. Appl. Polym. Sci.* 85 1496 (2002)

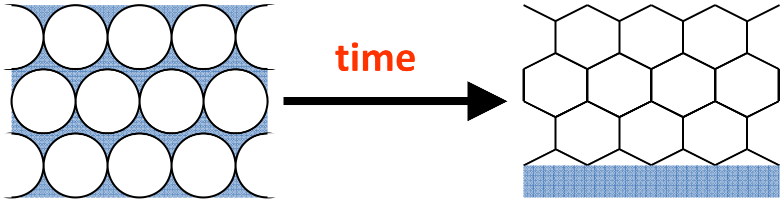
Liquid foam characterization is challenging

Opacity prevents direct observation

- 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

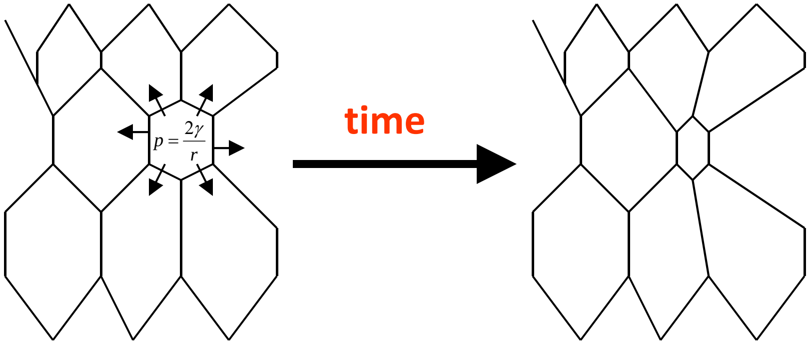
Structure is continuously evolving

Liquid Drainage



Coalescence and rupture also occur

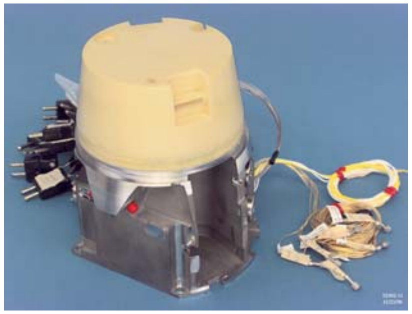
Cell Coarsening



Polyurethane (PMDI): Model Development

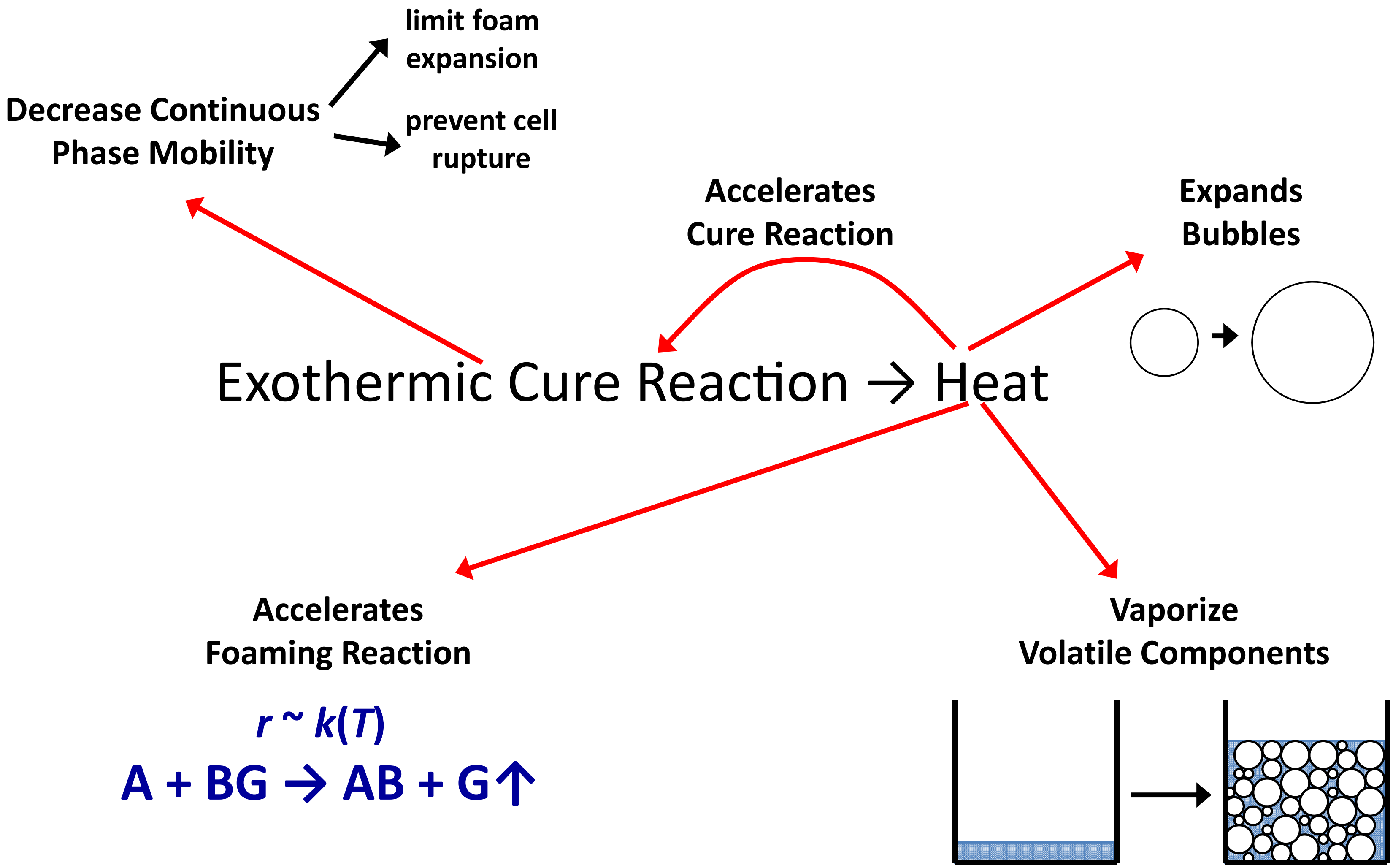
- At Sandia, we use a variety of physically and chemically blown foams.
- PMDI is used as an encapsulant for electronic components, to mitigate against shock and vibration
- We would like to develop a computational model to help us understand foam expansion for manufacturing applications.
- Polyurethane is a chemically blown foam having two primary, competing simultaneous reactions: CO_2 production and polymerization. Separating these reactions can be difficult.
- We use IR spectroscopy to track reaction rates in several isothermal experiments at different temperatures.
- IR does not provide a clear signal for the foaming reaction: Gas generation measured by free rise height.

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



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

Numerical Models are Useful for Polymeric Foams Because of Competing Physics



Decrease Continuous Phase Mobility

limit foam expansion

prevent cell rupture

Accelerates Cure Reaction

Expands Bubbles

Exothermic Cure Reaction → Heat

Accelerates Foaming Reaction

$r \sim k(T)$

$\mathbf{A + BG \rightarrow AB + G\uparrow}$

Vaporize Volatile Components

Cradle-to-Grave Modeling of Foam

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

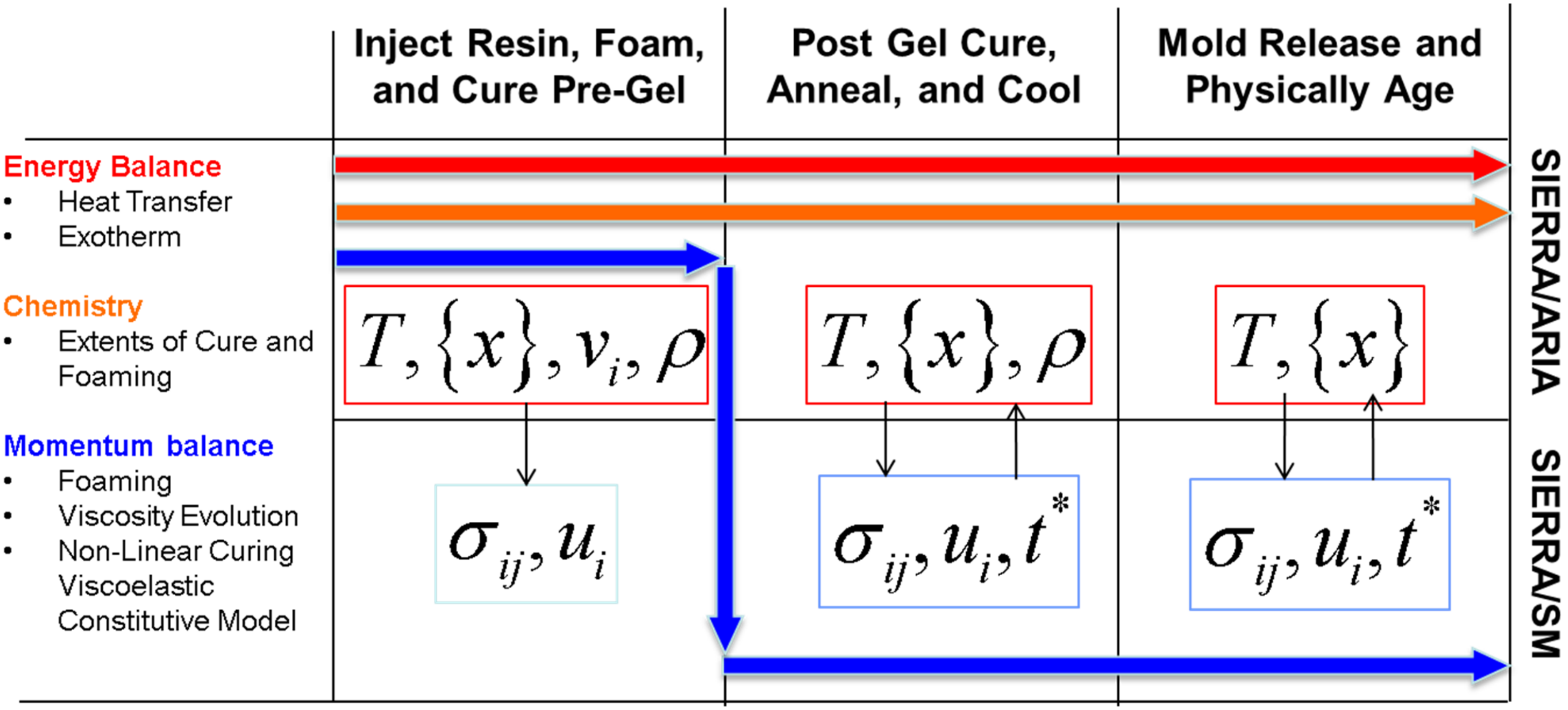
Once the polymer vitrifies, further gas production causes bubble pressurization without volume increase

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

Cradle-to-Grave Modeling of Foam



Inject Resin, Foam, and Cure Pre-Gel

Post Gel Cure, Anneal, and Cool

Mold Release and Physically Age

Energy Balance
- Heat Transfer
- Exotherm

Chemistry
- Extents of Cure and Foaming

Momentum balance
- Foaming
- Viscosity Evolution
- Non-Linear Curing Viscoelastic Constitutive Model

$T, \{x\}, v_i, \rho$

$T, \{x\}, \rho$

$T, \{x\}$

σ_{ij}, u_i

σ_{ij}, u_i, t^*

σ_{ij}, u_i, t^*

SIERRA/ARIA

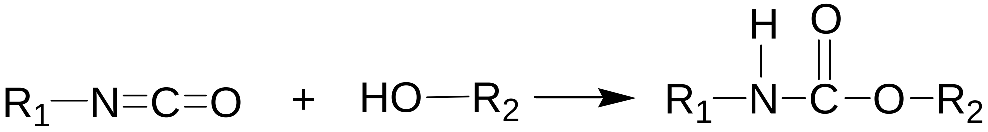
SIERRA/SM

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

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

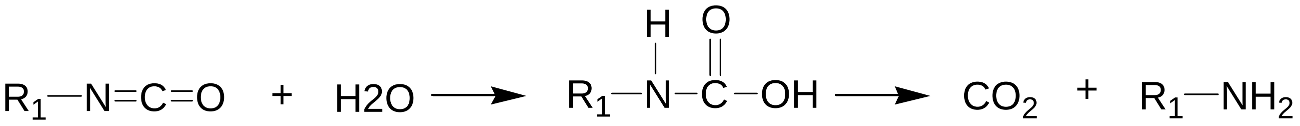
Polyurethane Resin Cure and Foaming Reactions

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



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

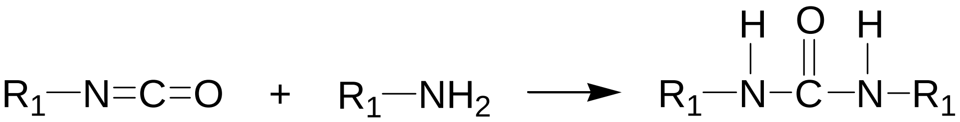
Urethane formation, crosslinking



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

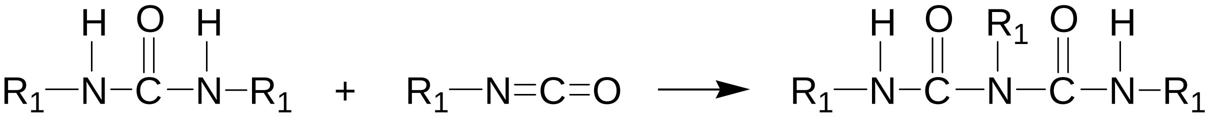
Foaming reaction yields CO_2 and amine

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



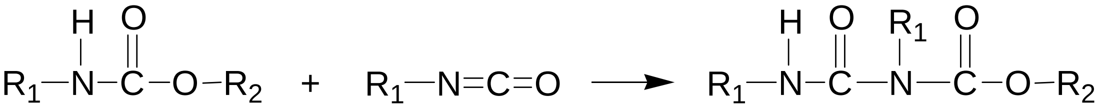
$$R_1{-}N{=}C{=}O \;+\; R_1{-}NH_2 \longrightarrow R_1{-}\overset{\overset{H}{|}}{N}{-}\overset{\overset{O}{\|}}{C}{-}\overset{\overset{H}{|}}{N}{-}R_1$$

Urea formation



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

Biuret formation



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

Allophanate formation

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

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

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

Use of Extent of Reaction Form Can Simplify the Model

- Decouple reactions assuming isocyanate is in excess during foaming
- Track two extent of reactions to give density (and volume) of foam with time, heat generated from the exothermic reactions, and viscosity of the foam
- Besides the moles of carbon dioxide and polymer, the moles of water, polyol, and isocyanate can all be derived from these two extent of reactions

ξ is the extent of polymerization reaction

$$\frac{d\xi}{dt} = k_0 e^{\Delta E / RT} (1-\xi)^q$$

$$S_{rxn} = \Delta H_{rxn} \rho \frac{d\xi}{dt}$$

$$\eta = \eta_{polymer} \eta_{\phi}$$

$$\eta_{\phi} = \eta_{polymer} \exp\left(\frac{\phi_g}{1-\phi_g} \right)$$

$$\eta_{polymer} = \eta_0 \left(\frac{\xi_c^b}{\xi_c^b - \xi^b} \right)^q$$

α is the extent of reaction generating CO_2

$$\frac{d\alpha}{dt} = \frac{k(1-\alpha)^n}{(1-\alpha)^m + M} \quad \text{where} \quad \begin{aligned} k &= A_1 \exp(-E_1 / RT) \\ M &= A_2 \exp(-E_2 / RT) \end{aligned}$$

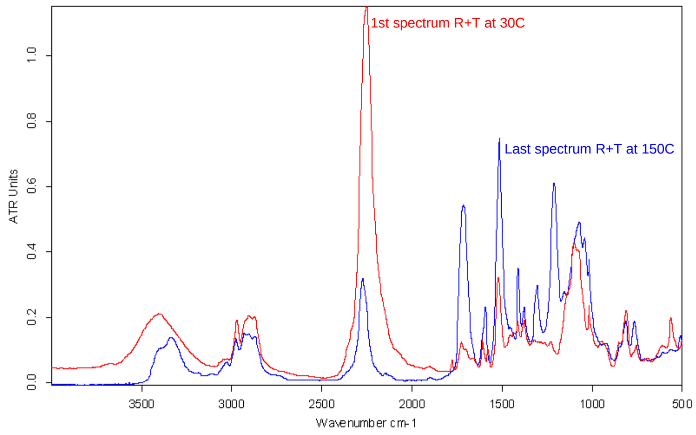
$$n_{CO_2}(t) = n_{CO_2}^{init} + \alpha(t) n_{CO_2}^{\max}$$

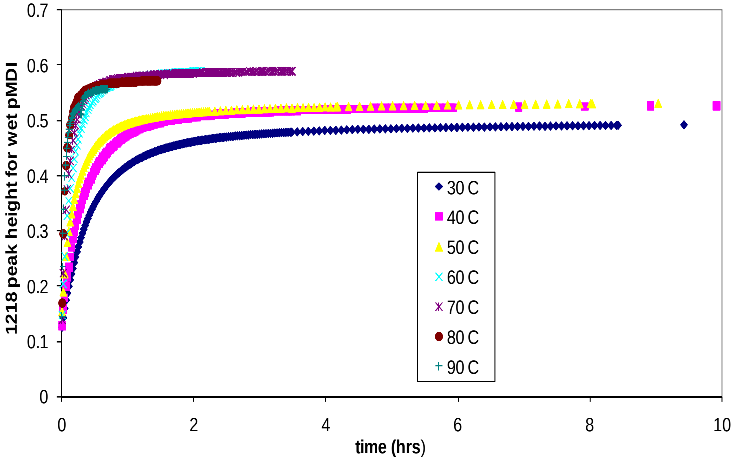
$$\phi(t) = \frac{n_{CO_2} MW_{CO_2} / \rho_{CO_2}}{n_{CO_2} MW_{CO_2} / \rho_{CO_2} + V_{liquid}}$$

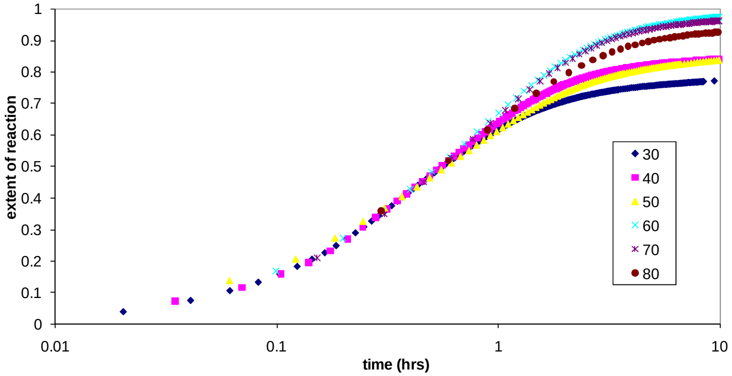
$$\rho_{foam} = (\rho_{CO_2} - \rho_{liquid}) \phi(t) + \rho_{liquid}$$

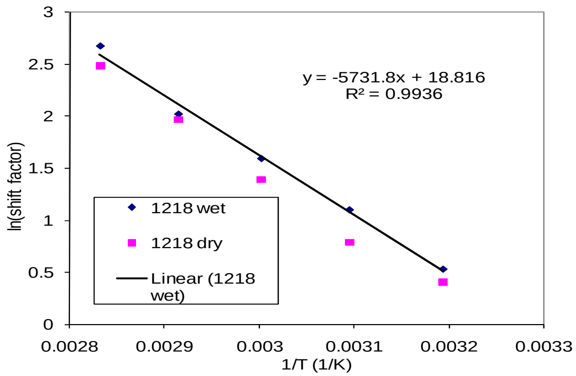
Extent of Reaction for Polymerization

- Use IR to monitor polyol-isocyanate urethane reactions in both wet and dry polyurethane
- Peak height as a function of time for the 1218 cm^{-1} peak
- Isothermal tests were carried out for various temperatures ranging from 30°C to 90°C.









- Normalize the peak height by the maximum height at the highest temperature to obtain extent of reaction
- Shifted extent of reaction for isothermal tests carried out for various temperatures
- Natural log of the shift factor versus the reciprocal temperature in Kelvin, gives the activation energy for the Arrhenius rate constant for the polymerization reaction.

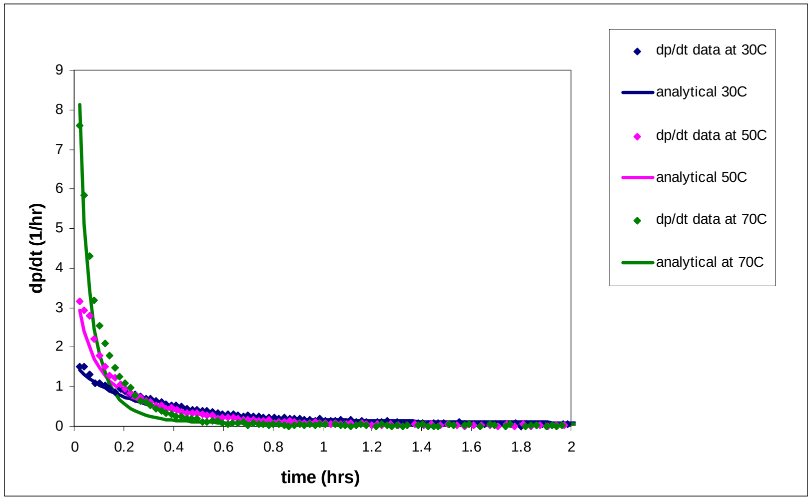
Extent of Reaction for Polymerization

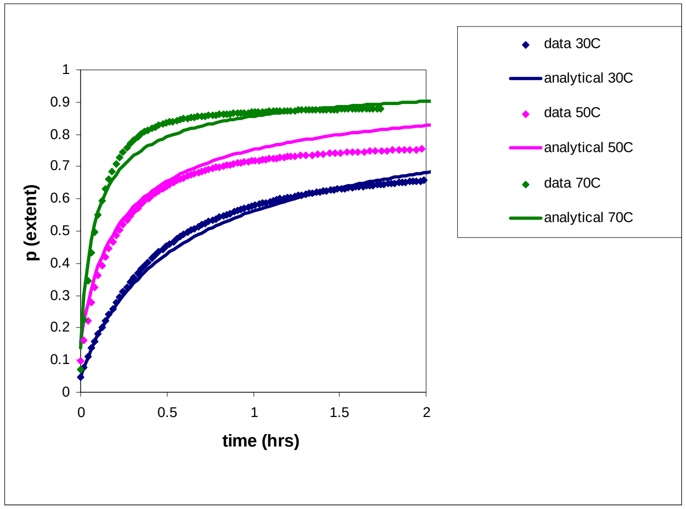
- Numerically differentiate the extent of reaction, ξ, to obtain the rate
- Fit the rate and the extent of reaction simultaneously to a standard equation form, where only the exponent is unknown
- Form of between 2^{nd} and 3^{rd} order reaction fits data

$$\frac{d\xi_{cure}}{dt} = k_0 e^{\Delta E/RT}\left(1-\xi_{cure}\right)^{2.75}$$

k_0=2.96 x 10^8 1/hr,
ΔE/R=-5731.8 K

- "Wet" vs. "dry" slightly different rates – used full PMDI-4 (wet) formulation results



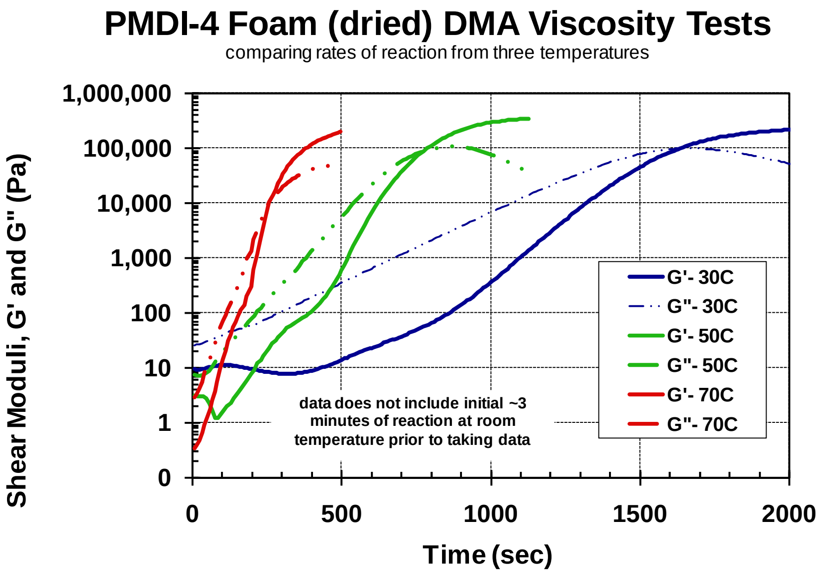


From polyol-isocyanate urethane reactions (Peak 1218 in PMDI-4 foaming)

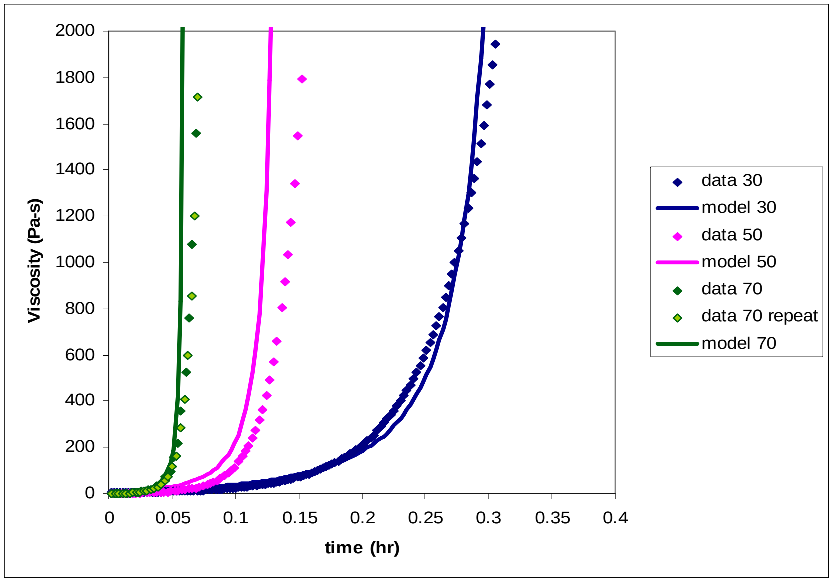
- The lumped heat of reaction was measured through differential scanning calorimetry to be 240.3 J/g for the wet (foaming) formulation

Resin Continuous Phase Viscosity

- Storage and loss modulus for dry polyurethane at 30^{o}C, 50^{o}C, and 70^{o}C measure in oscillatory rheometer.
- The cross over point of G’ and G’’ gives an approximate gel point and gel time of the polymer. Allow to be a function of T.
- Viscosity is correlated to extent of reaction and compared to data.



Measurements by Doug Adolf

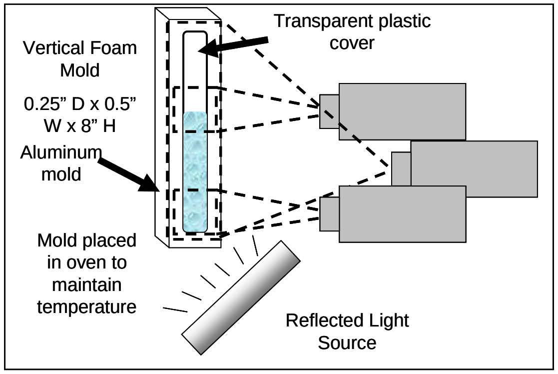


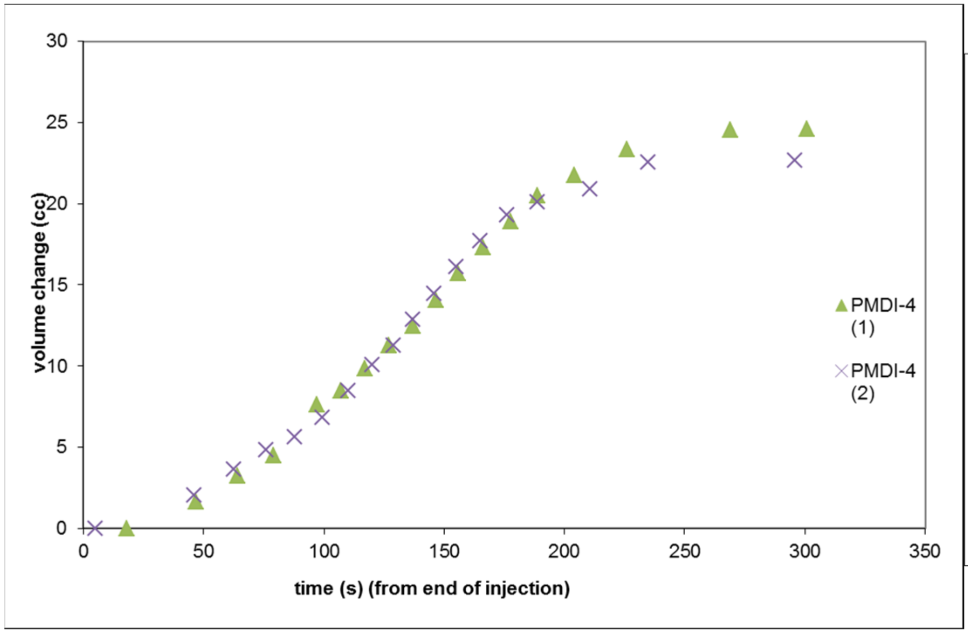
$$\eta_{cure} = \eta_0^0 \left(\frac{\xi_c - \xi}{\xi_c}\right)^{-2.0} \qquad \xi_c = 0.003T(K) - 0.5525$$

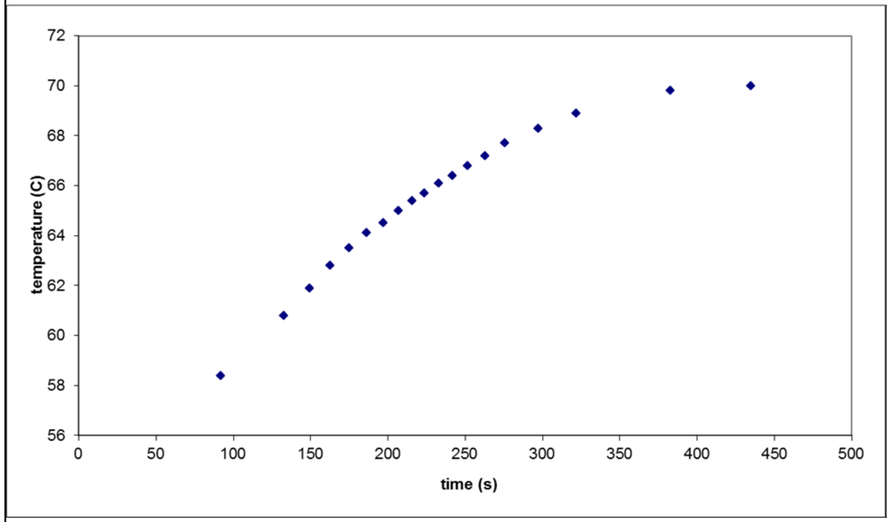
$$\eta_0^0 = 2.74x10^{-9} \exp\left(\frac{6400[cal/mol]}{R[cal \cdot gmole^{-1} \cdot K^{-1}]T[K]}\right) Pa \cdot s$$

Measure Height Change in Simple Geometry to Quantify Foaming Reaction

- Data have most uncertainty at early times because reaction is occurring during mixing and injections, but bubbles are being destroyed in these processes, too.
- We can only measure height change after these processes.
- CO_2 loss from bubble breakage at top surface? BUT bottom line: engineering model to predict volume change
- The foam cannot be preheated, so during the foam rise the temperature is not steady.

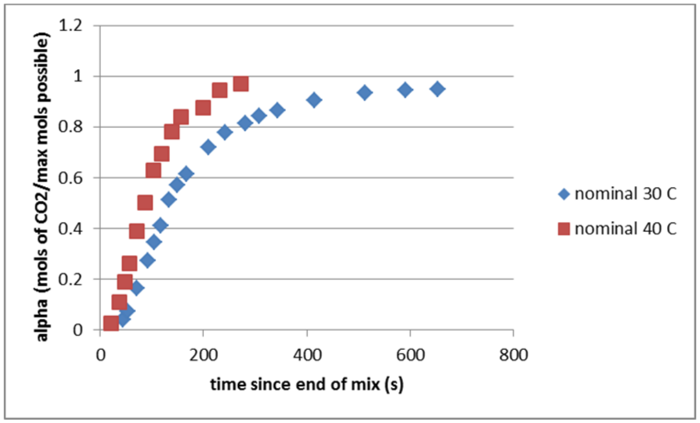




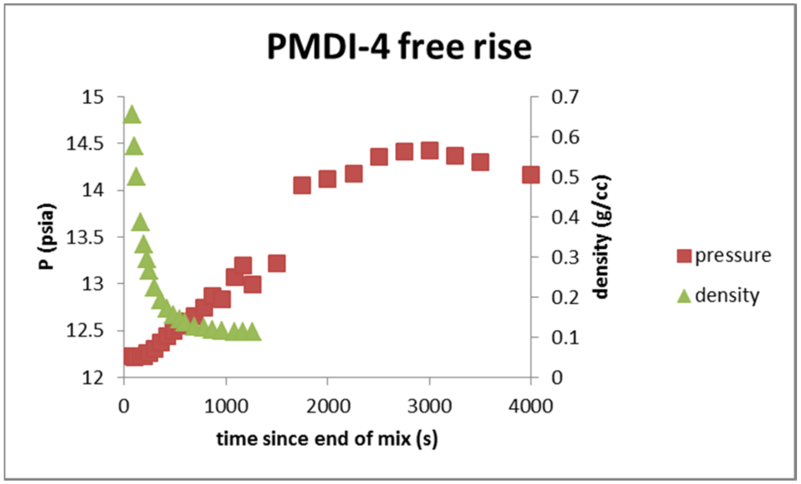


Volume Change, Temperature, and Pressure Determines CO_2 Concentration

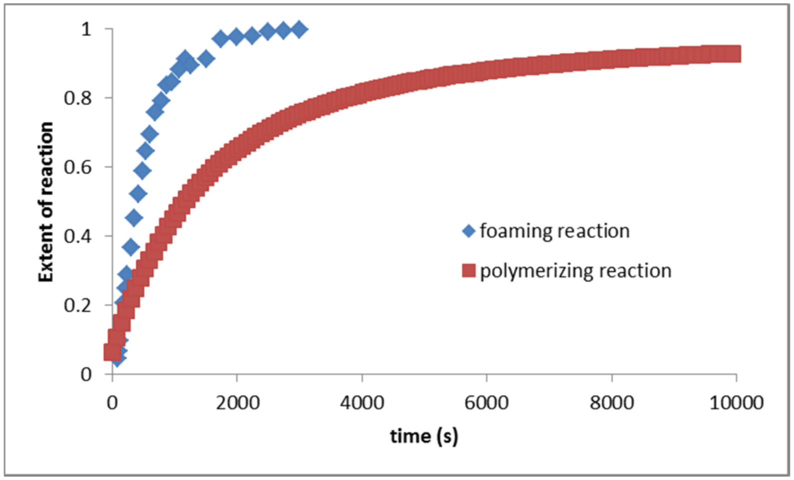
- As expected, reaction progresses faster at higher temperatures
- Pressure continues to rise after foam has stopped expanding.
- Implies CO_2 reaction progressing after foam viscosity restricts expansion.
- Comparing to IR, we see that polymerizing reaction is slower than foaming reaction (at 30C reaches a maximum polymerization in about 4 hours vs. P max at less than 1 hr).



Foam rise data with a fast catalyst at two temperatures.

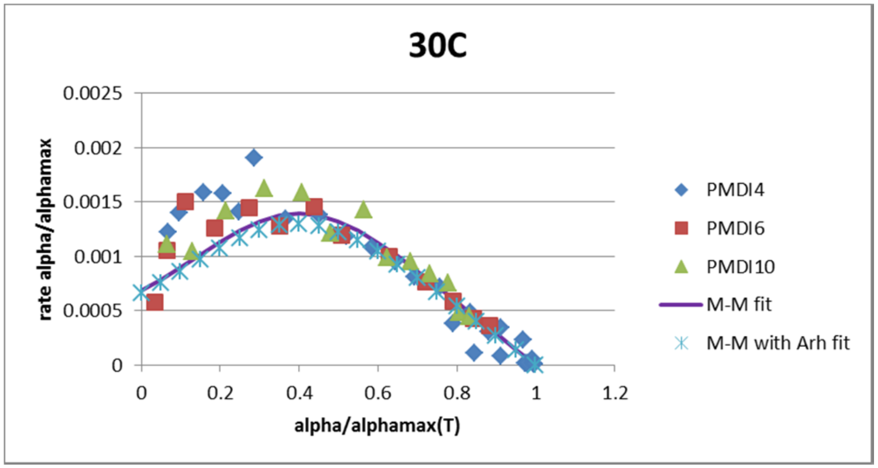


Foam rise data for a slower reacting foam at a nominal temperature of 30C



Comparison of foam rise and IR data for a slower reacting foam at a nominal temperature of 30C

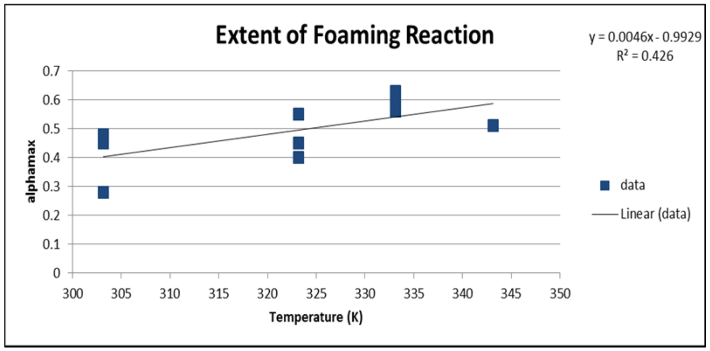
Michaelis-Menten Reaction Form for CO_2

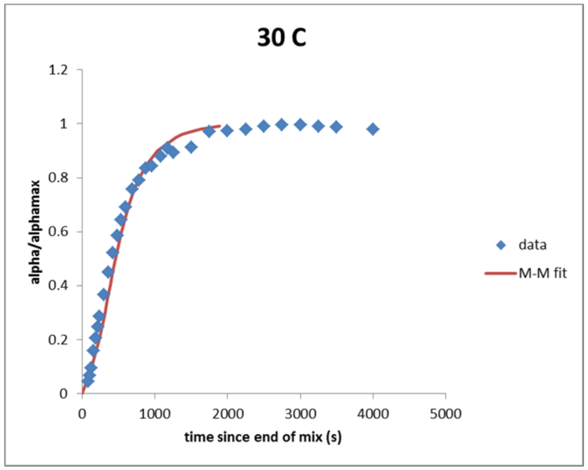


$$\frac{d\alpha / \alpha_{\max}}{dt} = \frac{k(1-\frac{\alpha}{\alpha_{\max}})^n}{(1-\frac{\alpha}{\alpha_{\max}})^m + M}$$

$$\alpha_{\max} = 0.0046[1/K]T[K] - 0.9929$$

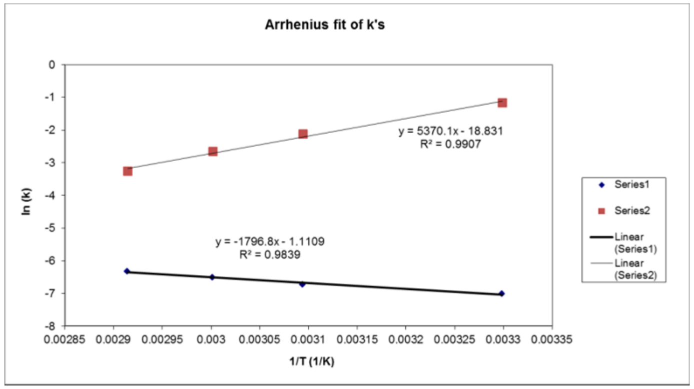
Foam formulations vary slightly (besides H_2O content) so a universal α_{max} is probably not appropriate





$$t + C = \frac{1}{k}\int (1-\alpha)^{m-1} d\alpha + \frac{M}{k}\int (1-\alpha)^{-1} d\alpha$$

$$= \frac{1}{k}\left[\frac{(1-\alpha)^m}{-m}\right] - \frac{M}{k}\ln(1-\alpha).$$

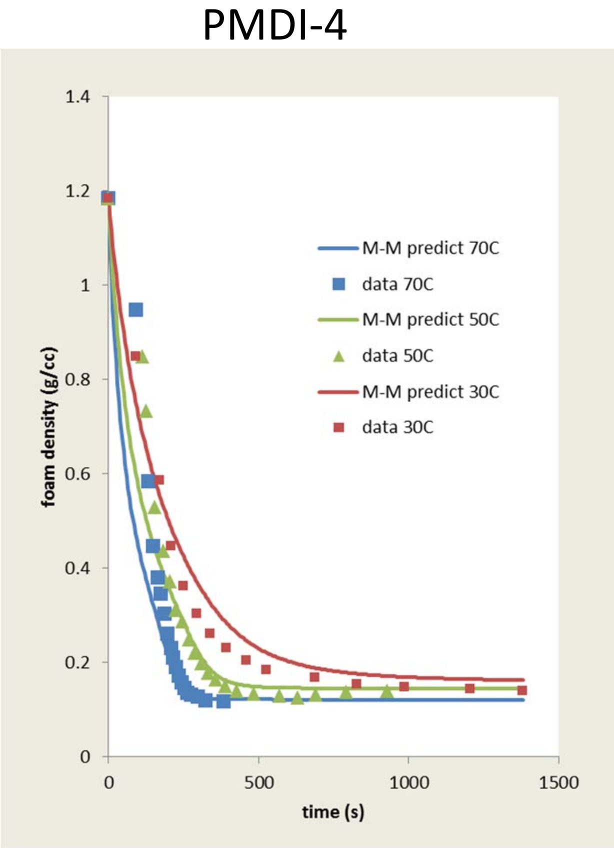


$$k = A_1 \exp(-E_1 / RT)$$

$$M = A_2 \exp(-E_2 / RT)$$

New Polyurethane Gas Generation Model

- First step achieved:
  - Detailed, consistent, kinetic model of gas evolution to produce CO_2 (Michaelis-Menten form)
  - Populate kinetic model via experimental data for several types of PMDI and several temperatures
  - Model can accurately predict the density and possibly density gradients
  - Model implemented in Sierra/Aria



α is the extent of the conversion of water to CO_2
$\alpha_{\max}$ is the maximum conversion for a universal correlation

$$\frac{\partial \alpha^*}{\partial t} = \frac{k(1-\alpha^*)^n}{(1-\alpha^*)^m + M} \qquad k = A_1 \exp(-E_1/RT)$$

$$M = A_2 \exp(-E_2/RT)$$

$$\alpha^* = \frac{\alpha}{\alpha_{\max}}$$

n_{Co2}, the moles gas, can be calculated from α and $\alpha_{\max}$

$$n_{CO_2} = n^{i}{}_{CO_2} + \alpha^* \alpha_{\max} n^{\max}{}_{CO_2}$$

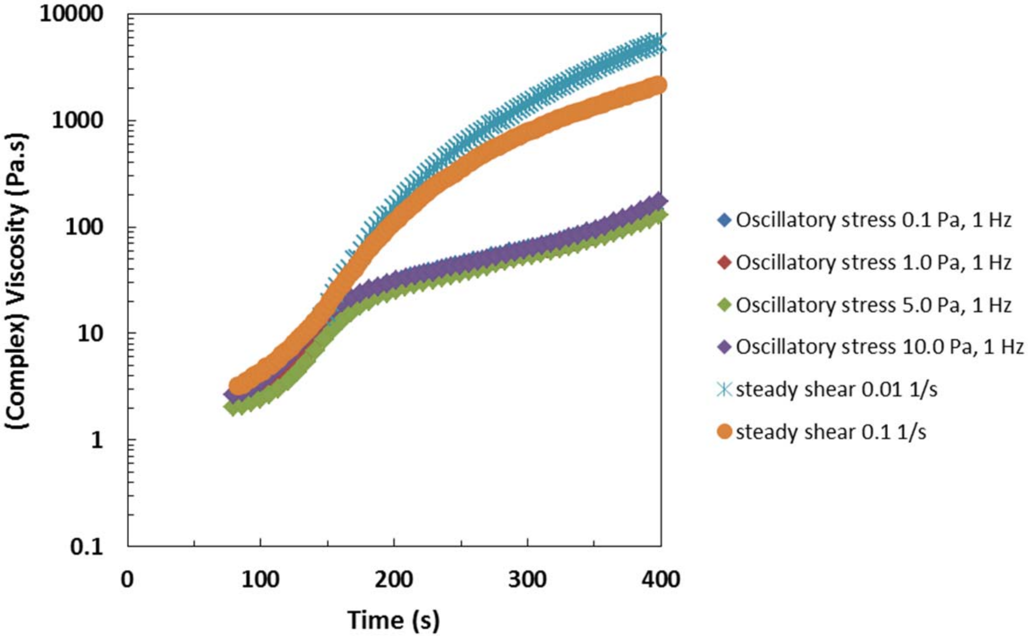
$$\alpha_{\max} = f(T) = \alpha_1 T(K) - \alpha_1$$

$\phi(t)$, the volume fraction of gas, is related to n
ρ_{foam}, the density of foam, is now a prediction from the model

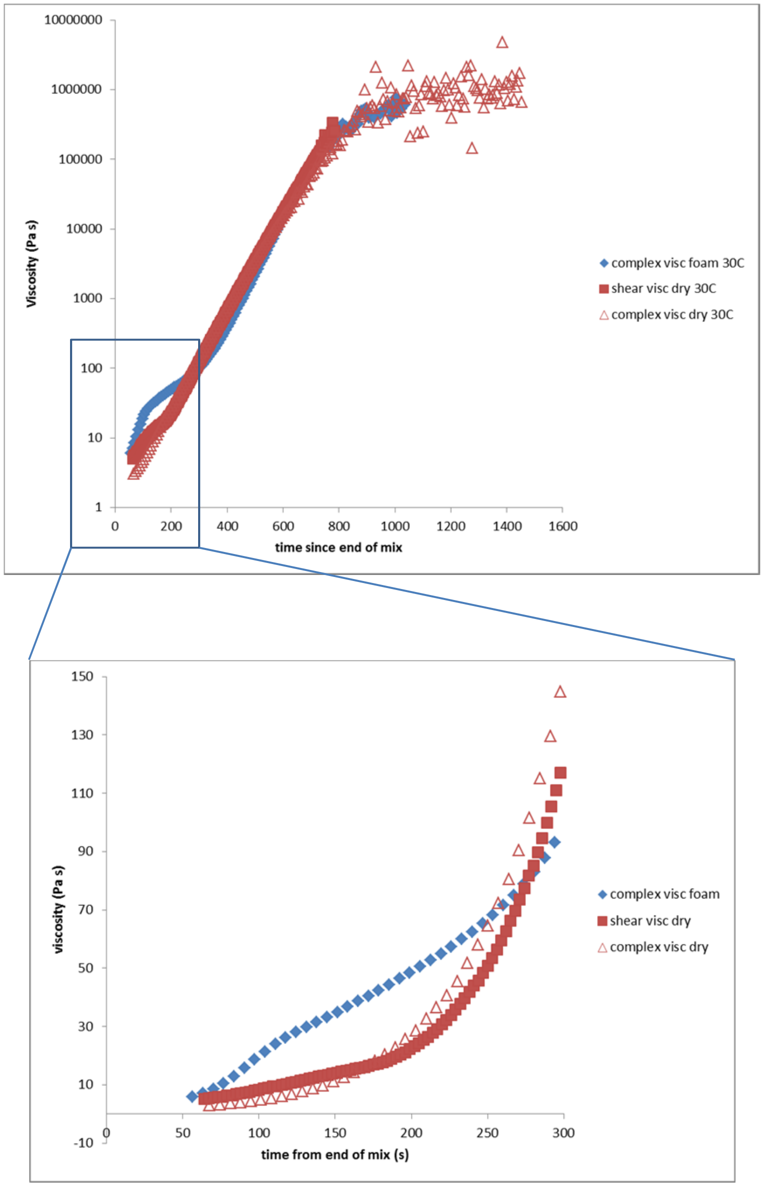
$$\phi(t) = \frac{n_{CO_2} MW_{CO_2} / \rho_{CO_2}}{n_{CO_2} MW_{CO_2} / \rho_{CO_2} + V_{liquid}}$$

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

Polyurethane: Foam Viscosity



- Dynamic and shear viscosity measured at 30^{o}C, 50^{o}C, and 70^{o}C for material during foaming
- At longer times, viscosity dominated by polymerization effects

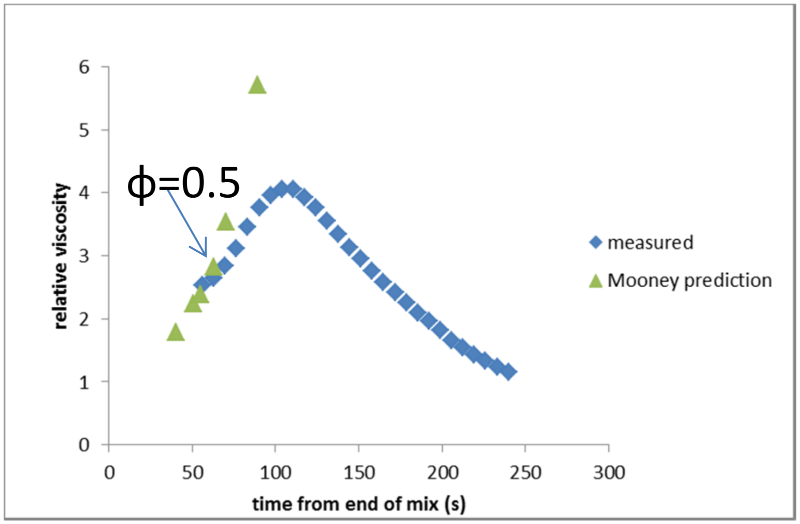


Rheology of a fast-reacting foam – foam rise stops at approximately 500 s.

Foam Viscosity Model

- Knowing density evolution from separate foam rise experiments we relate the gas fraction and the foam viscosity
- Mooney prediction (for $\phi_{gas} < 0.5$)

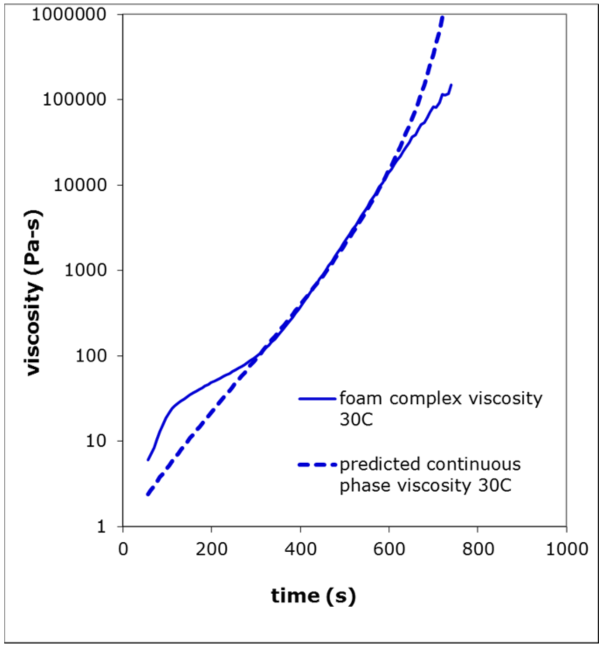
$$\eta_{foam} = \eta_{cure} \exp\left(\frac{\phi_{gas}}{1-\phi_{gas}}\right)$$



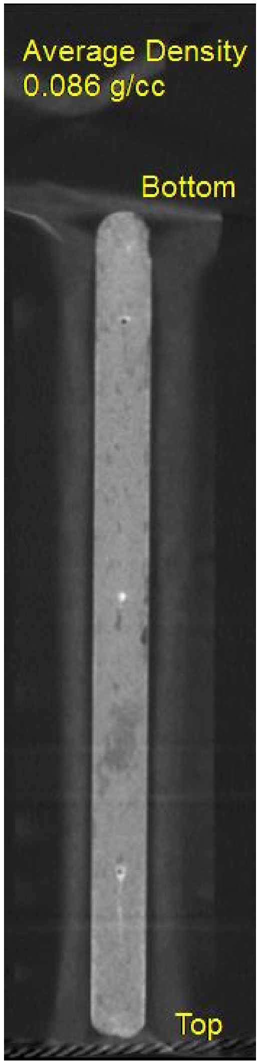
- Recall continuous phase viscosity during curing:

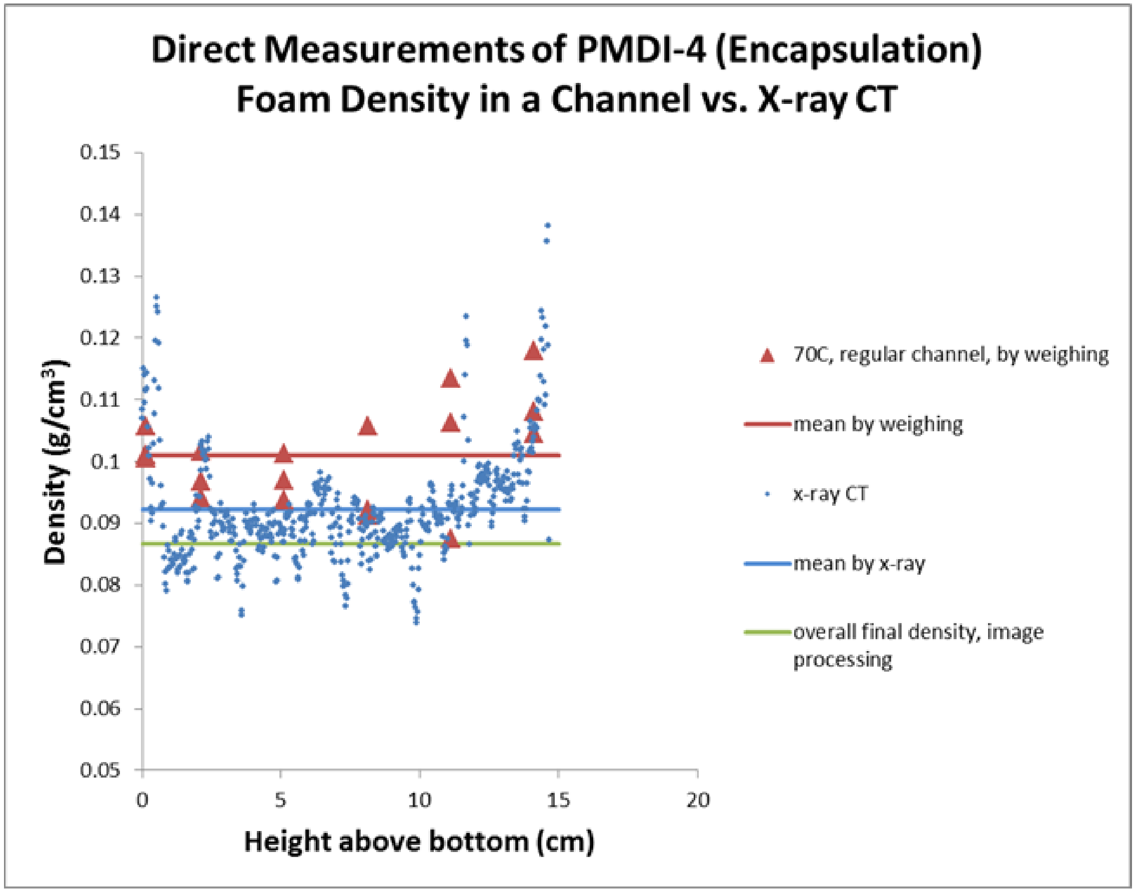
$$\eta_{cure} = \eta_0^0 \left(\frac{\xi_c - \xi}{\xi_c}\right)^{-2.0}$$

- For $\phi_{gas} > 0.7$ estimate $\eta_{foam} = \eta_{cure}$



Experimental Post-Test Density Variation

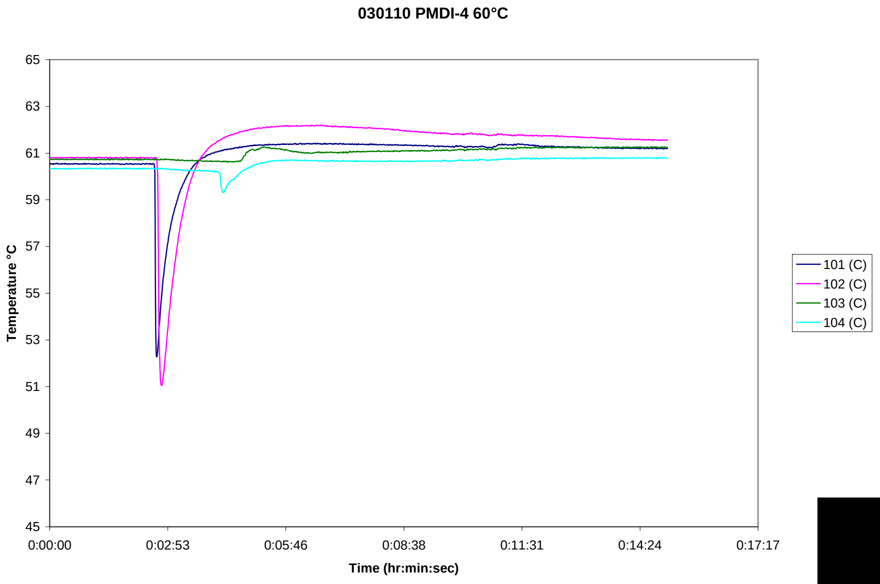




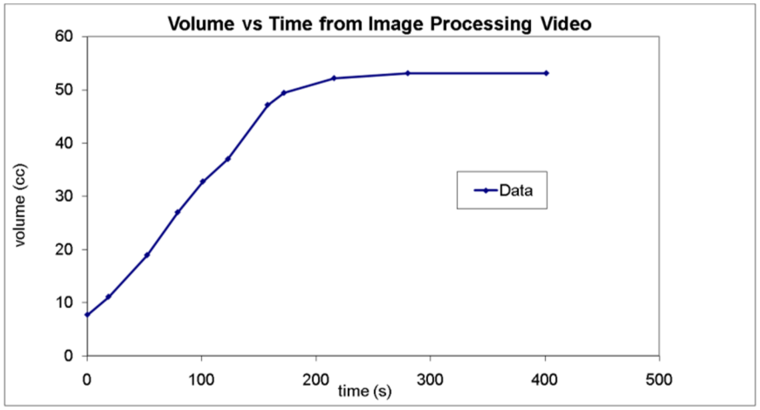
- 15% variation of density from highest to lowest
- Different techniques give 10% difference in average density

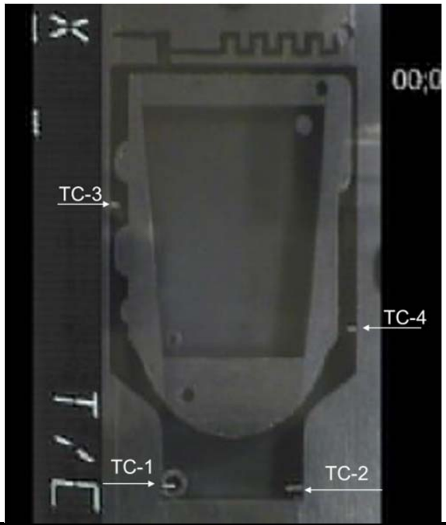
Next step: model foam rise experiment and fit data simultaneously so we can include gradients in the parameter estimation

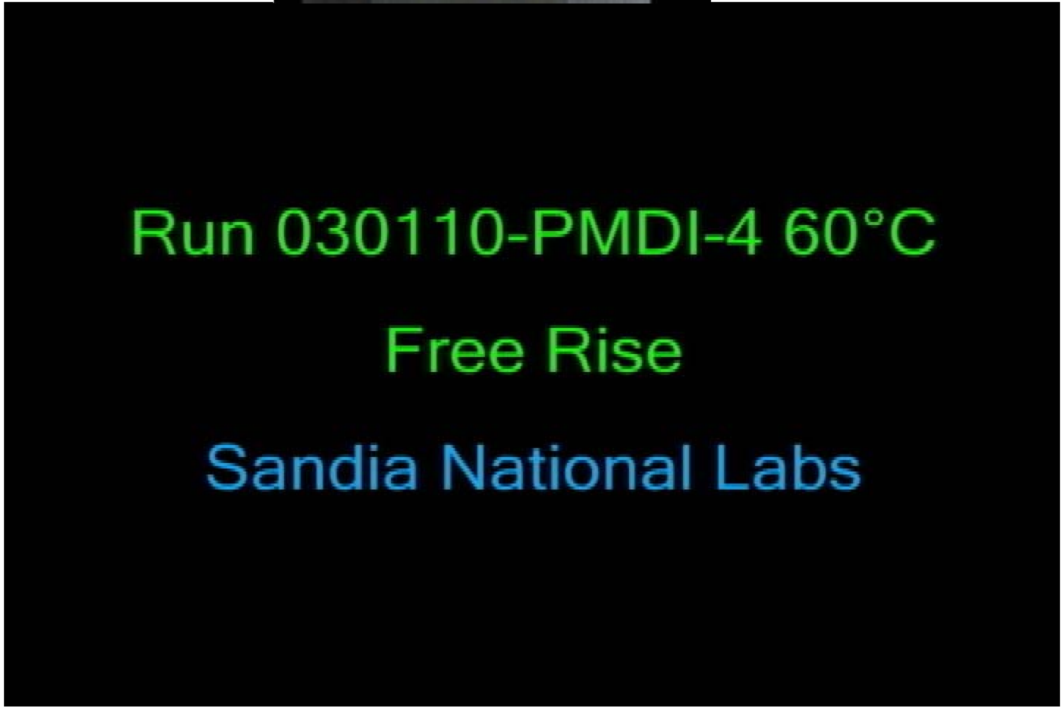
PMDI-4 Temperature-Instrumented Flow Viz



- Front location, temperatures , fill rate analysis







Run 030110-PMDI-4 60°C

Free Rise

Sandia National Labs

- Video of polyurethane

Equations of Motion Include Evolving Material Models

Momentum equation and continuity have variable density, shear viscosity, and bulk viscosity

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

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

Energy equation has variable heat capacity and thermal conductivity including a source term for heat of reaction for foaming and curing reactions

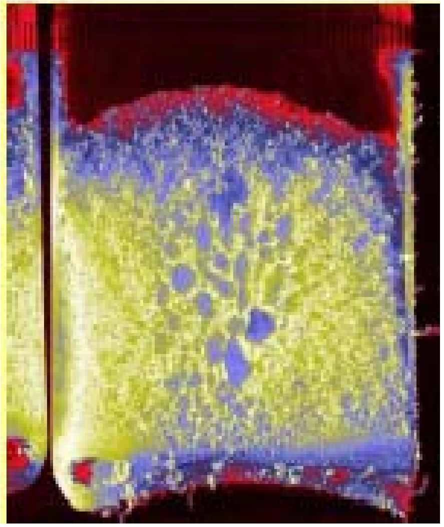
$$\rho C_{pf} \frac{\partial T}{\partial t} + \rho C_{pf} v \bullet \nabla T = \nabla \bullet (k \nabla T) + \rho \varphi_e \Delta H_{rxn} \frac{\partial \xi}{\partial t}$$

Extent of reaction equation for polymerization: condensation chemistry

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

Extent of reaction equation for foaming reaction: Michaelis-Menten

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



NMR imaging shows coarse microstructure (Altobelli, 2006)

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

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

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

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

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

Thermal properties depend on gas volume fraction and polymer properties

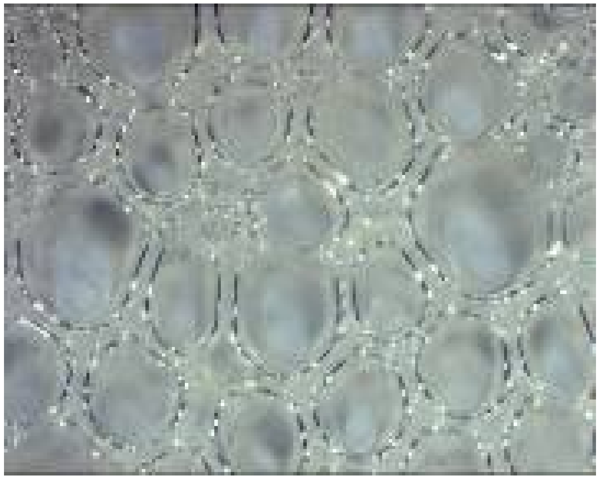
$$k = \frac{2}{3}\left(\frac{\rho}{\rho_e}\right)k_e + \left(1 - \frac{\rho}{\rho_e}\right)k_v$$

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

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

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

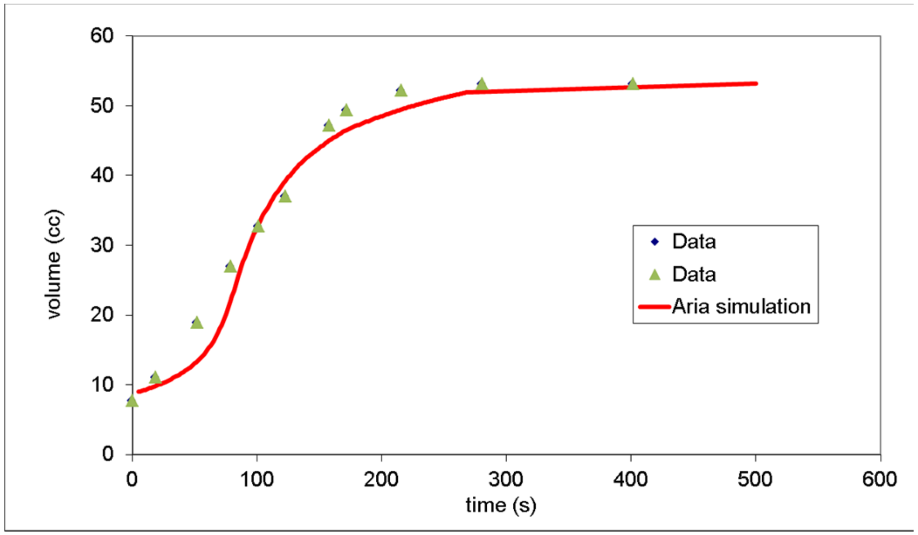
$$\lambda = \frac{4}{3}\mu_0 \frac{(\phi_v - 1)}{\phi_v}$$

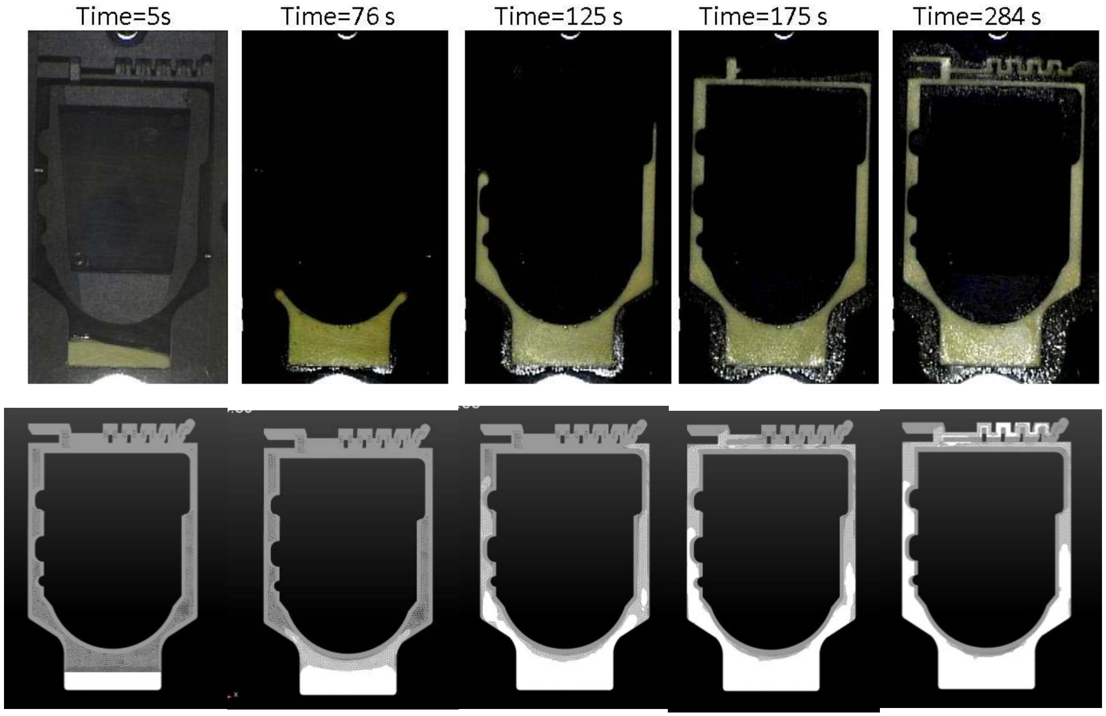


Epoxy foam is a collection of bubbles in curing polymer

- 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)

PMDI-4 Free Surface Validation Study





- Model tracks density change from foaming in full system
- But validation data show that model foams too slow and then too fast
- Current work:
  - Improve density model
  - Add a function to tie foam generation to gelation and vitrification

Coupled Finite Element Method/Level Set to Solve Foam Dynamics

- Given fluid velocity field, u(x,y,z), evolution on a fixed mesh is according to:

$$\frac{\partial \phi}{\partial t} + u \cdot \nabla \phi = 0$$

- Purely hyperbolic equation … fluid particles on ϕ(x,y,z) = 0 should stay on this contour indefinitely
  - Does not preserve ϕ(x,y,z) as a distance function
  - Introduces renormalization step.

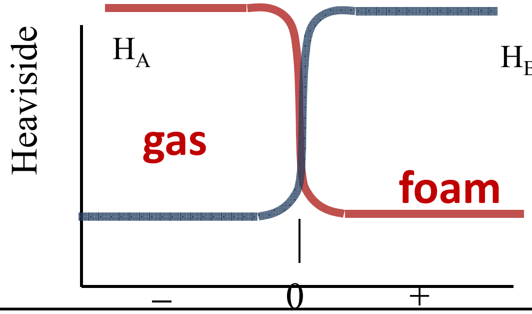
- Equations of motion, kinetics and energy balance averaged based on level set, ϕ

$$H_A \rho_A \frac{Du}{Dt} + H_B \rho_B \frac{Du}{Dt} = -\nabla P + H_A \nabla \cdot (\mu_A \dot{\gamma}) + H_B \nabla \cdot (\mu_B \dot{\gamma}) + (H_A \rho_A + H_B \rho_B) g + I.T.,$$

$$H_A \frac{D\rho_A}{Dt} + H_B \frac{D\rho_B}{Dt} + (H_A \rho_A + H_B \rho_B) \nabla \cdot u = 0$$

$$H_A + H_B = 1$$

Rao et al, IJNMF, 2011



Numerical Solution Methods for Interfacial Motion

Tracking motion of interface between two distinct phases appears often:

- Phase changes
- Film growth
- Fluid filling

Interface tracking:

- Explicit parameterization of location
- Interface physics more accurate
- Moving mesh
- Limits to interface deformation
- No topological changes

Examples:

- Spine methods (*Scriven*)
- ALE

Embedded Interface Capturing:

- Interface reconstructed from higher dimensional function
- Fixed mesh
- “Diffuse” interface physics
- Interface deformation theoretically unconstrained

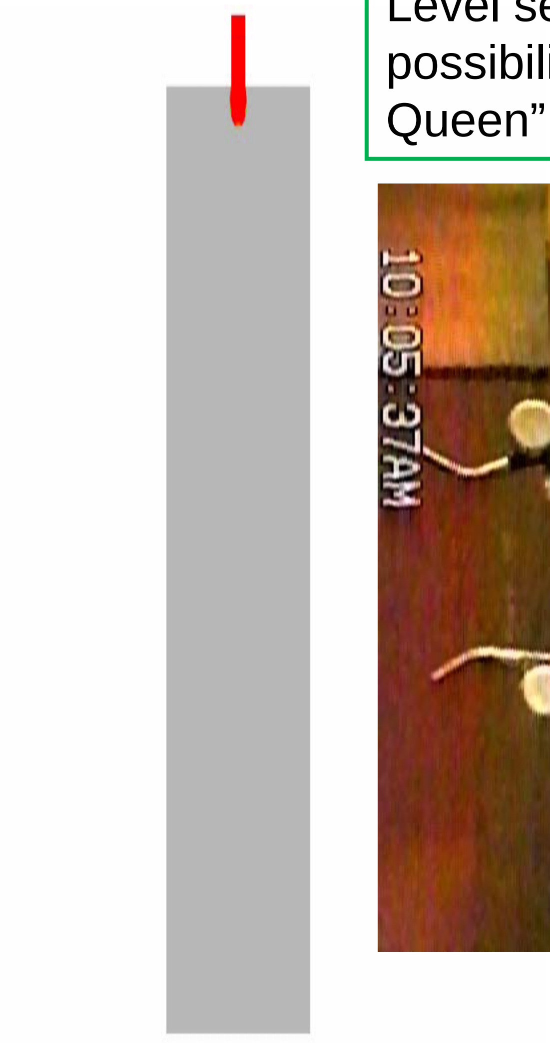
Examples:

- Volume-of-Fluid (*Hirt*)
- Level Sets (*Sethian*)

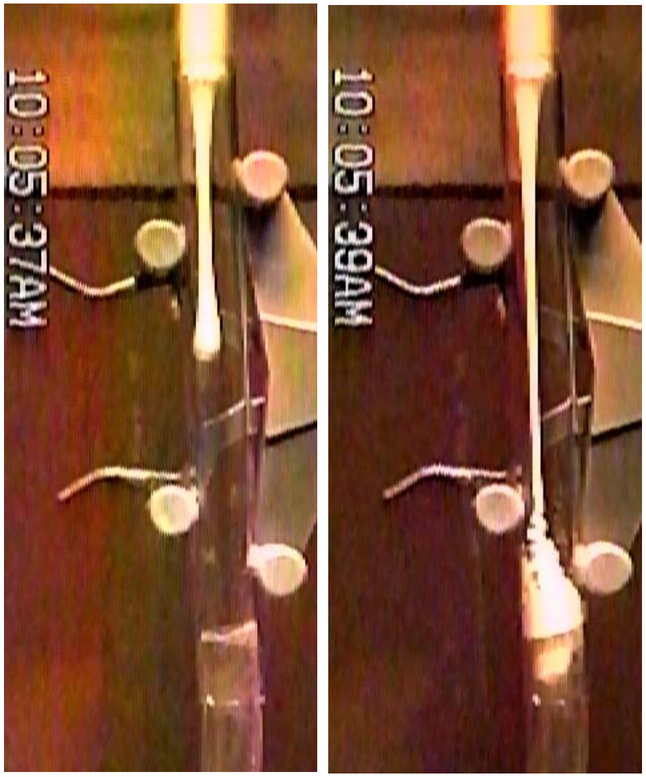
PA Sackinger, PR Schunk, RR Rao, “A Newton-Raphson pseudo-solid domain mapping technique for free and moving boundary problems: A finite element implementation,” *J. Comp. Physics*, 125, 83, 1996.

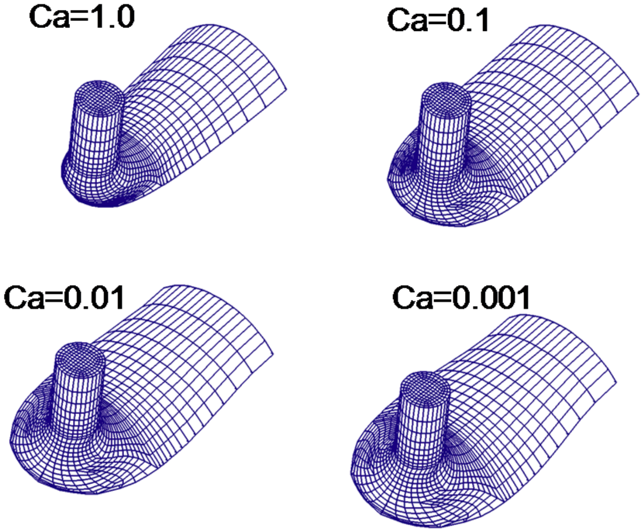
Embedded Interface Methods Can Capture Topological Changes

Level set method has possibility of modeling “Dairy Queen” effect

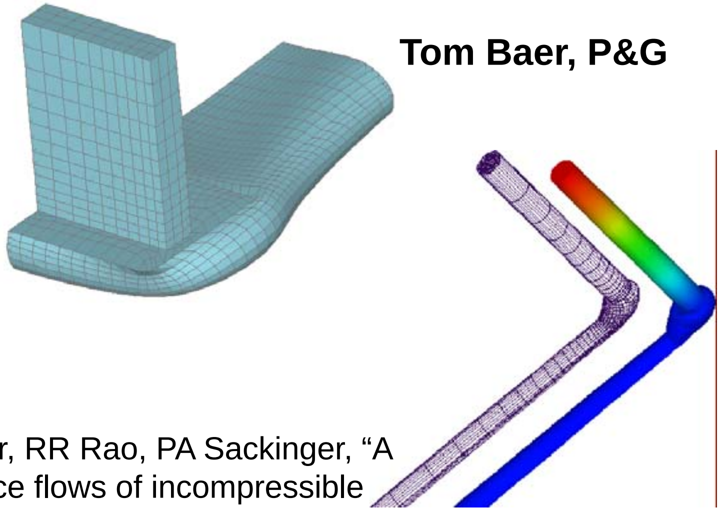


Scott Roberts, SNL





Tom Baer, P&G



RA Cairncross, PR Schunk, TA Baer, RR Rao, PA Sackinger, “A finite element method for free surface flows of incompressible fluids in three dimensions. Part I. Boundary fitted mesh motion,” IJNMF, 33, 375, 2000.

Evolving Level Set ϕ for Fluid Filling

- Given fluid velocity field, u(x,y,z), evolution on a fixed mesh is according to:

$$\frac{\partial \phi}{\partial t} + u \cdot \nabla \phi = 0$$

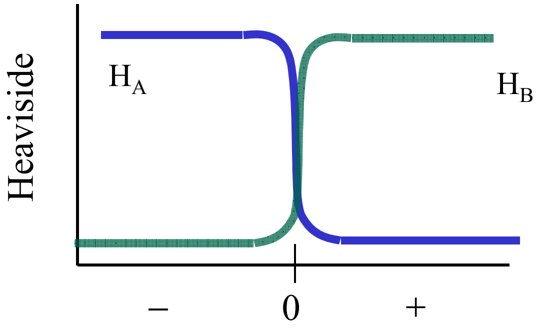
- Purely hyperbolic equation … fluid particles on ϕ(x,y,z) = 0 should stay on this contour indefinitely
  - Does not preserve ϕ(x,y,z) as a distance function
  - Introduces renormalization step.

- Equations are averaged depending on the level set, ϕ

$$H_A \rho_A \frac{Du}{Dt} + H_B \rho_B \frac{Du}{Dt} = -\nabla P + H_A \nabla \cdot (\mu_A \dot{\gamma}) + H_B \nabla \cdot (\mu_B \dot{\gamma}) + (H_A \rho_A + H_B \rho_B) g + I.T.,$$

$$H_A \frac{D\rho_A}{Dt} + H_B \frac{D\rho_B}{Dt} + (H_A \rho_A + H_B \rho_B) \nabla \cdot u = 0$$

$$H_A + H_B = 1$$



Finite Element Implementation

- **Approximate variables with trial function, e.g.**

$$u \approx \sum_{i=1}^{n} u_i N_i \quad v \approx \sum_{i=1}^{n} v_i N_i \quad w \approx \sum_{i=1}^{n} w_i N_i \quad p \approx \sum_{i=1}^{m} p_i N_i^{'}$$

- **Substitute into equations of motion, weight residual with shape function for Galerkin implementation**

$$Weighted\text{-}Residual = \int N_i R_i dV$$

- **Gaussian quadrature**
- **Solve discretized system**

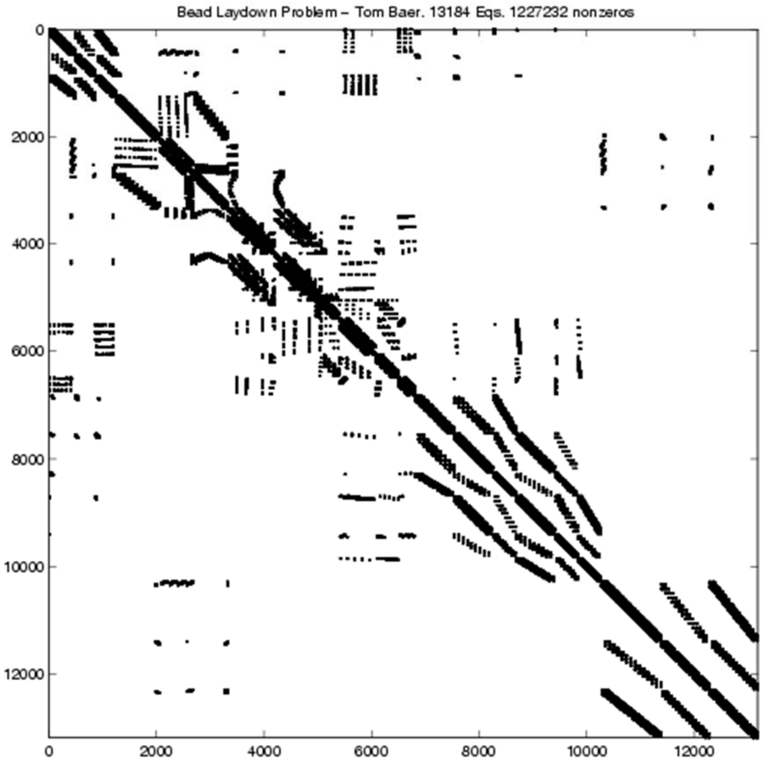
$$\underline{\underline{A}}\,\underline{x} = \underline{b}$$

- **Issues: Linear system solved with Krylov-Based iterative solvers => require stabilization**

Why Are 3D Free Surface Problems Hard?

$$\rho \frac{Du}{Dt} = -\nabla P + \mu \nabla^2 v + \rho g$$

$$\nabla \cdot u = 0$$



Typical problem graph for incompressible flow

- Formulation uses a coupled u-p solve with a decoupled level set solve
- Incompressibility constraint and distinguishing conditions and boundary conditions lead to non-diagonally dominant matrices
- In 2D, direct solver can be used with LBB elements
- In 3D, only Krylov-based iterative solvers are feasible
- Stabilization for the continuity equation is used to allow for equal order interpolation and improve the matrix condition number
- Stabilized methods that may work well on single phase flows, have difficulty handling the pressure jumps associated with the level set method
- Solution requires heavy duty preconditioner-solver pairing such as ILUT(1-3)/GMRES, which are not very scalable
- Mass loss issues must be ameliorated
  - Remediated via new boundary conditions, stabilization methods, renormalization, and time-stepping algorithm

SOME STABILIZATION METHODS FOR 3D COUPLED FLOWS

- **Pressure Stabilized Petrov-Galerkin Method (Q1/Q1) (PSPG) (Hughes et al. 1986)**

$$R_i^{c} = \int_D \phi^i \left[\nabla \cdot u\right] dV$$

$$+ \sum_{Elem} \int_D \tau_{pspg} \nabla \phi^i \cdot [\rho \frac{\partial u}{\partial t} + \rho (u - u_m) \cdot \nabla u + \nabla p - \boxed{\mu \nabla^2 u} - f\,] dV$$

- **Dohrman-Bochev Stabilization (Q1/Q1)(PSPP) (Dohrmann, and Bochev, 2004)**

$$R_i^{c} = \int_D \phi^i \left[\nabla \cdot u\right] dV + \sum_{Elem} \tau_{pspp} (\phi^i - \pi \phi^i)(p - \pi p) dV$$

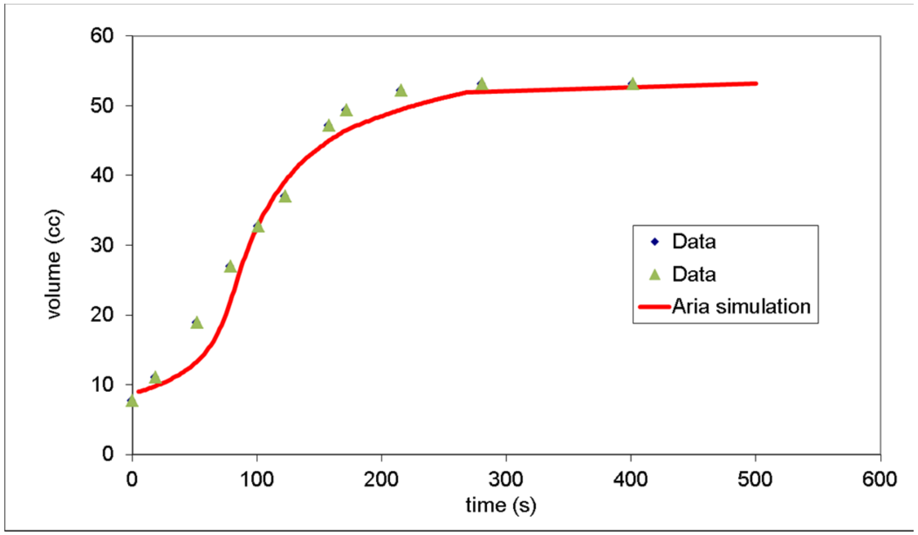
$$\pi p = \int_{V_e} p dV \Big/ \int_{V_e} dV$$

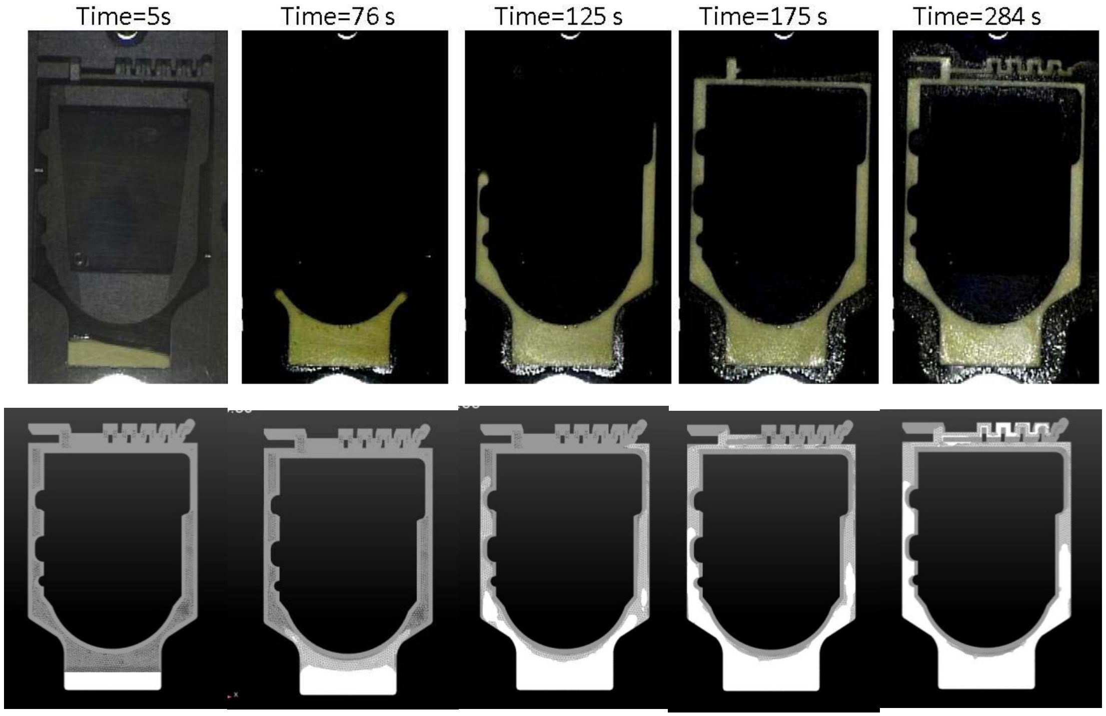
- **Dohrman-Bochev Stabilization on Transient Pressure (Q1/Q1)(PSPP_T)**

$$R_i^{c} = \int_D \phi^i \left[\nabla \cdot u\right] dV + \sum_{Elem} \tau_{pspp} (\phi^i - \pi \phi^i)(\frac{\partial p}{\partial t} - \pi \frac{\partial p}{\partial t}) dV$$

$$\pi \frac{\partial p}{\partial t} = \int_{V_e} \frac{\partial p}{\partial t} dV \Big/ \int_{V_e} dV$$

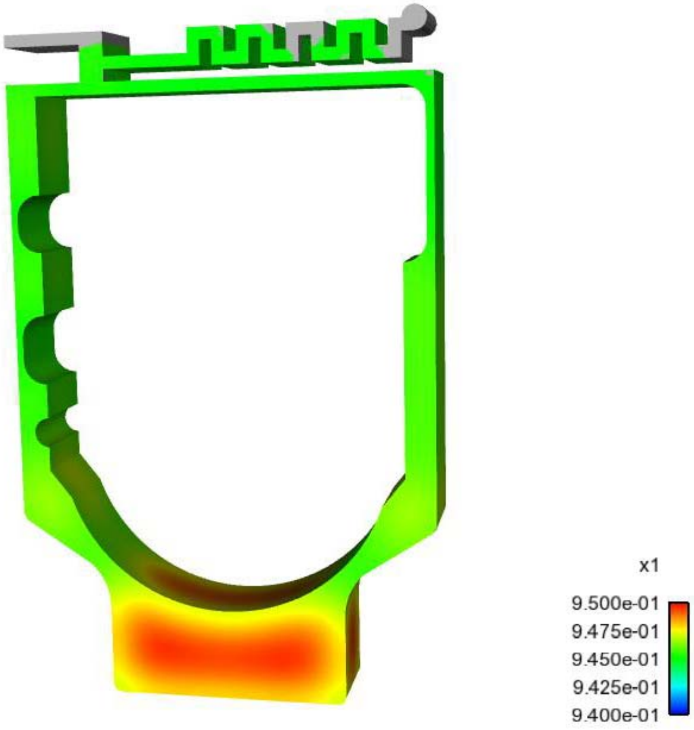
PMDI-4 Free Surface Validation Study

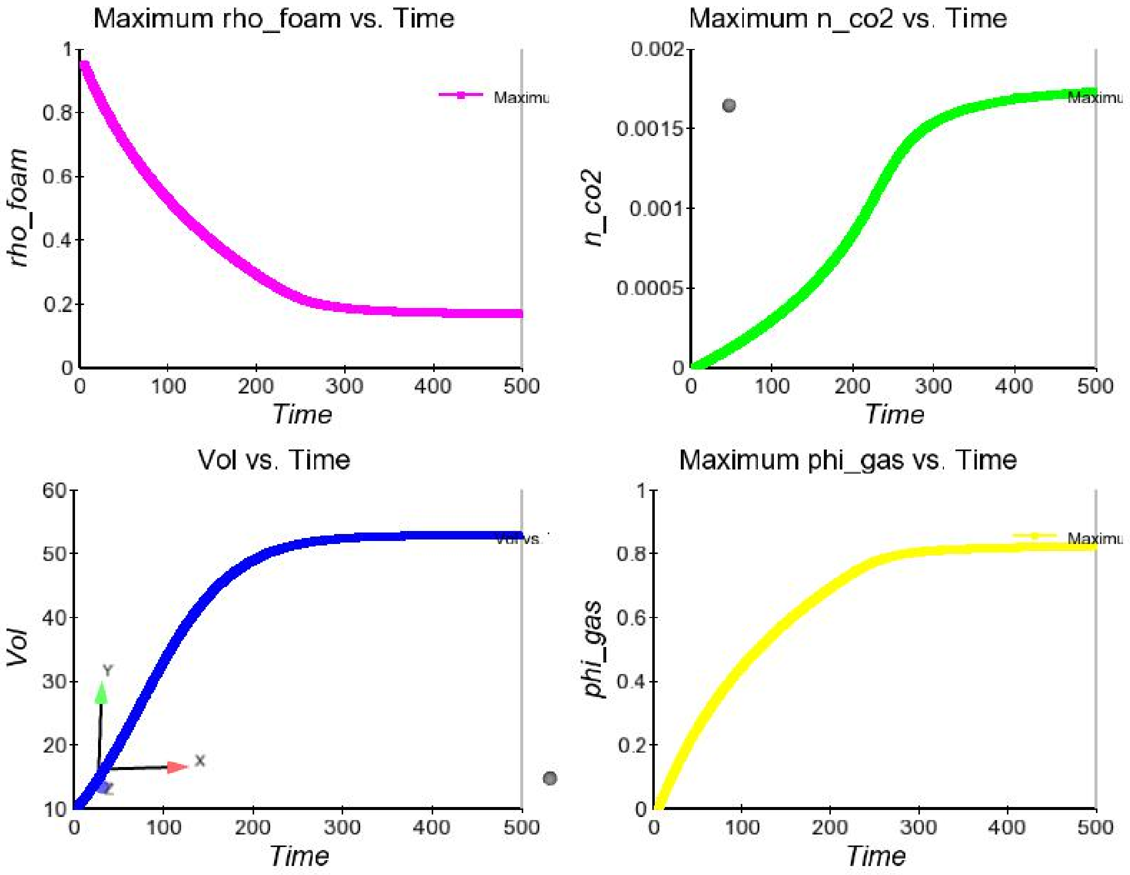




- Model tracks density change from foaming in full system
- But validation data show that model foams too slow and then too fast
- Current work:
  - Improve density model
  - Add a function to tie foam generation to gelation and vitrification

New Model Predicts Moles CO_2 and Density for Polyurethane Foams

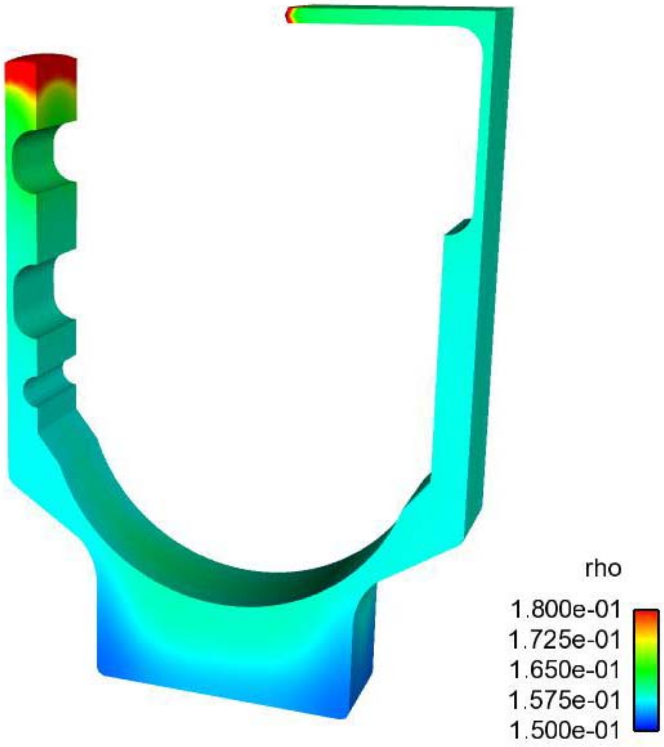




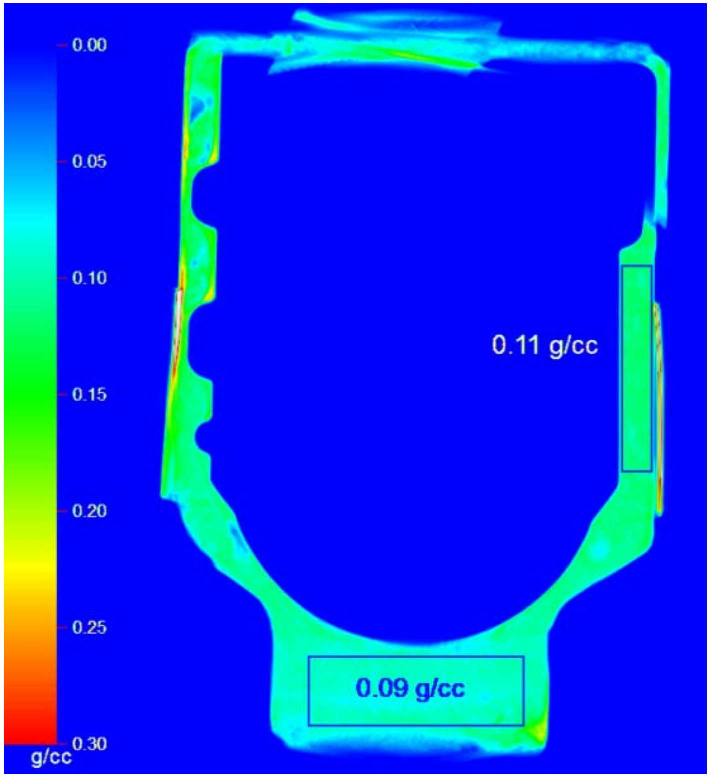
Modeling extent of reaction for CO_2 generation can give trends to help understand foam density variations

Density Gradients Occur in Polyurethane Foams

- X-ray CT of PMDI-4 part shows density gradients

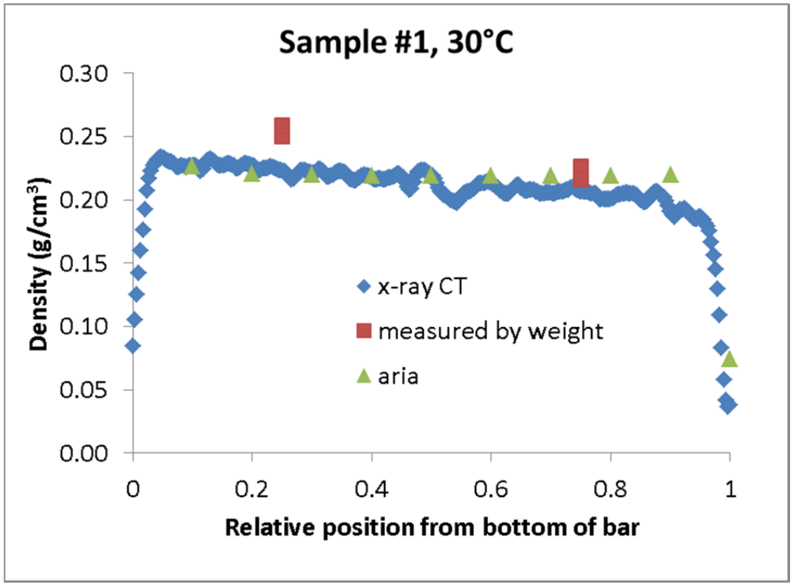


Modeling extent of reaction for CO_2 generation can give trends to help understand foam density variations

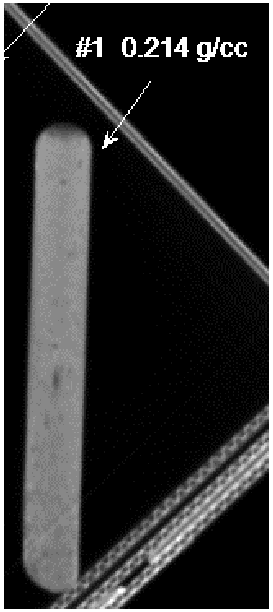


Experimental CT gives density gradients in artifact mold (CT courtesy of Kyle Thompson, SNL)

Structural Foam Density Predictions:



Density for PMDI-10 foam free rise at 30ºC : x-ray CT, weight measurement, and Sierra Aria run



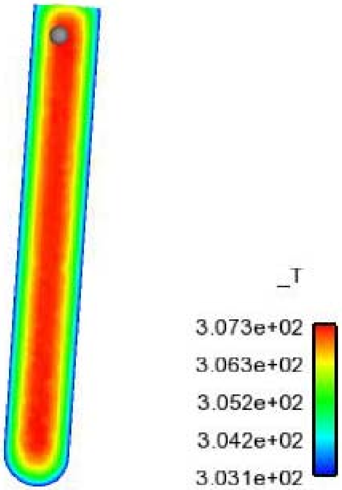
X-ray CT of PMDI-10 foam free rise at 30ºC

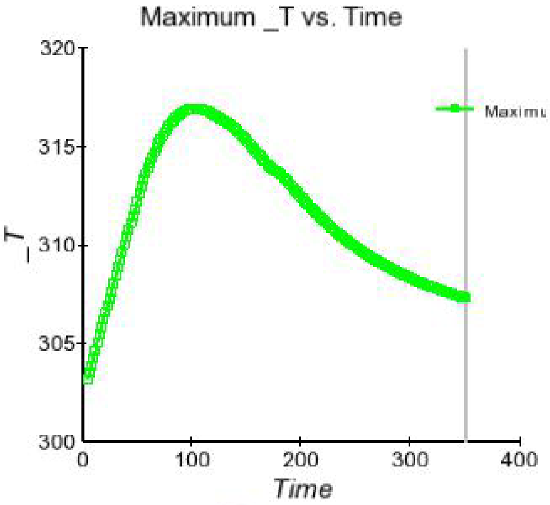
Structural mold filling demonstrates ability of the model to predict filling and density in complex geometries

Validation efforts showed areas for improvement

:

- Missing divergence term in energy equation
  - What form does the pressure dependence take for a foam, which is a mixture of incompressible liquid and compressible gas bubbles?
- Exotherm in thin geometry of 10ºC not seen in experiment



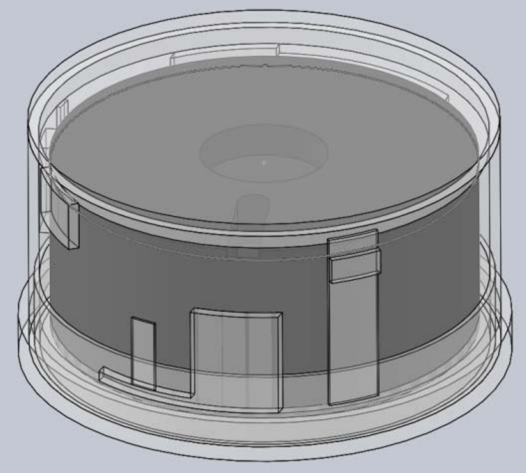


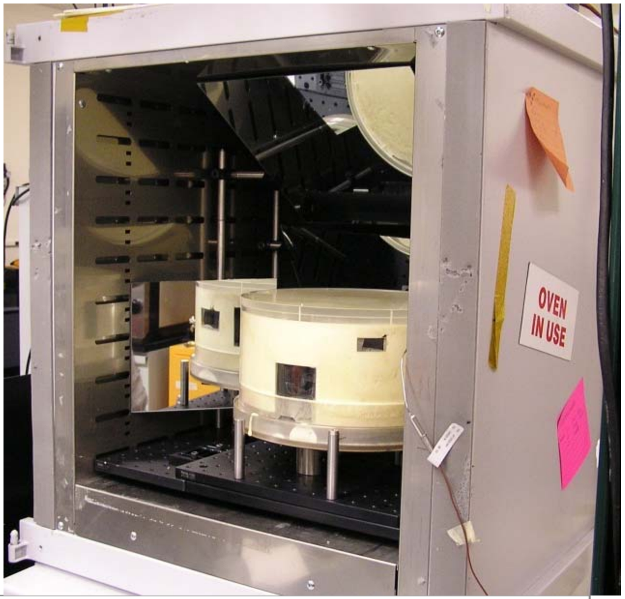
Exotherm causes 10ºC temperature rise not seen in experiment. However, temperature gradients shows that thermocouple placement is critical.

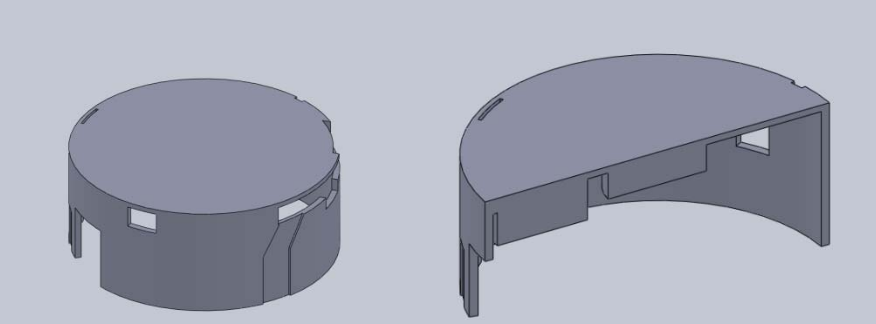
$$\rho C_p \frac{\partial T}{\partial t} + \rho C_p \mathbf{v} \bullet \nabla T = \nabla \bullet \left(k \nabla T \right) \boxed{- T(\partial P / \partial T)_P (\nabla \bullet \mathbf{v})} + S_{rxn}$$

Simplified Structural Support Validation Tests

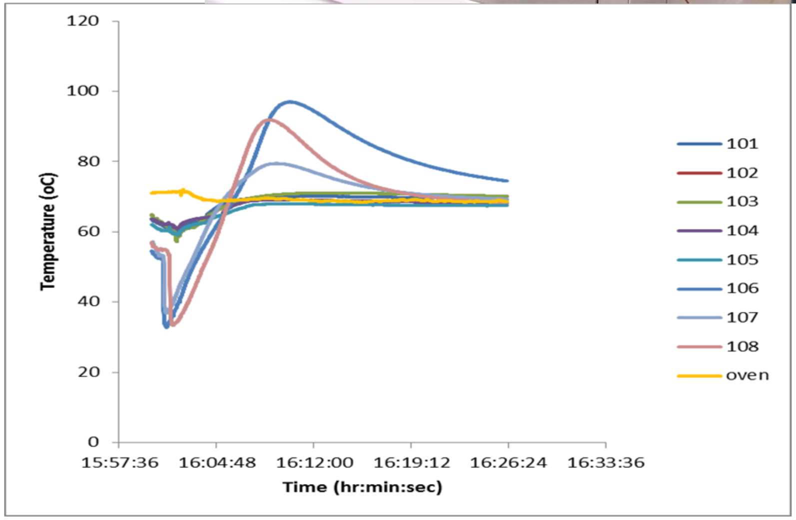
- Inspired by a legacy mold that had trouble filling
- KC gave us a solid model of the part; we inverted it to design a transparent mold
- Temperature instrumented with four camera views





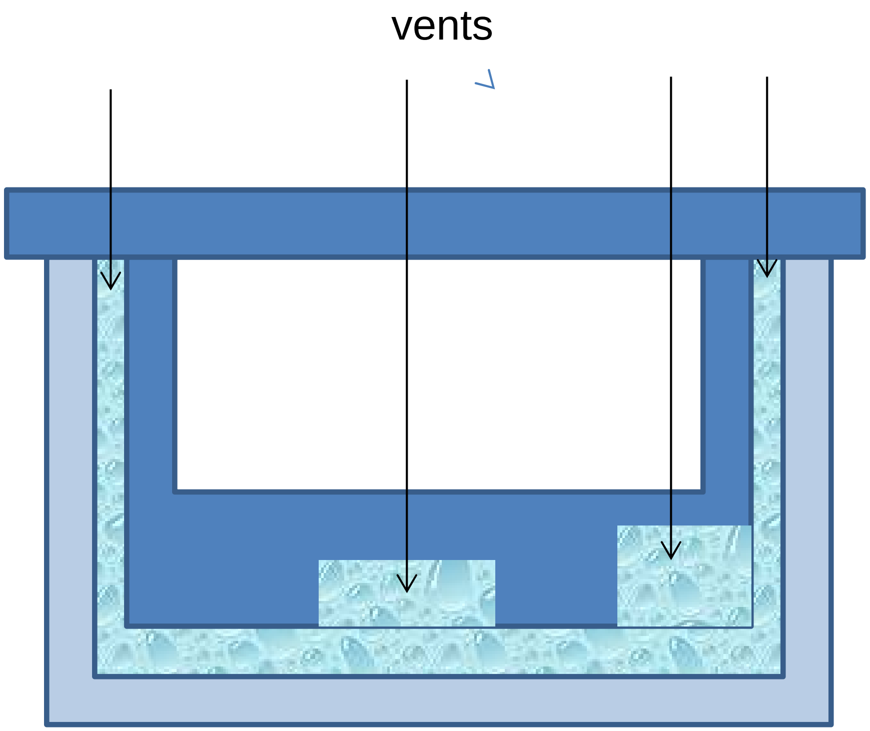


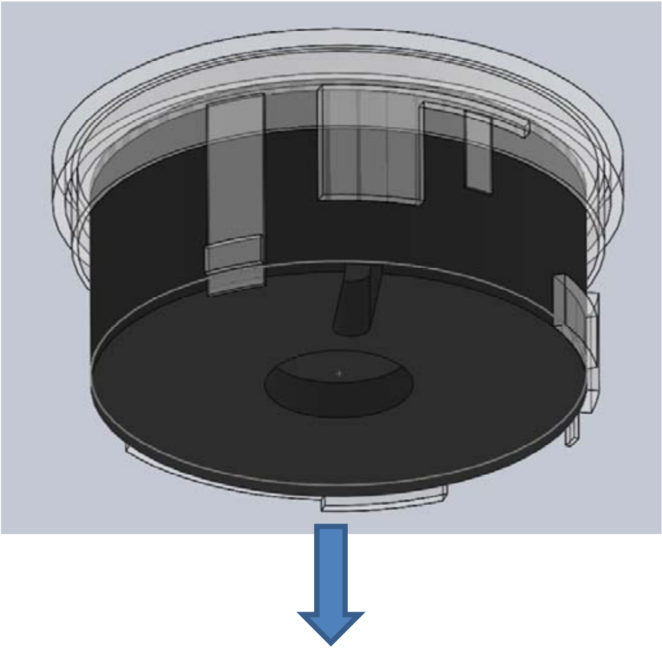
Simplified Part



Simplified Structural Support Mold Test 3

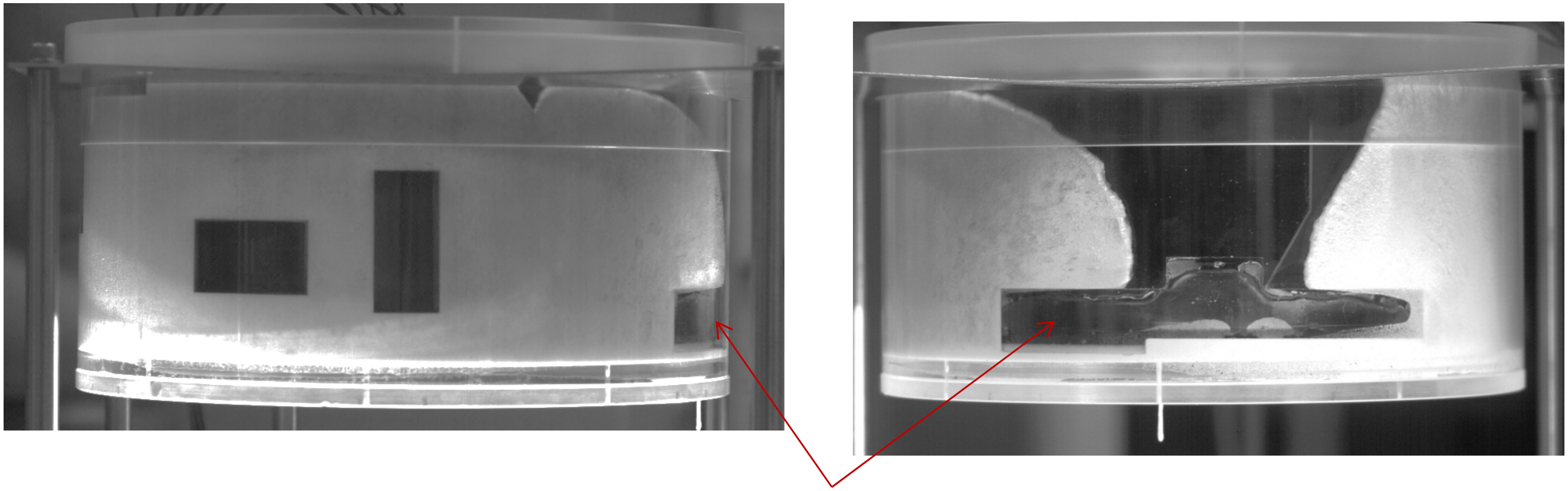
- Used 10 pcf free rise structural PMDI foam, filled to produce a 13 pcf part
- To speed up process and slow down foam reaction rates:
  - No preheats
  - Mixed 30 seconds instead of 1 minute
  - Pour all foam into one reservoir, the lid of the upside down part
- Temperature instrumented with four camera views





Push inside mold down into bowl that once was the lid

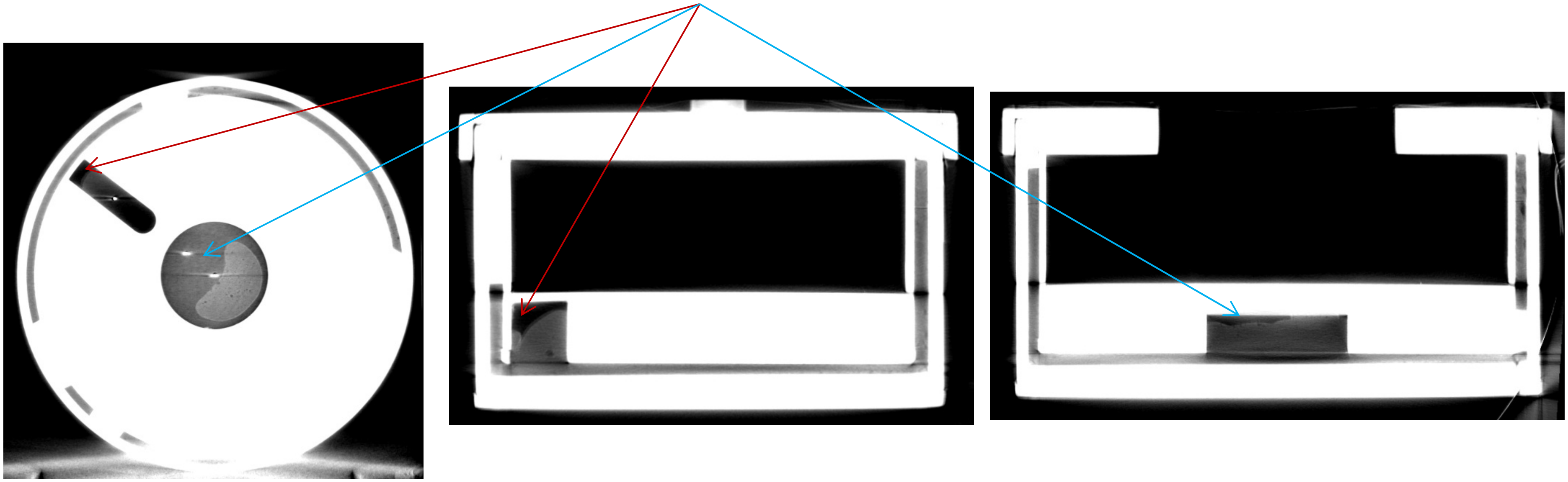
Last Place to Fill Now on Other Side of Largest Feature



Largest feature

Accidentally put in less foam than encapsulation test 1,
but reaction proceeded faster gelling foam before could finish rising

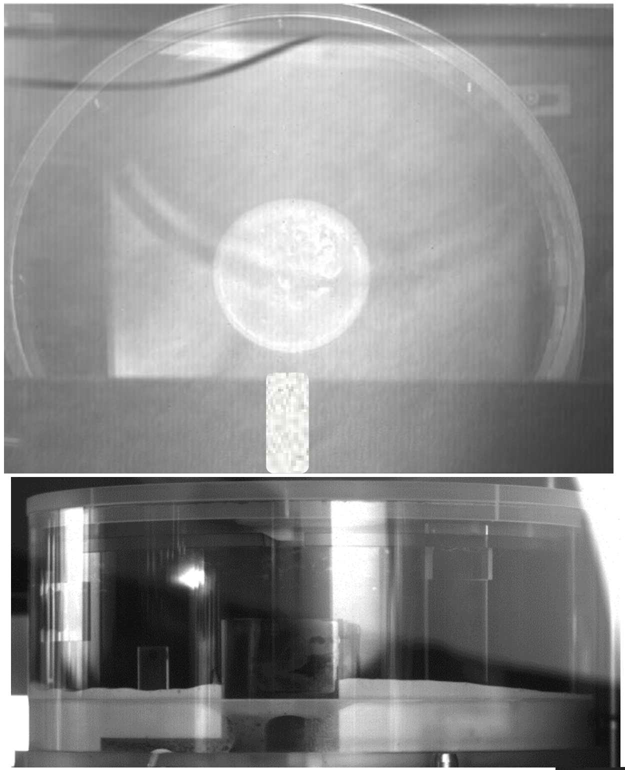
X-Ray CT Shows That Cavities Are Left with Voids



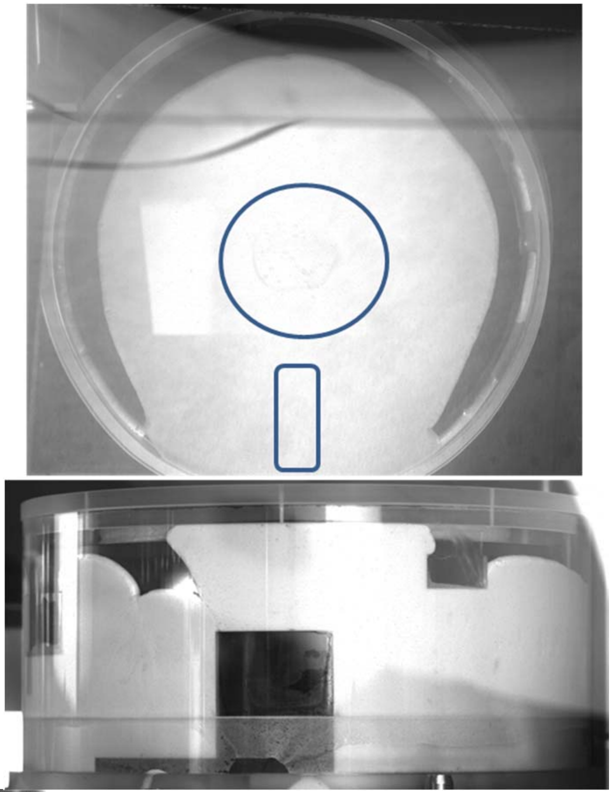
voids

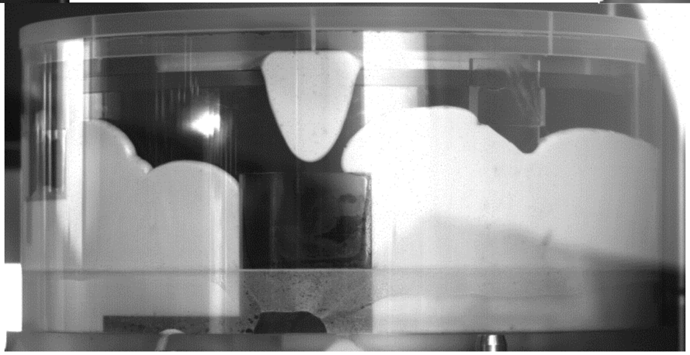
- Artifacts occur near large areas of plastic or metal (bright thermocouples)
- Imaging tricks and/or machining away the plastic mold will allow better images
- X-ray CT will also give us information on density gradients.

Filling Method Creates Knit Lines



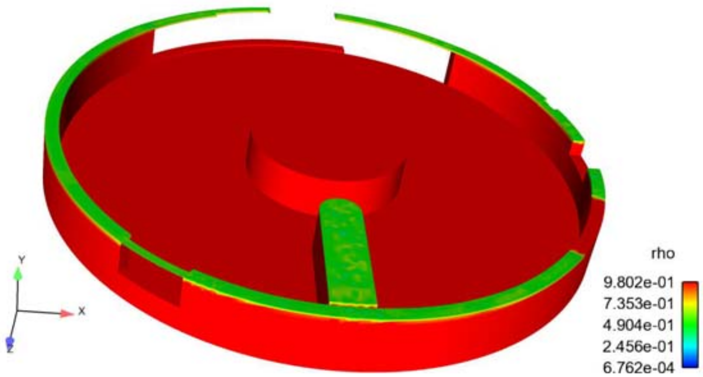
Foaming material is originally placed in top rectangular and cylindrical reservoirs and in bottom rim reservoir, to simulate legacy KC filling method



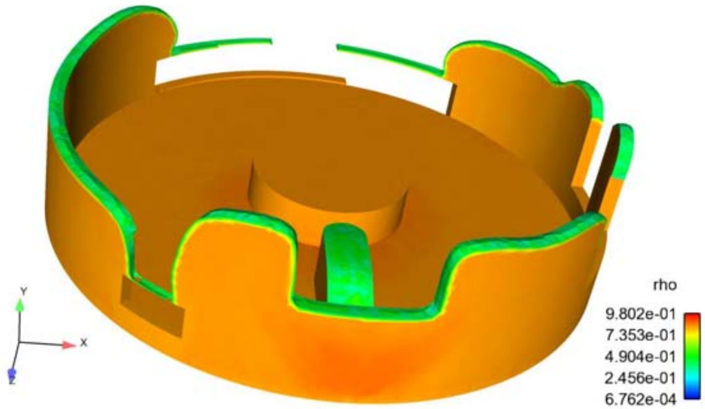


Filling and Density Gradients of a Structural Part Mockup

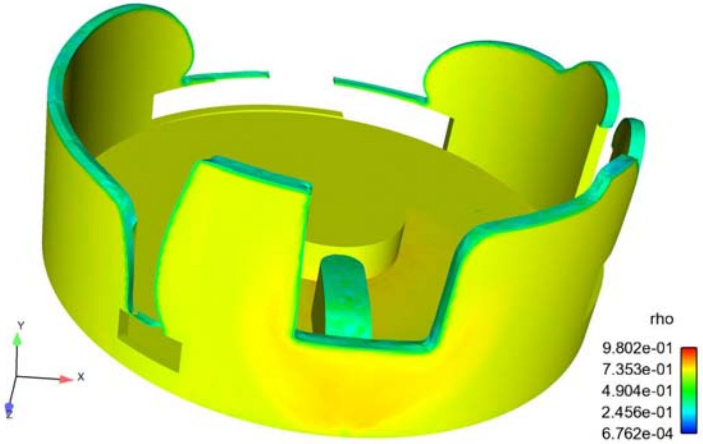
Time = 24.531



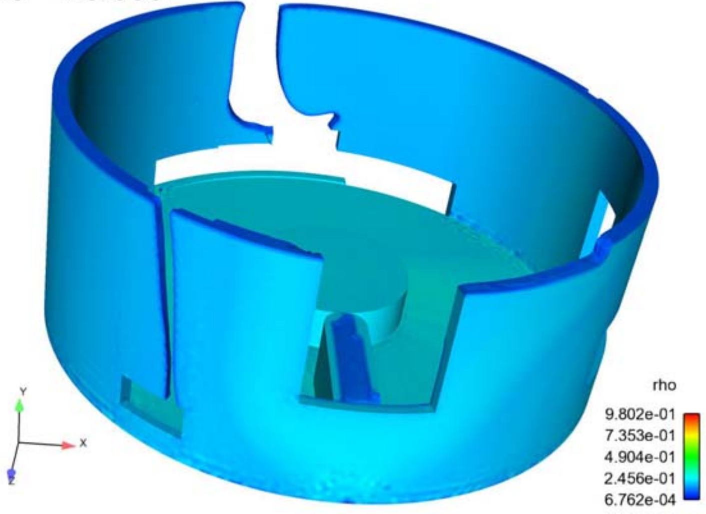
Time = 29.315



Time = 32.136



Time = 73.666



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)

$$\begin{aligned}
\underline{\underline{\sigma}} = {} & \left\{\mathrm{K_g}(T(t)) - K_\infty(T(t))\right\}\int_0^t ds\ \mathrm{f}_1\left(t^* - s^*\right)\frac{d\mathrm{I}_1}{ds}(s)\ \underline{\underline{\mathrm{I}}} \ - \ \left\{\mathrm{K_g}(T(t))\ \beta_g - K_\infty(T(t))\ \beta_\infty\right\}\int_0^t ds\ \mathrm{f}_1\left(t^* - s^*\right)\frac{dx}{ds}(s)\ \underline{\underline{\mathrm{I}}} \\
& - \left\{\mathrm{K_g}(T(t))\delta_g(T(t)) - K_\infty(T(t))\delta_\infty(T(t))\right\}\int_0^t ds\ \mathrm{f}_1\left(t^* - s^*\right)\frac{dT}{ds}(s)\ \underline{\underline{\mathrm{I}}} \\
& + \ 2\left\{G_\mathrm{g}(T(t), x(t)) - G_\infty(T(t), x(t))\right\}\ \int_0^t ds\ \mathrm{f}_2\left(t^* - s^*\right)\ \frac{d\underline{\underline{\varepsilon}}_{dev}}{ds}(s) \\
& + \left\{K_\infty(T(t))I_1 - K_\infty(T(t))\delta_\infty(T(t))\left[\mathrm{T(t)} - \mathrm{T_{sf}}\right] - K_\infty(T(t))\ \beta_\infty\left[\mathrm{x(t)} - \mathrm{x_{sf}}\right]\right\}\ \underline{\underline{\mathrm{I}}} \ + \ 2\int_0^t G_\infty(s)\ \frac{d\underline{\underline{\varepsilon}}_{dev}}{ds}\,ds
\end{aligned}$$

Material Clock

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

Density Scaling

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

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

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

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

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

Glass Transition Evolution

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

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

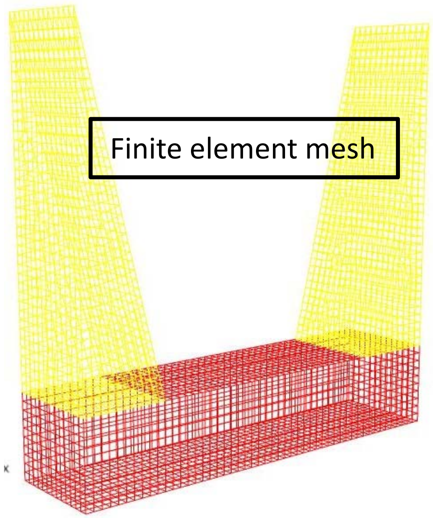
Shear Modulus

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

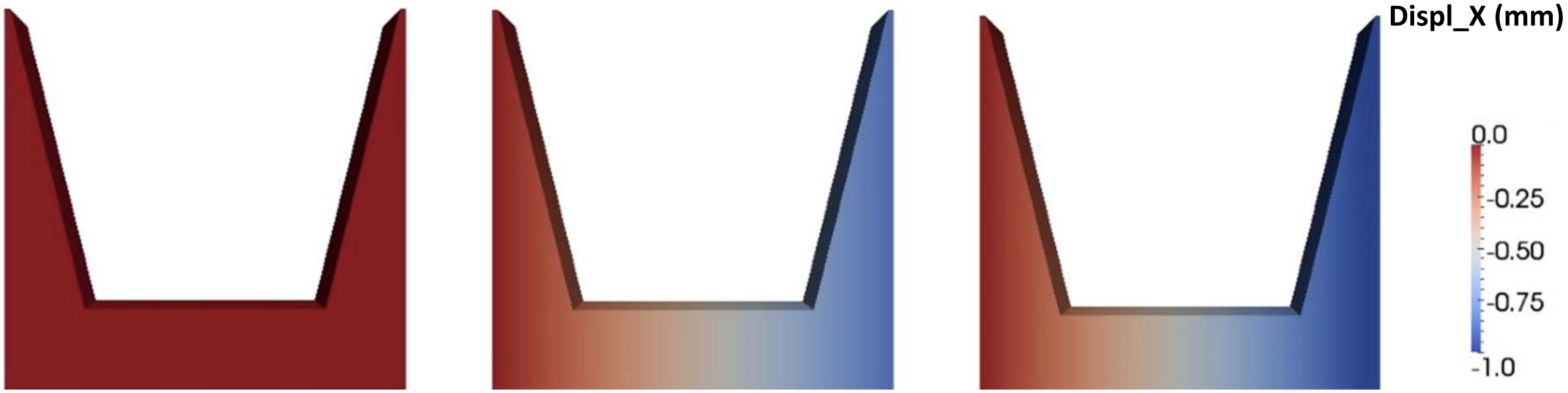
$$G_\infty(T) = \left\{ G_{\infty ref} + \frac{\partial G_\infty}{\partial T}(T - T_{ref}) \right\} \left[\frac{\mathrm{x}^{\mathrm{m}} - x_g^m}{x_{ref}^m - x_g^m} \right]^n$$

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

Homogeneous Material Properties Give Only an Isotropic Response



- **The foam is cooled in the mold and then released**
- **It is then aged for 1 year under traction free conditions.**
- **The foam deforms spherically due to viscoelasticity; the shape does not distort.**


Initial State

Post Release
1 hour

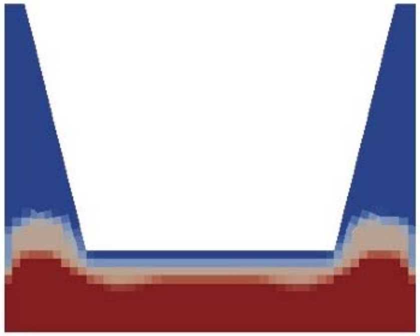
Post Release
1 year

Scenario in which the solid foam is uniform after curing.

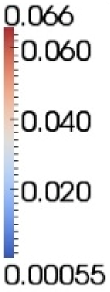
In the Real Manufacturing Process, Gradients in Density and Cure Exist

- **Density variations develop during foaming and polymerization**
- **Foam volume generation is locked in at gelation, though gas production can lead to bubble pressurization**
- **Polymerization is approximately locked in a vitrification**

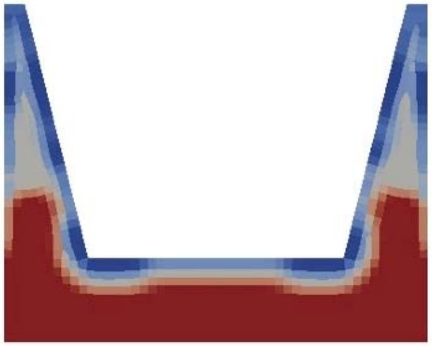
Foaming after 0.25 hour



Density (g cm^{-3})

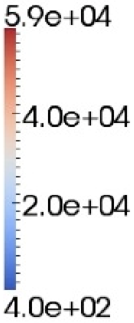


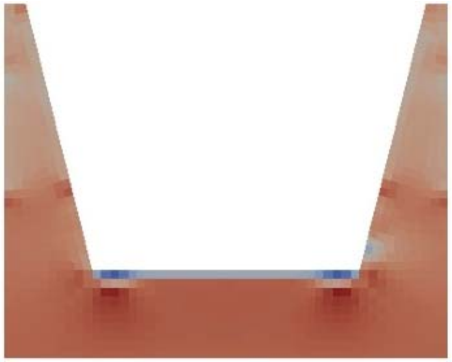
Gelation at 0.5 hour



Post Cool Down
Immediately Pre-Release

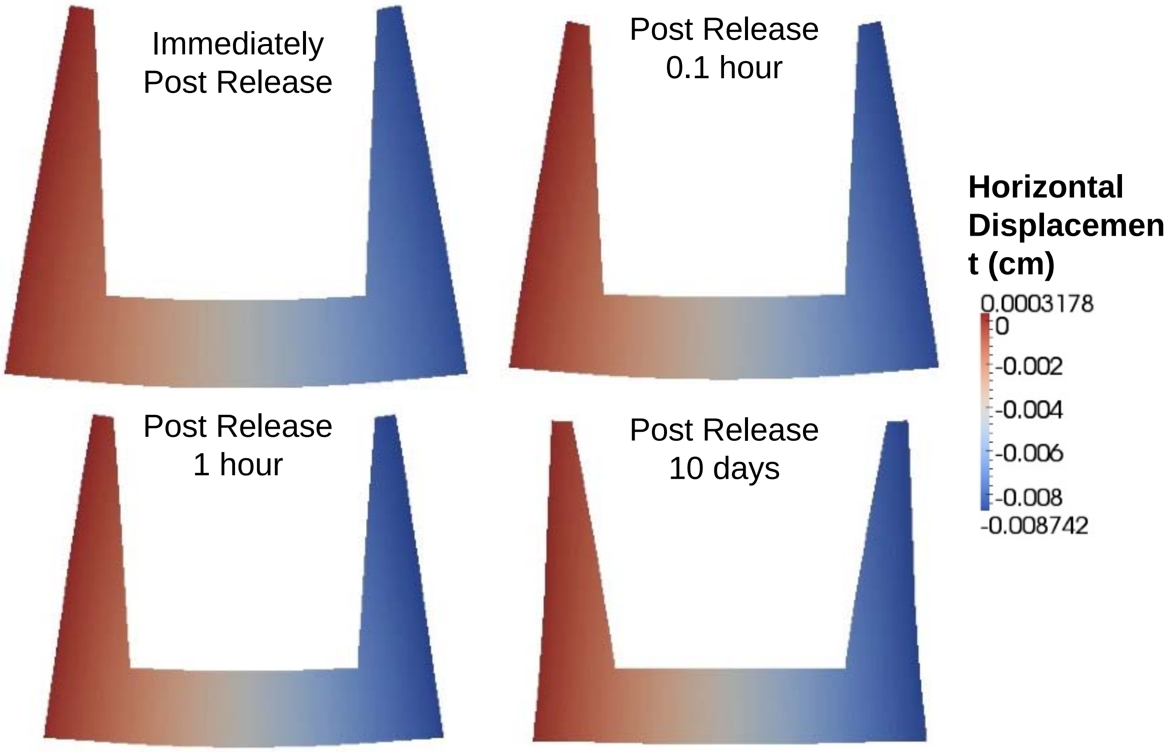
Stress (dyne cm^{-2})





Residual stresses build due to variations in material properties and temperature

After Mold Release, Residual Stresses Relax Leading to Shape Change



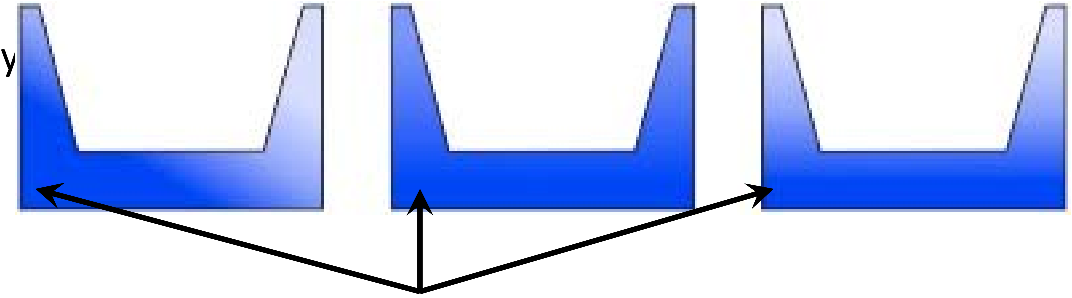
After release, residual stresses redistribute and relax causing the structure to distort. Note, these displacements have been amplified by 1000 to show the shape change. Simulated warping displacements are ~10 microns

Modeling the Sensitivity of Density on Manufacturing Conditions

Wide Array of Manufacturing Inputs

- Mixing Methods
- Formulation stoichiometry
- Injection Direction
- Applied Mold Temperature History
- Humidity

Different Manufacturing Schedules May
Generate Density and State of Cure Variations



Common Resin Injection Site
Different Mold Temperatures
Different Curing Times

→ Filling/Curing Variations

We Can Determine Which Processing Parameters Cause the Greatest Variation in Foam Density and Cure

Modeling the Sensitivity of Shape Stability on Predicted Density and Cure

Carry out sensitivity study for parameters to determine the most important to measure first

Given Different Density and State of Cure Variations Initial Conditions, How Does the VE Response Change?

Difficult to measure all input parameters from the model

Residual Stresses Drive Time Dependent Shape Change Dependent on Property Variations

We Can Determine Which Processing Parameters Cause the Greatest Warping in Foamed Components

Thoughts on Uncertainty Quantification of the Shape Stability Based on the Manufacturing Process

Uncertainty in Experimental Data:

- Initial density uncertain since it foams during mixing and injections
- Local volume of gas produced => experiment measures average gas production from macroscopic volume
- Variations in spatial distributions of temperature, pressure, gas volume fraction, and degree of polymerization assumed to be minimal, though temporal changes are monitored

Assign Uncertainties to Process Variables in the Mold

- Temperature, pressure, and extent of reaction distribution

Propagate parameter uncertainty to give bounds on maximum variation

- Define validation/UQ metric, possibly final density and density variation
- Sensitivity study to determine most important parameters

Propagate error from density distribution into structural properties

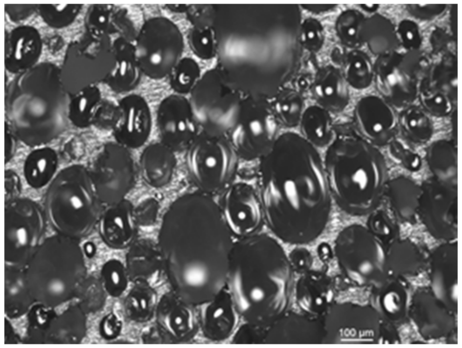
- Final warpage predictions will depend on both experimental uncertainties and uncertainty for initial conditions from density model
- Determining all necessary parameters for NLVE model is difficult
- Use maximum displacement as validation/UQ metric for structural response

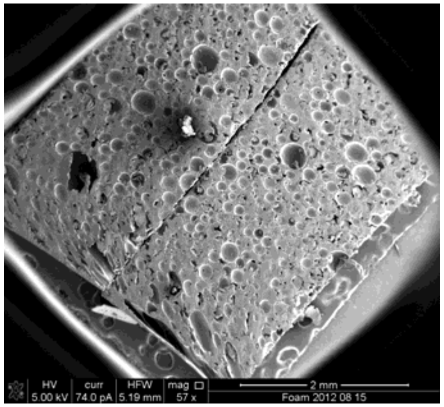
Coupled mechanics add complexity to uncertainty quantification

Model Form Uncertainty: Missing Physics in the Model

- Homogenized model ignores localized effects of bubbles and bubble-scale interactions
  - surface tension, creaming, drainage, coalescence, coarsening, migration
  - Bubble pressurization, deformation, and rupture
  - Cure shrinkage and thermal stresses in bubbly polymers
- Accurate slip coefficients
- Model insensitive to viscosity – how do we include this effect?
- Evolving fluid viscoelasticity
- Fluid and gas compressibility
- Effect of vitrification on polymerization kinetics
- Numerical Uncertainty: Effect of mesh refinement on density variation, level set length-scale, etc

SEM of foam showing polydispersity





Bubble at walls are elongated and show coarsening

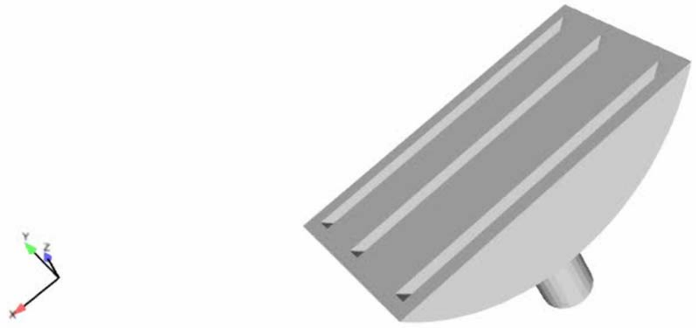
Hierarchy of Model Fidelity

- 0th order model → Arrows
- 1st order model → Qualitative results, trends, timescale
- 2nd Order Model → Design, void size, density trends
-
-
- Nth Order Model → Fully predictive solutions

Model maturity must be obtained through an iterative V&V process, before UQ can be truly meaningful

Conclusions and Future Work

- **Current model is adequate for production calculation**
    - Determining metering, initial placement, voids, gate, and vent location
    - Investigate encapsulation of new geometries of interest
    - Improve density predictions and conduct validation in more complex geometries
    - The current model is "first order." We are now trying to include secondary effects to make the model more predictive
- **Model uncertainty is still one of the largest areas of uncertainty**
    - Key sub-models such as gas generation and polymerization
    - Effect of pressurization and temperature still must be investigated
    - Air is too viscous and leaves unphysical voids
- **Next steps**
    - Bubble-scale modeling to include gelation and gas pressure in density model to make it more predictive
    - Drainage/creaming term could help make gradient larger
    - Full fluid-thermal-structural response for a complex geometry



Computational Modeling of Filling of Complex Mold