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Models and Experiments to Understand Physically Blown Foams

Rekha Rao, Lisa Mondy, Thomas Baer, Doug Adolf, Edward Russick, Anne Grillet, Ray O. Cote, Jeremy Lechman, Andy Kraynik

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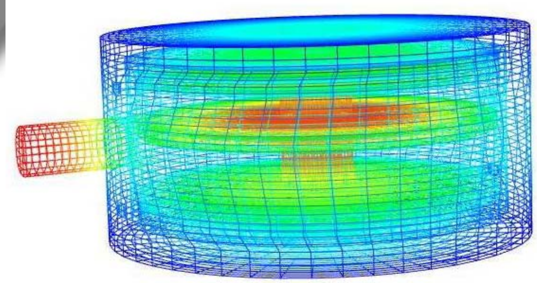
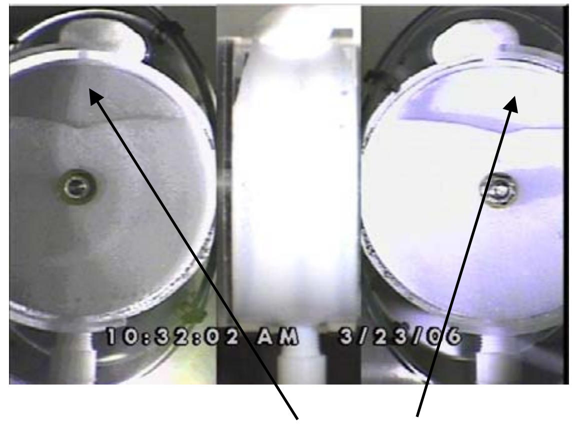
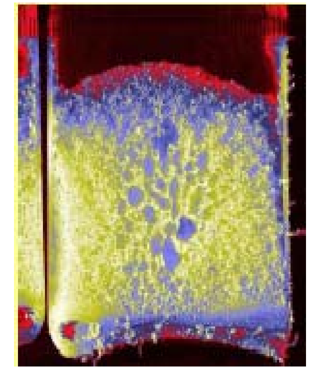
Foam Processing





Flow visualization shows voids



NMR imaging shows coarse microstructure (Altobelli, 2006)

Problem Description:

•Many electronic components are encapsulated with blown foams
•Foam materials critical for structural support and shock/vibration isolation
•Foaming can be unpredictable leading to unacceptable voids
•Inhomogeneities in foam material can lead to property variations & potential structural issues

Technical Approach/Challenges:

Coupled Computational Modeling

- Model development closely linked to experimental work
- Kinetics
- Rheology
- Blowing agent transport
- Thermal modeling
- Fluid mechanics
- Free surface flow
- Microscale and mesoscale modeling
- Validation experiments

Foam of Interest is Physically Blown

Vision: Develop a continuum model with volume source terms, and include relevant physics in these terms. Single phase, homogenized model

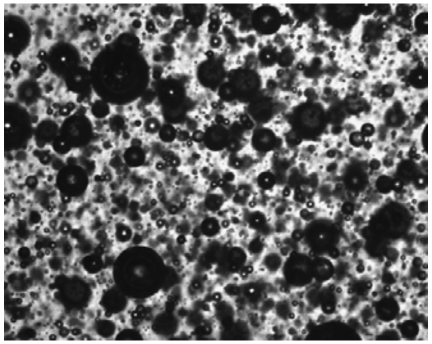
Process

- Two part epoxy, starts as an emulsion
  - Part B (shaken to distribute components)
    - Cabosil M-5 (particulate for nucleation sites)
    - curing agent
    - surfactant
    - FC-72 Fluorinert (blowing agent immiscible with curing agent)
  - Mixed with Part A, the resin
- Foam is blown by heating
  - 65^{o}C oven (FC-72 boils at 53^{o}C)

Bubbles in a soft drink nucleate homogenously, responding to a decrease in pressure

What we need to know

- Reaction kinetics, thermal properties, rheology of continuous phase, etc
- Nucleation mechanism
- Growth stage physics
  - How much blowing agent is used and how much lost?
  - Emulsion/foam microstructure
- Foam properties
  - Heat transfer & rheology
  - Density & bubble size
  - Wetting/slip at walls



Epoxy foam starts out as an emulsion and probably nucleates heterogeneously

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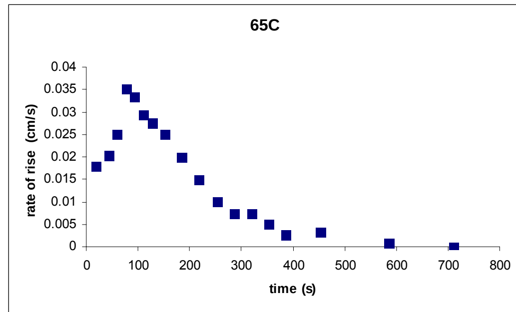
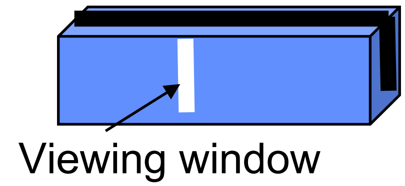
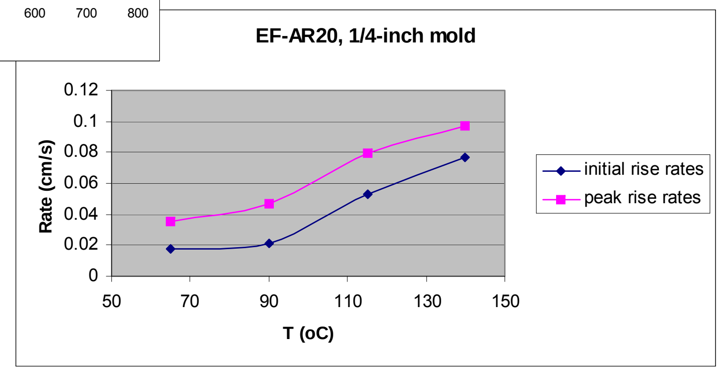
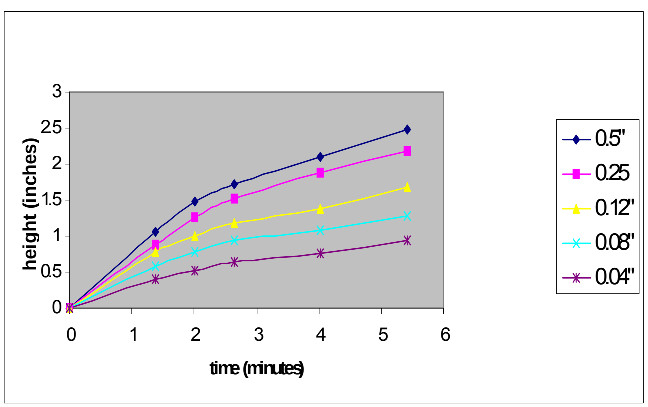
Foam Rise Experiments

- Foam expansion in narrow (1/4") slots
- Foam rise velocity increases over first minute or so, then decreases because gas is used up and/or viscosity of polymerizing resin increases
- Rise rate is dependent on temperature
- Rise rate is dependent on channel size in simple geometry
- Interplay of these effects in a complex geometry not obvious without modeling (see next slide)









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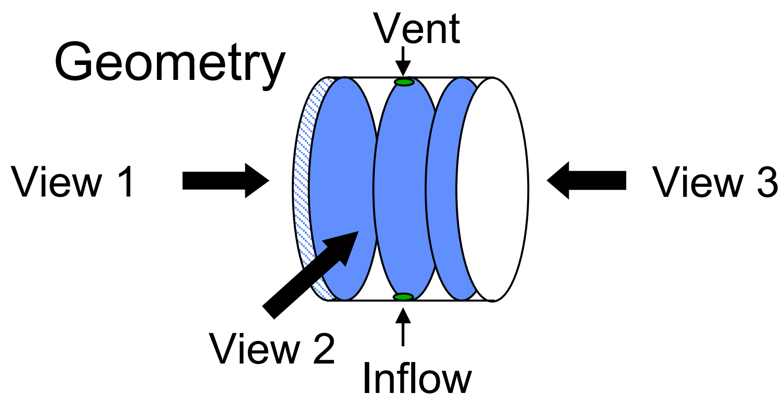
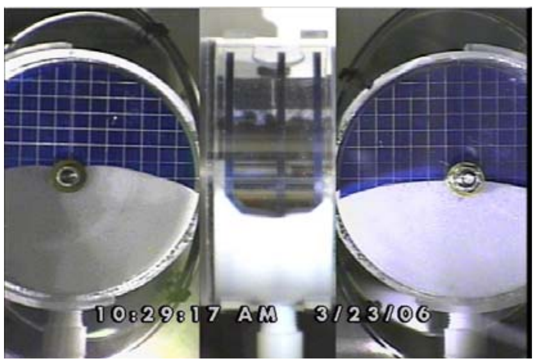
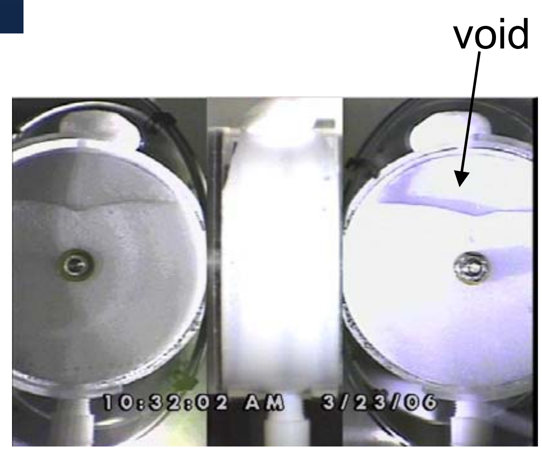
Foam Rise Experiments in More Complex Geometry

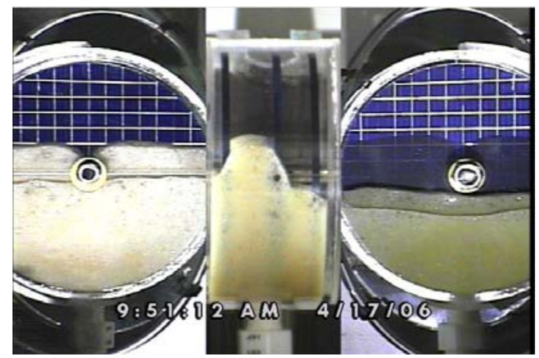




Early: unlike in simple geometry experiments, epoxy foam (EF-AR08) fills *faster* in the *narrow* gaps between plates.



A few minutes later: foam speeds up in the big gaps and slows in the narrow ones.



Foam with different epoxy, but same blowing agent does not complete fill.

Heat transfer from oven critical.
Competing effects → models needed.

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Current Continuum Blown Foam Model

Momentum: $\frac{\partial}{\partial t}(\rho_f \mathbf{v}) = -\nabla \bullet (\rho_f \mathbf{vv}) - \nabla p + \nabla \bullet (\mu_f (\nabla \mathbf{v} + \nabla \mathbf{v}^t)) - \lambda \nabla \bullet (\nabla \bullet \mathbf{v}) + \rho_f \mathbf{g}$

Dilatational viscosity, $\lambda = \frac{4}{3}\mu_0 \frac{(\phi_0 - \phi - 1)}{\phi_0 - \phi}$

Continuity: $\nabla \bullet \mathbf{v} = -\frac{1}{\rho_f}(\frac{\partial \rho_f}{\partial t} + \mathbf{v} \bullet \nabla \rho_f)$

Energy:

$$\frac{\partial(\rho_f C_{pf} T)}{\partial t} + v \bullet \nabla(\rho_f C_{pf} T) + \rho_f C_{pf} T(\nabla \bullet v) = \nabla \bullet (k_f \nabla T) + \rho_f (1-\phi)\Delta H_{rxn} \frac{\partial \xi}{\partial t} - \rho_f \lambda_{evap} \frac{\partial \phi}{\partial t}$$

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

Liquid phase volume fraction of blowing agent: rate dependent model

$$\frac{\partial x}{\partial t} = kx \qquad T \geq T_{boiling} \qquad \phi = \frac{\rho_f}{\rho_{fluorinert}} x_{fluorinert}$$

Density: $\rho_f = [(x_0 - x)\frac{RT}{pM} + (1 - x_0)\frac{1}{\rho_{epoxy}} + \frac{x}{\rho_{flourinert}}]^{-1}$

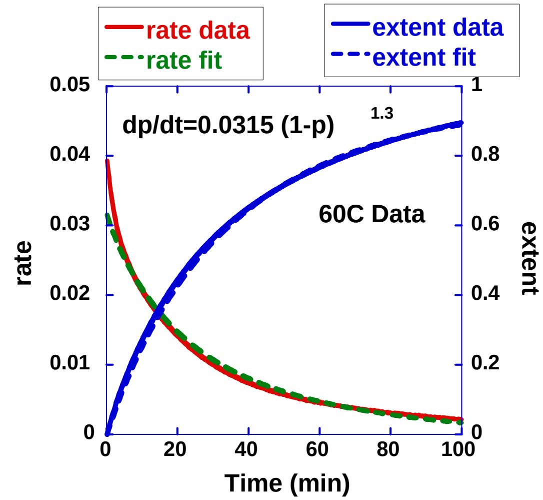
Viscosity: $\mu = \mu_0 \exp(\frac{\phi_0 - \phi}{1 - \phi_0 + \phi}), where \mu_0 = \mu_0^0 \exp(\frac{E_\mu}{RT})(\frac{\xi_c^{\,2} - \xi^2}{\xi_c^2})^{-4/3}$

- •Model strives to compute local density and viscosity gradients.
- •Must couple these complex equations with a method to locate the free surface over time
- •New model under development based on cavitation theory
- • Reference: Seo and Youn,Polymer, 2005; Marciano et al., Poly. Eng. Sci, 1986;

Reaction Kinetics and Rheology for Continuous Phase Determined Experimentally

- Reaction kinetics for foam determined by differential scanning calorimetry
- Polymerization of epoxy material follows condensation chemistry
- Reaction is exothermic (ΔH_{rxn} = 250 J/g)
- Heat produced drives the reaction faster
- k=1.145e5 ΔE=10kcal/mol, n=1.3

$$\frac{d\xi}{dt} = ke^{\Delta E/RT}(1-\xi)^n$$

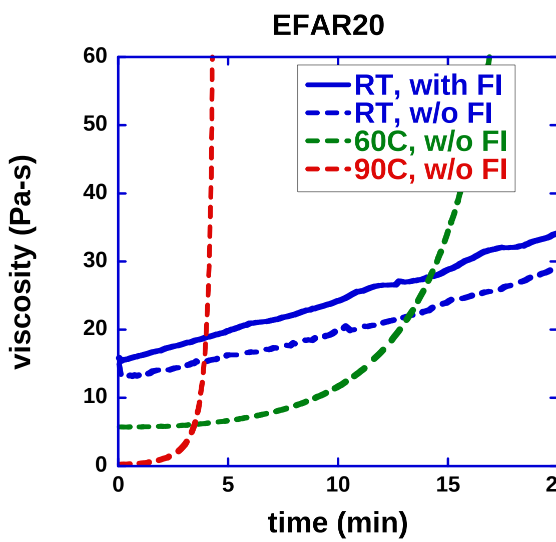


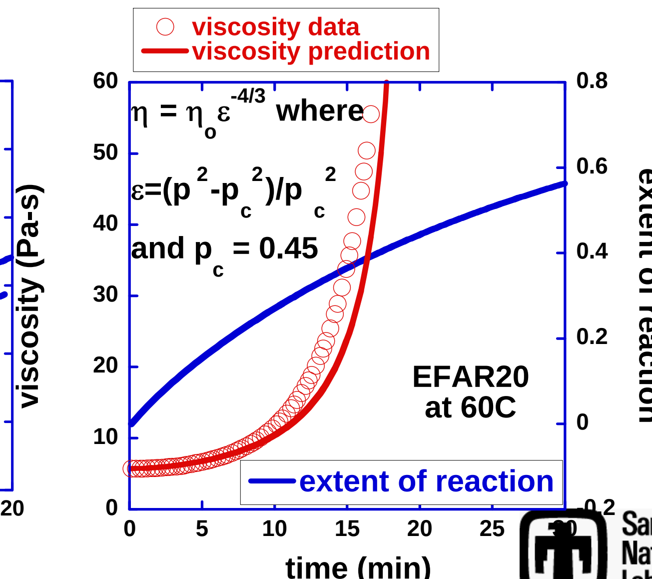
- Viscosity increases with cure
- Correlate viscosity with extent of reaction

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

- Viscosity is a function of void fraction

$$\mu = \mu_0 \exp(\frac{\phi_0 - \phi}{1 - \phi_0 + \phi})$$





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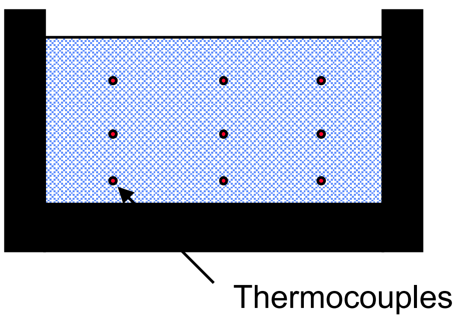
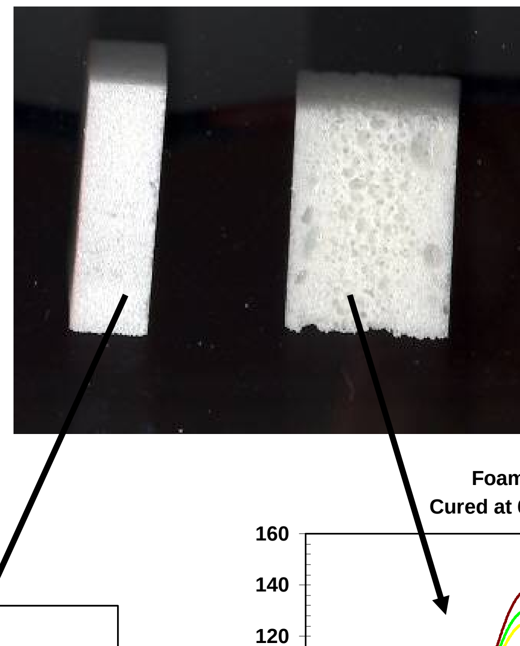
Foam Rise Experiment Offers Guidance for Manufacturing as well as Validation for Models

Schematic of Experiment

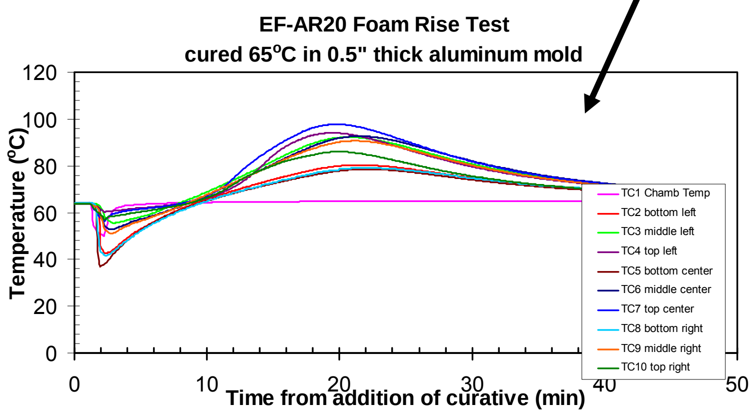


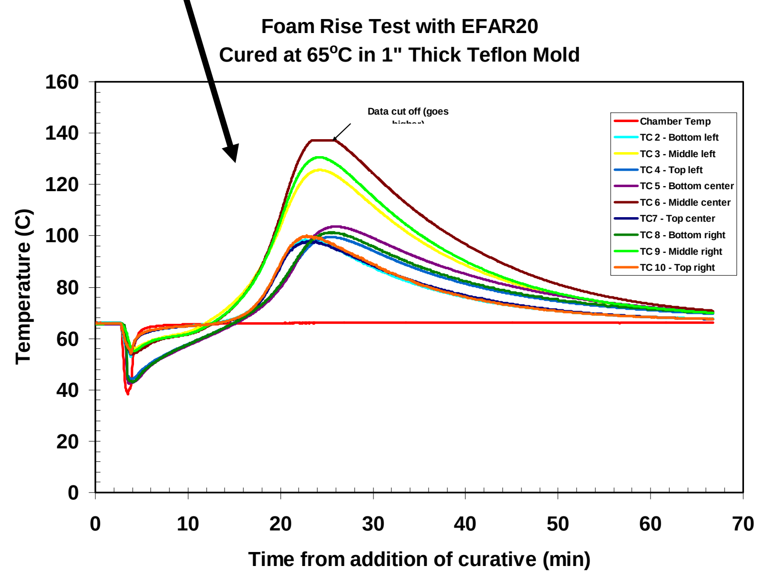
Vary thickness (out of the plane of the paper)

Photo of cured foam section from middle
Left ½ inch thick, Right 1 inch thick



- Thicker sections exotherm and produce coarser, lower density, more nonuniform foams





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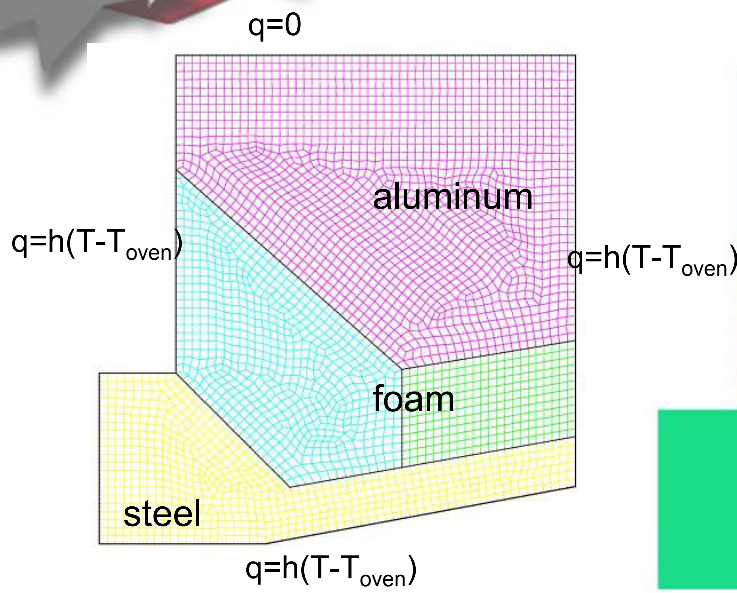
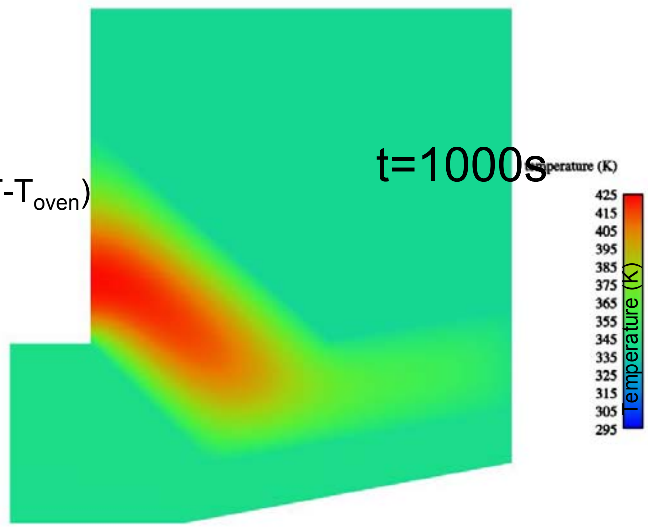
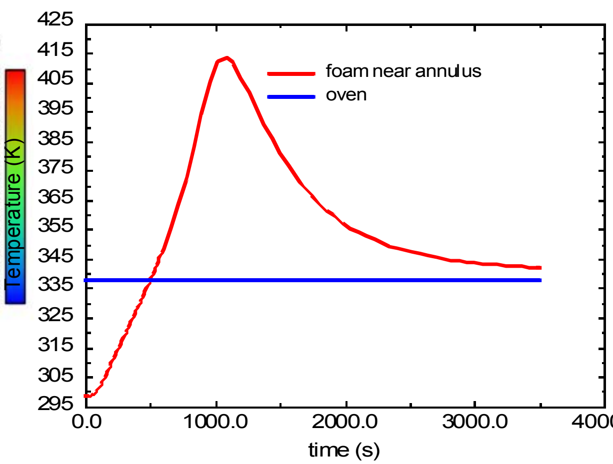
Thermal/Curing Analysis Of Foam Reaction



Axisymmetric mesh (Terry Hinnerichs)



Foam temperature after 1000s



Validation experiment (Chris O'Gorman)

- Foam initially at room temperature and is inserted into a mold preheated to the oven temperature
- Foam heats up to oven temperature, exotherms, and cools back down to oven temperature
- Transient thermal analysis with reaction kinetics show significant exotherm
- Foam heats up 80^{o}C higher than oven temperature
- Highest temperatures are seen 18 minutes after insertion into oven
- Experiment shows large bubbles in hottest regions

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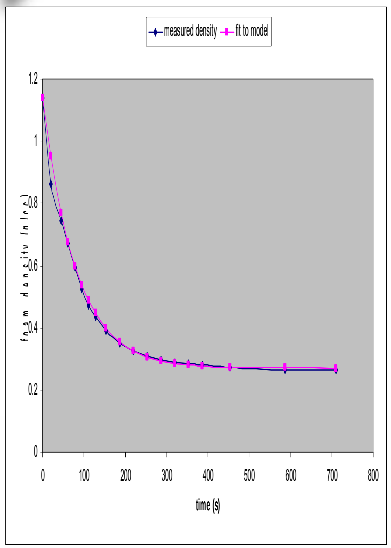
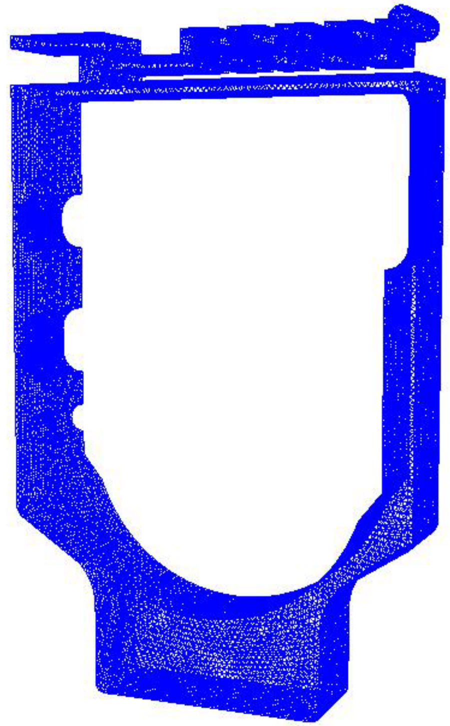
Variable Density as a Function of Time Only



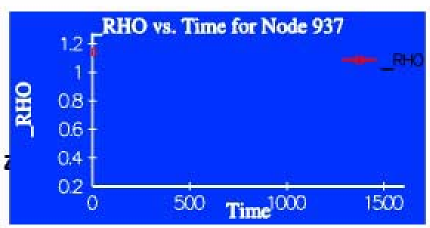


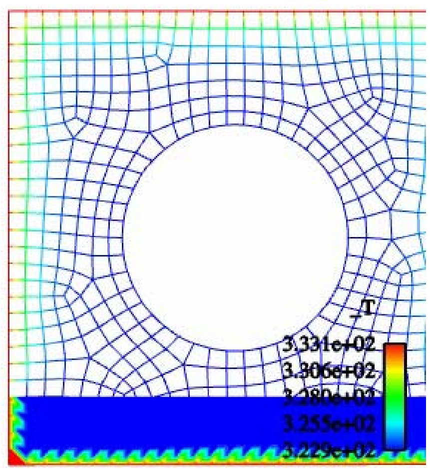
$$\rho = \rho_{final} + (\rho_{initial} - \rho_{final})e^{-kt}$$

- Parameters fit to experimental data:

ρ_{final} = 0.27 g/cm^3 (16.9lb/ft^3)
$\rho_{initial}$ = 1.14 g/cm^3
k = 1/80

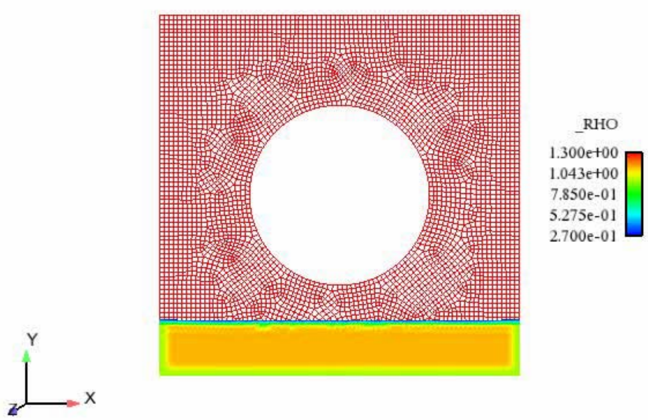
- Density is homogeneous spatially, but changes in time
- Numerically simple density model is empirical, but physics rich. Will be used for large component encapsulation simulations

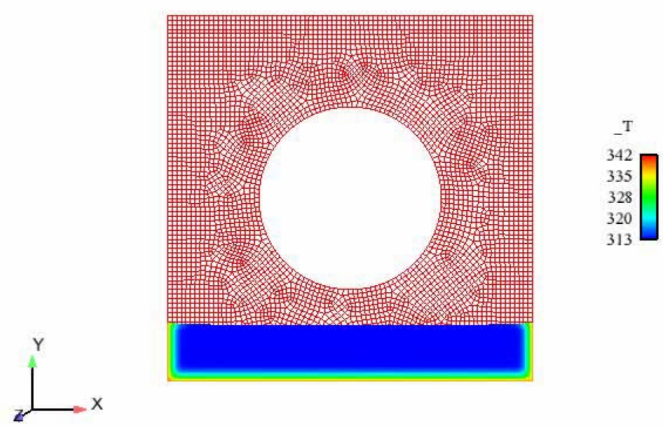




Variable Density as a Function of Fluorinert Concentration

$$\rho_f = [(x_0 - x)\frac{RT}{pM} + (1 - x_0)\frac{1}{\rho_{epoxy}} + \frac{x}{\rho_{flourinert}}]^{-1} \qquad \frac{Dx}{Dt} = kx$$





- First order kinetics give exponential decay for fluourinert concentration
- Local variations in density can be seen due to temperature and concentration
- More complex cavitation model is under development

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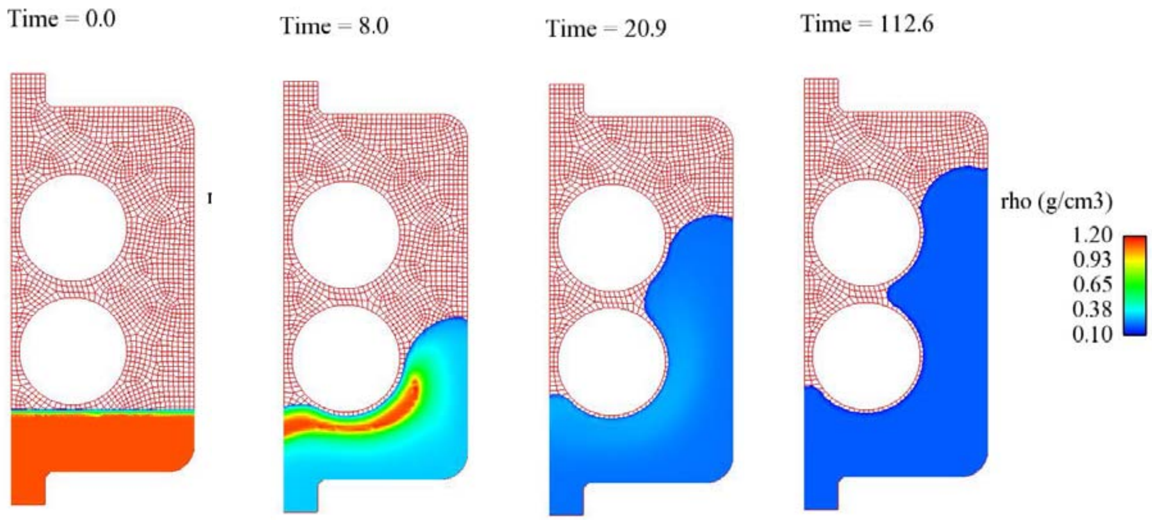
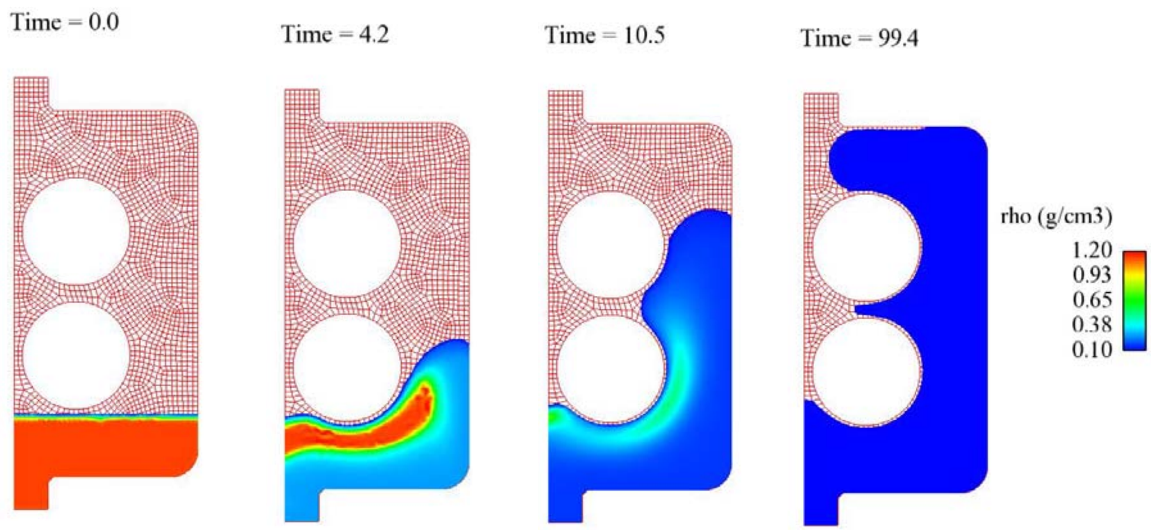
Modeling Can be Used to Aid in Material Selection and Metering



- Simulation show foam rise for 5% fluorinert initially



- Simulation show foam rise for 10% fluorinert initially
- Numerical loss of fluorinert limits expansion
- Improvements underway

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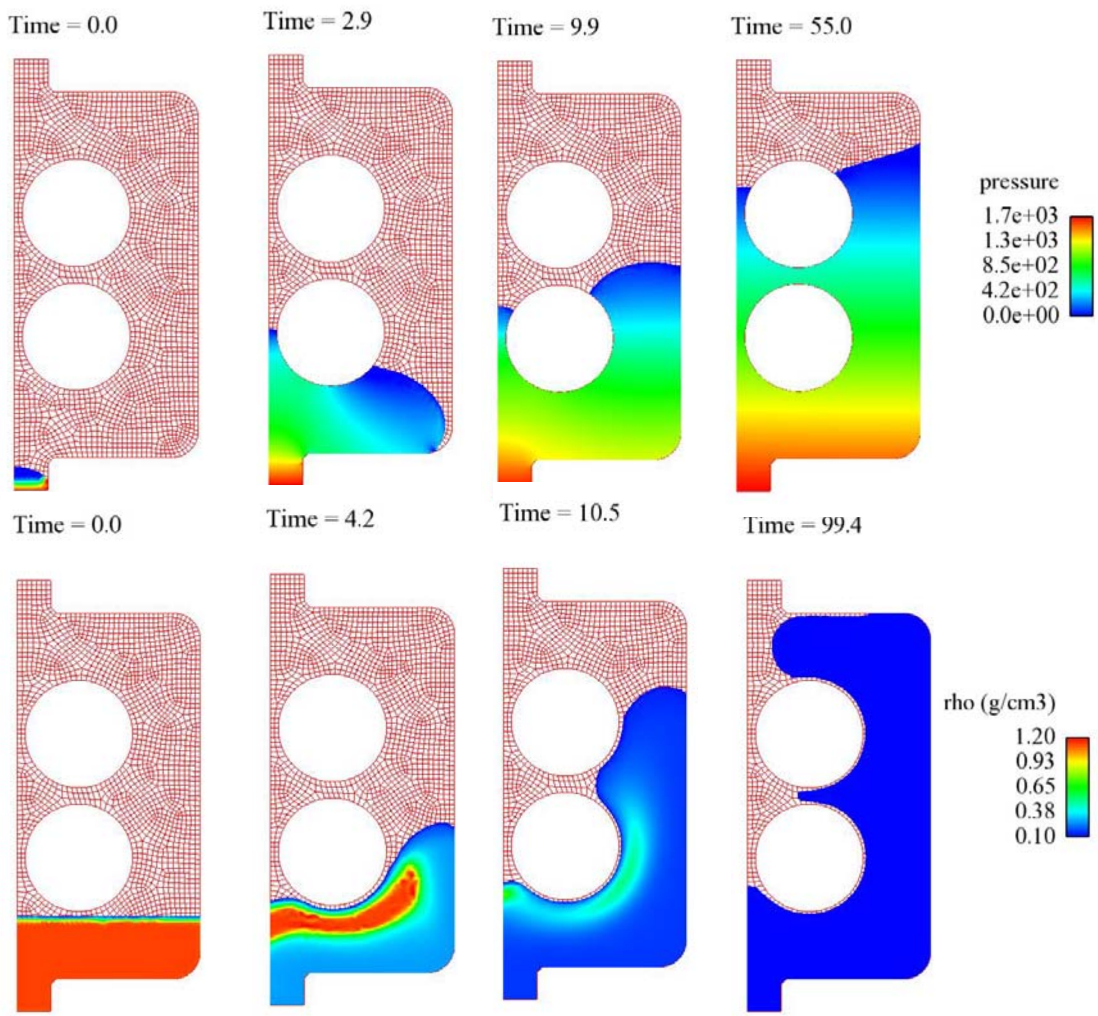
Pressure Driven Flow Profiles Different From Free Rise Foam

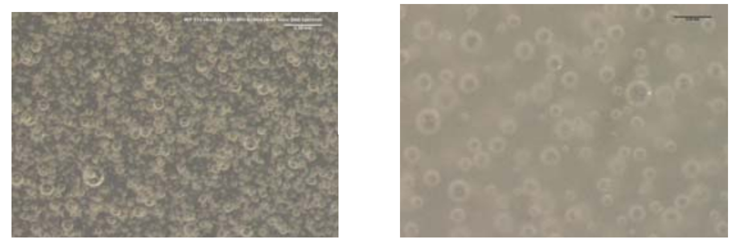


Pressure driven flow leaves smaller voids than free rising foam

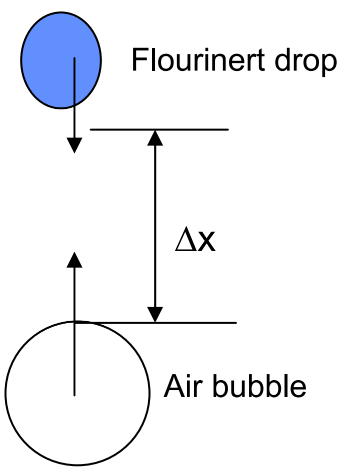
Free rising foam has trouble entering interstitial spaces

Single Droplet/Bubble Studies Elucidate the Nucleation Mechanism for Blown Foam

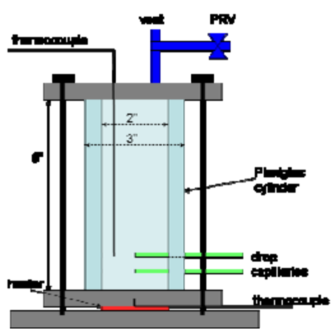
- Fluorinert blowing agent forms into droplets in mixing process
- Single droplet in mix will superheat without boiling – no boiling at typical oven temperatures
- Only “blows” when interacts with a bubble
- Droplet Rd ~ 10 μm and air bubble R_b ~ 100μm gives an average collision time on the order of minutes if Δx is on the order of 100μm.
- Explains why final foam density is dependent on mixing procedure – must incorporate air and have optimal droplet/bubble sizes



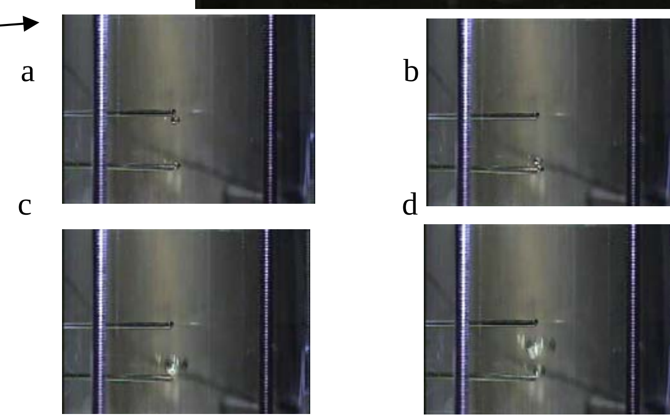
Mixing study (KCP): Left, “sweet spot” for good foam rise is between 800 and 1300 rpm. Right, foam rises only poorly when malt mixer at about 10,000 rpm is used.



Fluorinert droplet can be held Indefinitely above boiling temperature. Will boil if allowed to fall and interact with air bubble below.



Air bubble



Single droplet study: time 2.50, 2.84, 3.00, 3.04 s

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Conclusions and Future Work

- **Foams are complex, poorly understood, materials**
- **Coupled physics requires modeling**
  - **Current models shows areas for improvements in density and fluorinert vaporization models – new model based in cavitation theory underway**
  - **Gas phase transport must be added to model to allow prediction of density variation**
  - **Micro- and meso-scale modeling will be used to develop continuum foam expansion model and boundary conditions**
- **Experimental discovery and multiscale modeling used to develop continuum model for blown foams**
  - **NMR and confocal microscopy for droplet size, settling/flotation etc**
  - **Initially we will use a description of the cell size evolution determined by simplified Rayleigh-Plesset equations**