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Physical Blowing of an Epoxy Foam

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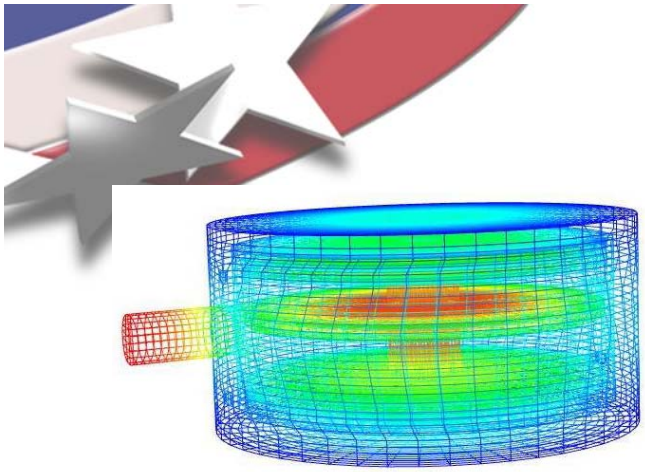
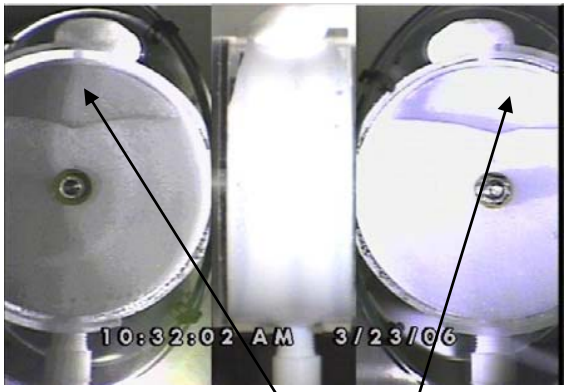
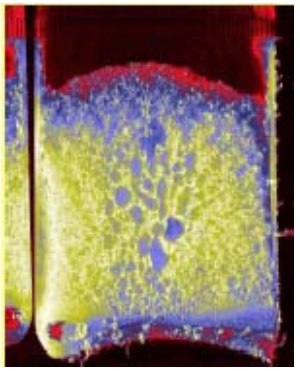
Foam Processing





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
- Multiphase transport
- Thermal modeling
- Fluid mechanics
- Free surface flow
- Validation experiments

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Foam of Interest is Physically Blown

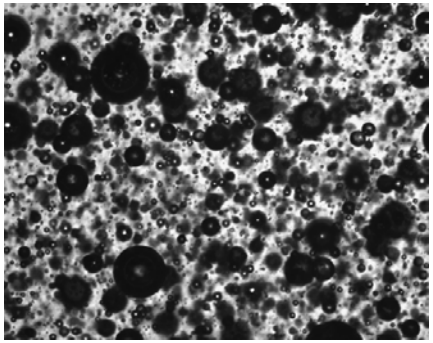
Vision: Develop a continuum model with volume source terms, and include relevant physics in these terms. Single phase, homogenized model

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)

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 capacity, thermal conductivity, & viscosity
  - Density & bubble size
  - Wetting/slip at walls



Epoxy foam starts out as an emulsion with air bubbles incorporated through mixing

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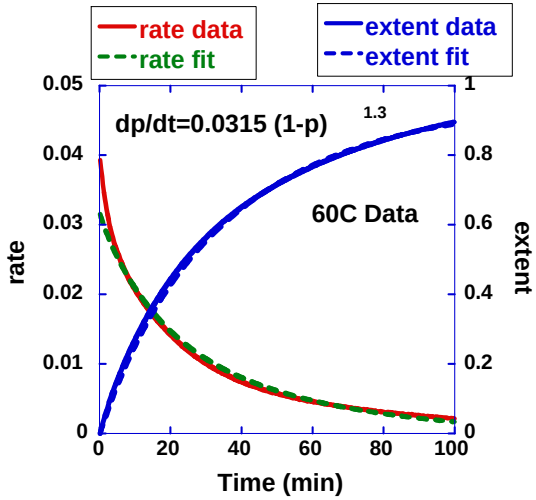
Reaction Kinetics and Rheology for Continuous Phase Determined Experimentally

- 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

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

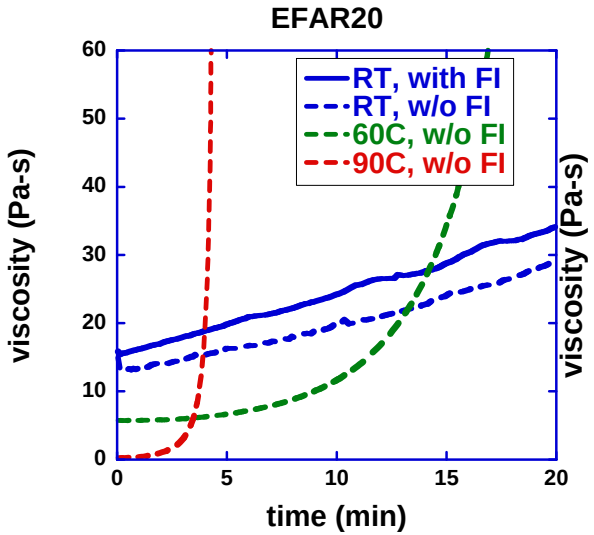


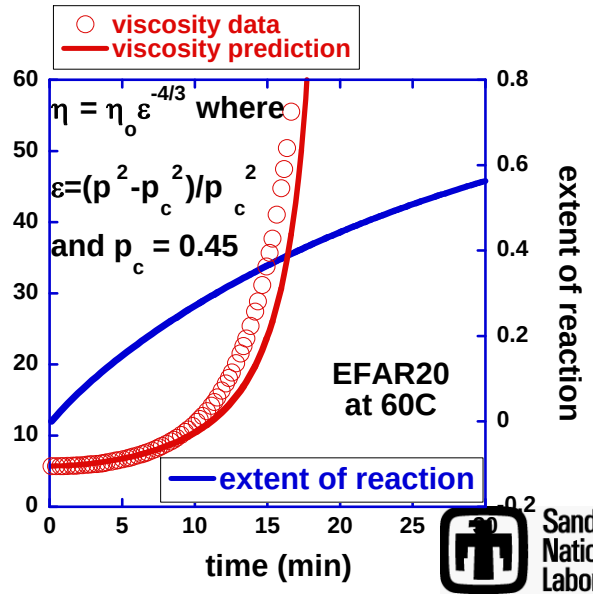
- Viscosity increases with cure
- Correlate viscosity with extent of reaction

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

- Overall foam viscosity is a function of void fraction (discuss later)

$$\mu = \mu_0 \exp\left(\frac{\phi_{gas}}{1-\phi_{gas}}\right)$$





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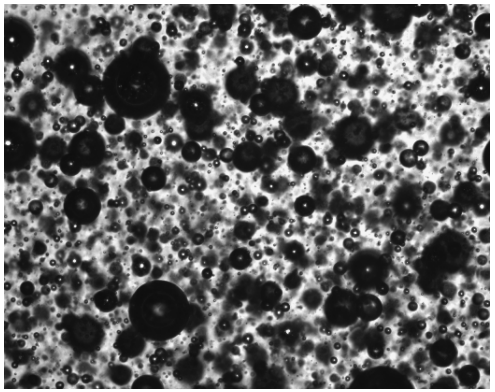
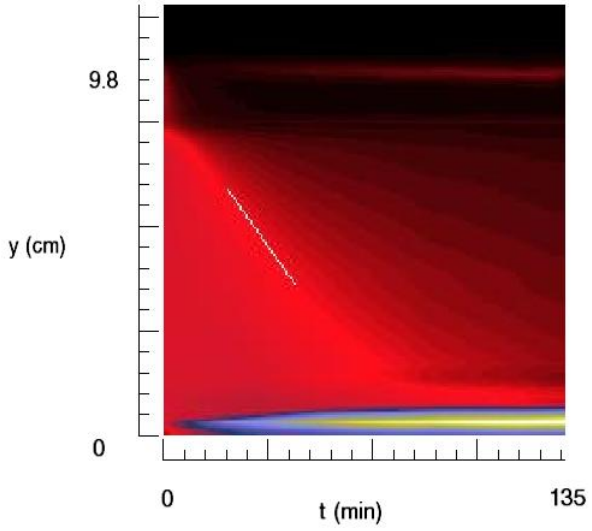
Foam Growth Theories Require Knowledge of Microstructure of Precursor Foam

- Dark circles are emulsion droplets or air bubbles about 10 - 100 microns in diameter
- Typical foam cell size O(100 microns)



Microscopy: which are emulsion droplets and which are bubbles?

- ^{19}F NMR 1-D Imaging shows separation of blowing agent in Part B
- Line indicates average settling velocity of 0.0013 cm/s
- Equivalent to Stokes velocity of a 10 micron diameter sphere
- Also used NMR to show Fluorinert is only slightly soluble in Epoxy mix



NMR imaging of Flourinert droplet concentration

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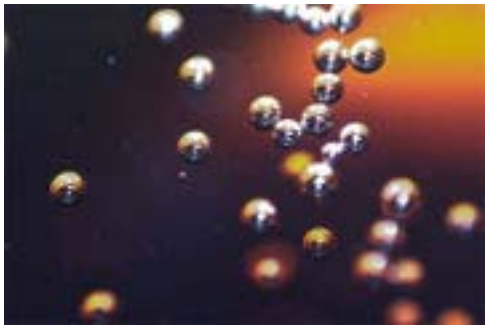
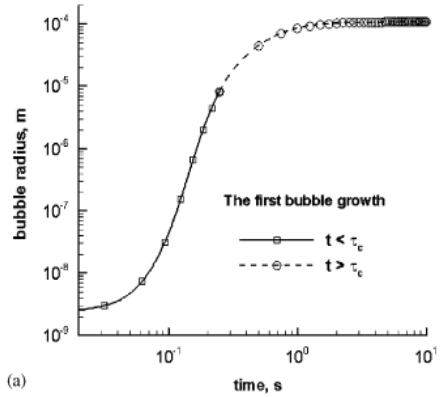
Microscale Models Predict Faster Foam Growth than Observed

- **Diffusion limited**
  - **Mao, Edwards, Harvey model for thermoplastic foams**
  - **Assume gas dissolved in continuous phase**

Chemical Engineering Science 61 (2006) 1836 – 1845

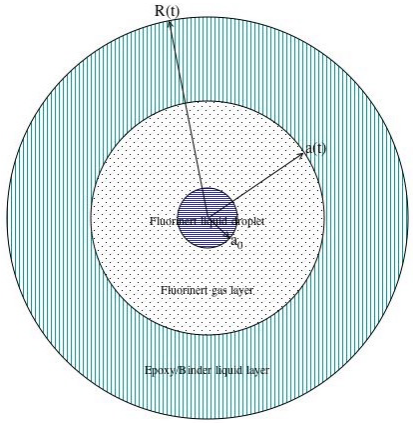


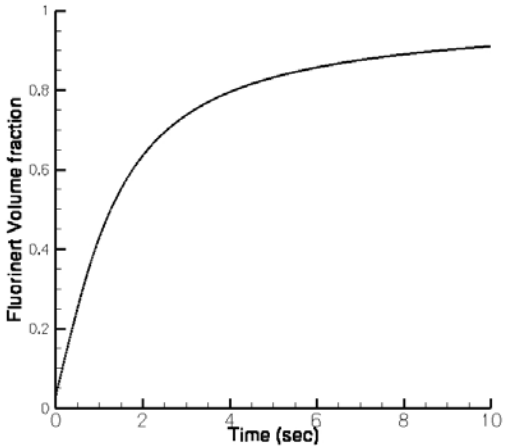
Bubbles in a soft drink nucleate homogenously, responding to a decrease in pressure



- **Heat transfer limited**
  - **Net heat flux to droplet determines rate of volume expansion depending on heat of vaporization**

$$\mathcal{H}_{vap}\frac{dn_{gas}}{dt} = 4\pi k_{eff}\Delta T a - 4\pi\frac{k_{eff}\Delta T}{\alpha_T}\left(1-\frac{a}{R}\right)a^2\frac{da}{dt}$$





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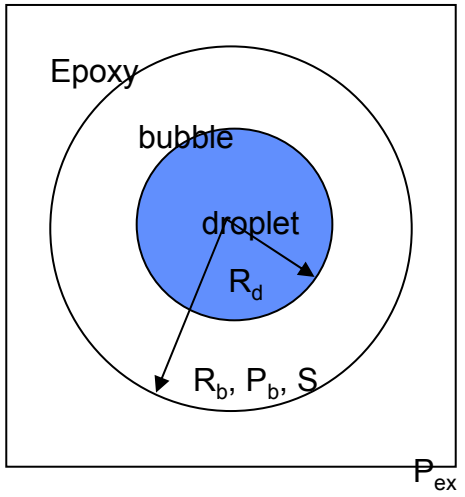
Microscale Foam Expansion Models (cont'd)

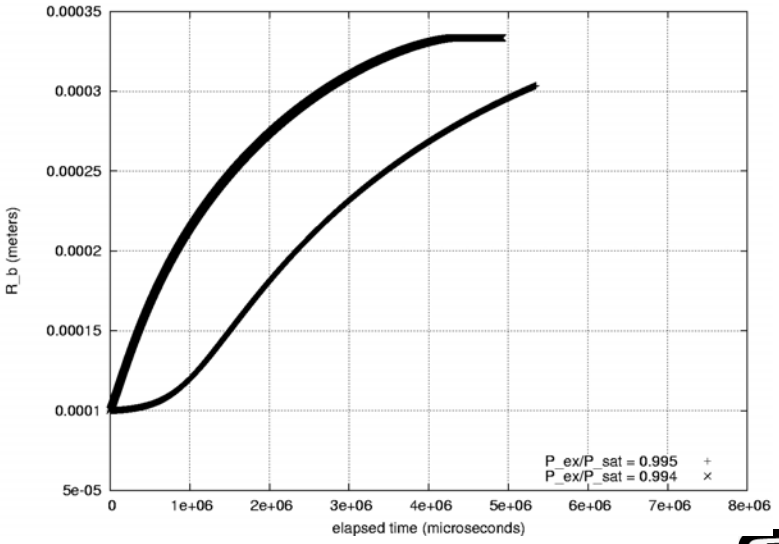
- **Equilibrium limited**
  - **Driving mechanism: initial droplet bigger than equilibrium size with vapor (Kelvin relation)**

$$R_d = \frac{v_m \sigma_{db}}{R_G T \ln S}; \quad S = P_b / P_{sat}$$

Where v_m is the molecular volume, R_G gas constant, σ_{db} surface tension, P_{sat} vapor pressure at coexistance for a planar interface



  - **For typical materials S < 0.99 gives R_d ~ *O*(1 - 100nm)**
  - **Experimentally, R_d ~ 10-100μm**
  - **Therefore, droplet will evaporate**
  - **0.16% change in P_{ex}/P_{sat} can have a factor of ~2 change in the bubble expansion time**



Expansion time is several seconds

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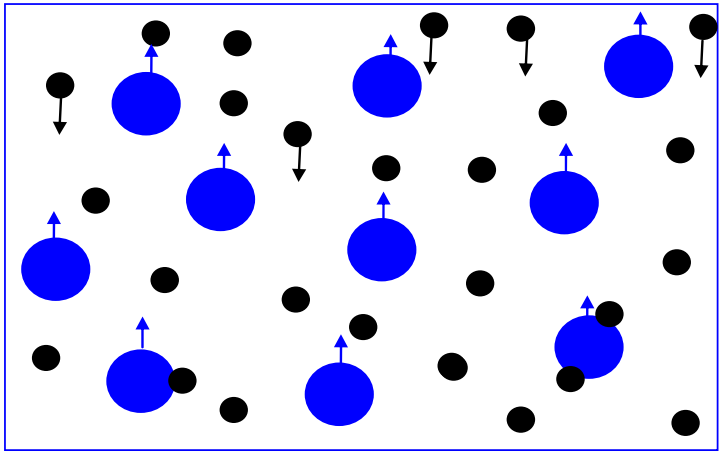
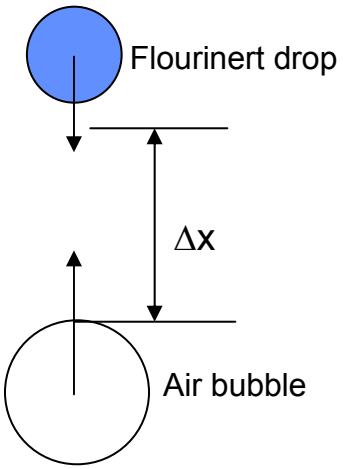
Foaming Is Nucleation Limited, And Nucleation Is Collision Limited



- Relative motion of early bubbles/droplets from density differences leads to collisions
- Gravitational coagulation kernels from cloud physics (e.g. Williams & Loyalka 1991)
- Relative motion can be increased if sheared



- Droplet Rd ~ 10 mm and air bubble Rb ~ 100mm gives an average collision time on the order of minutes if Dx is on the order of 100mm.
- Explains why final foam density is dependent on mixing procedure – must incorporate air and have optimal droplet/bubble sizes

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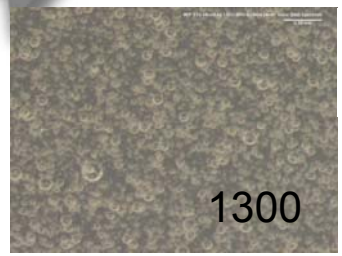
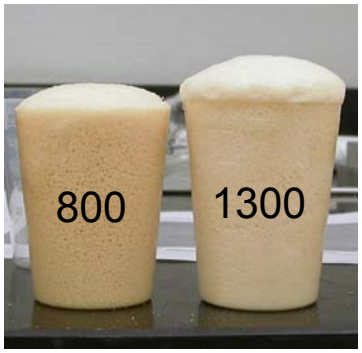
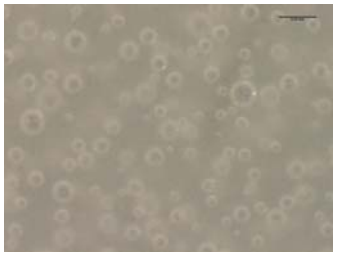
Single Droplet/Bubble Studies Elucidate the Nucleation Mechanism for Blown Foam



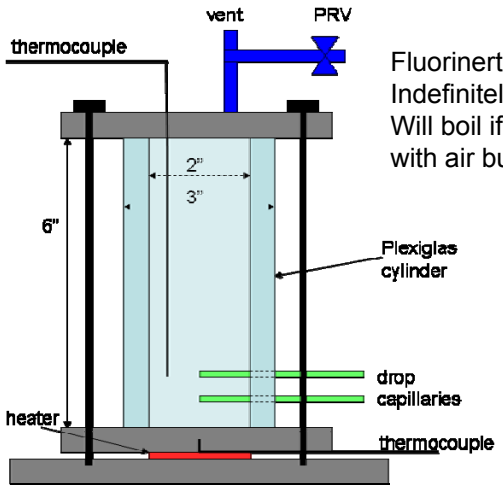
Mixing study: "Sweet spot" for good foam rise is between 800 and 1300 rpm





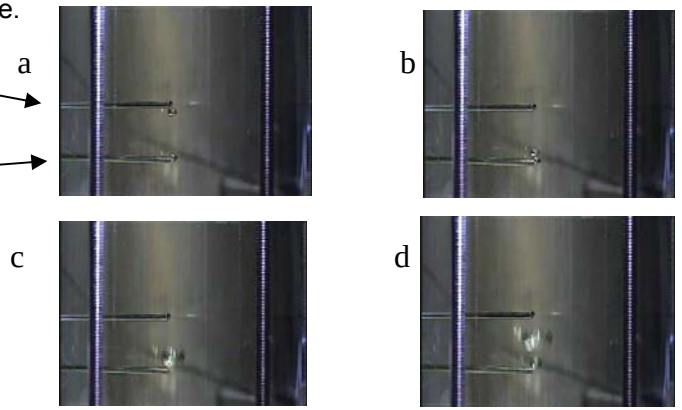
Foam rises only poorly when malt mixer at about 10,000 rpm is used.

- 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



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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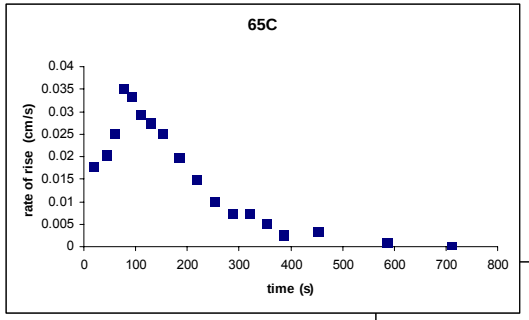
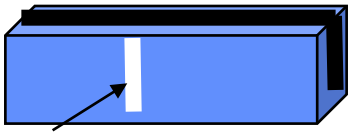
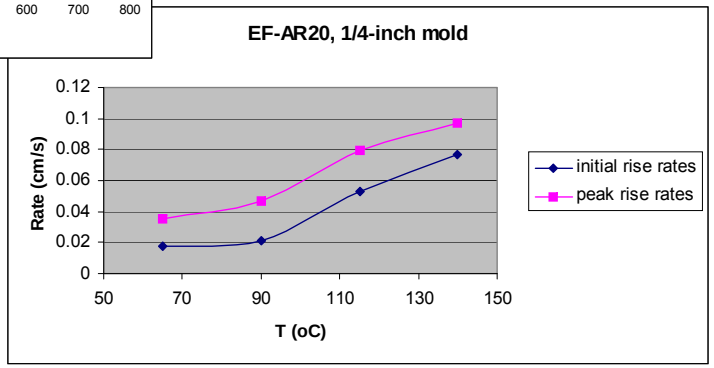
Foam Rise Experiments

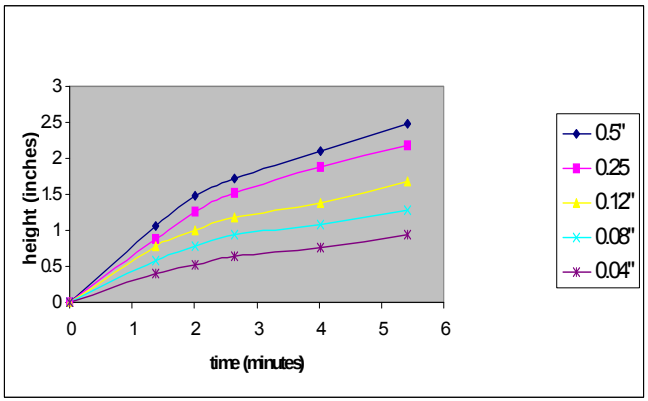
- Foam expansion in narrow (1/4”) slots
- Foam rise velocity increases over first minute or so, then decreases because gas is used up and/or viscosity of polymerizing resin increases
- Rise rate is dependent on temperature
- Rise rate is dependent on channel size in simple geometry
- Interplay of these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





Viewing window





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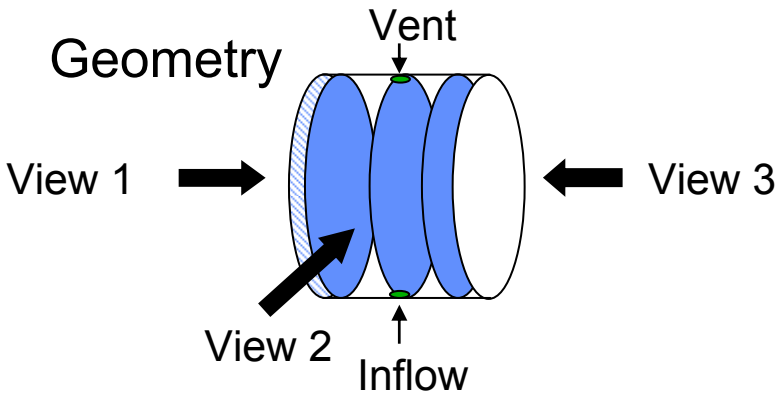
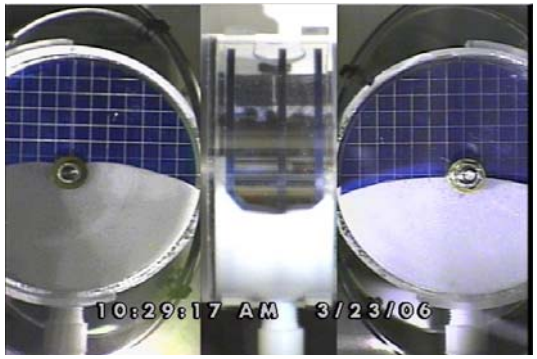
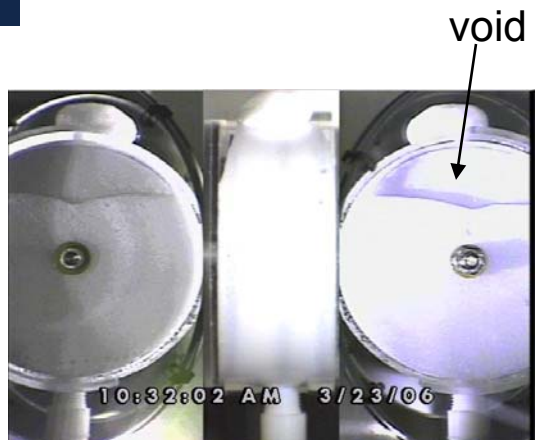
Foam Rise Experiments in More Complex Geometry

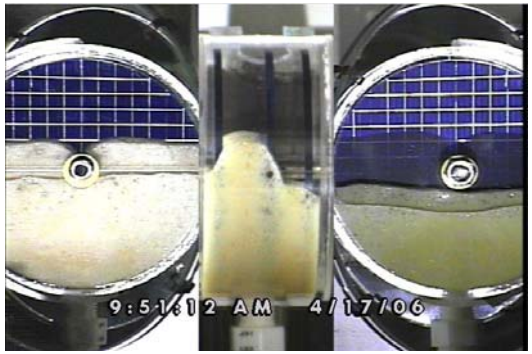




Early: unlike in simple geometry experiments, epoxy foam (EF-AR08) fills *faster* in the *narrow* gaps between plates.



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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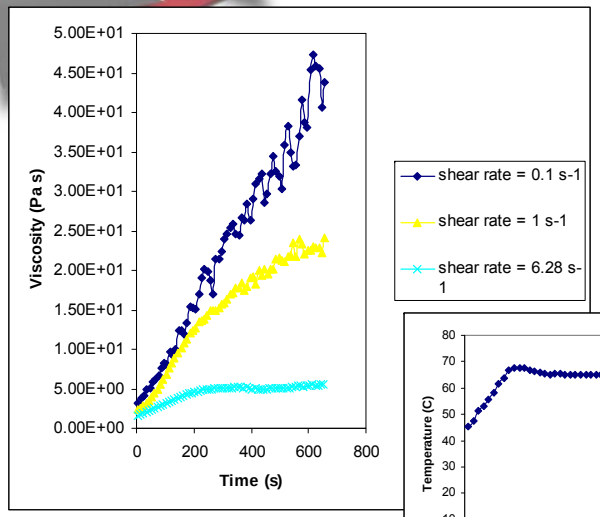
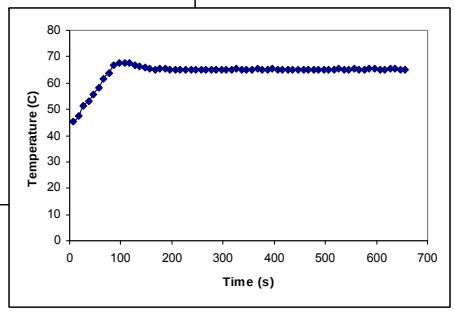
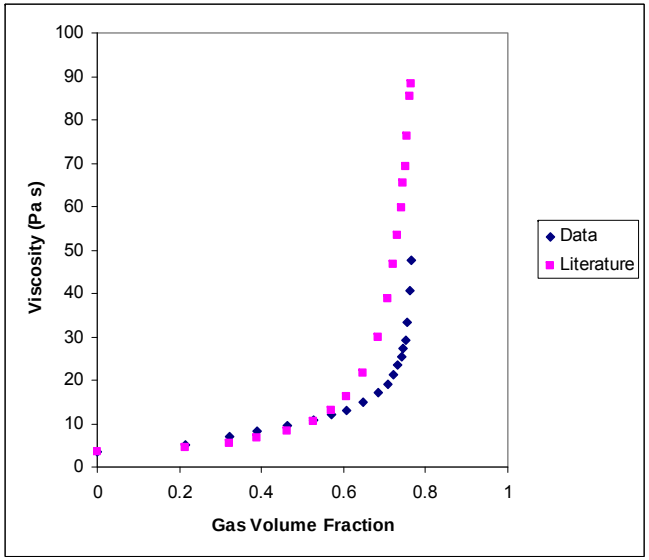
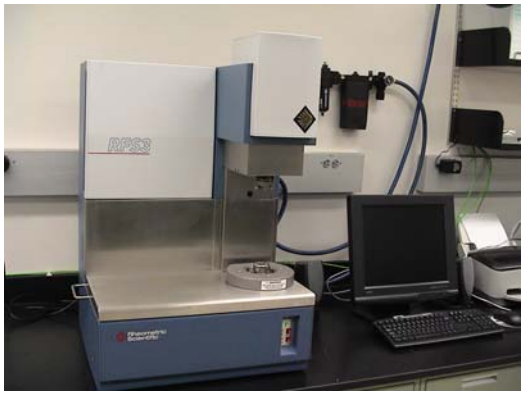
Foam Rheology









- Foaming rheology difficult
  - nonisothermal or loading problems
  - changing volume
  - changing microstructure
  - shear rate/sensitivity limits of rheometers
  - oscillatory: Cox-Merz rule doesn't apply
- Used two decoupled experiments to determine viscosity and volume fraction with time and temperature
- Results: For low shear rates foam shear viscosity follows Taylor-Mooney relationship

$$\mu = \mu_0 \exp\left(\frac{\phi_{gas}}{1-\phi_{gas}}\right)$$

- Expected to hold only if ϕ_{gas}<0.5

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

- 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;

Variable Density as a Function of Time Only

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

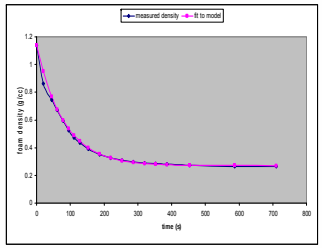
- Parameters fit to experimental data:

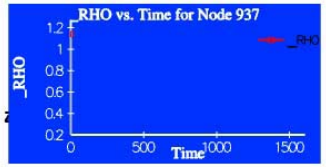
$\rho_{final} = 0.27\ g/cm^3\ (16.9 lb/ft^3)$

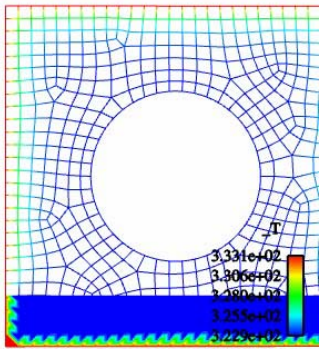
$\rho_{initial} = 1.14\ g/cm^3$

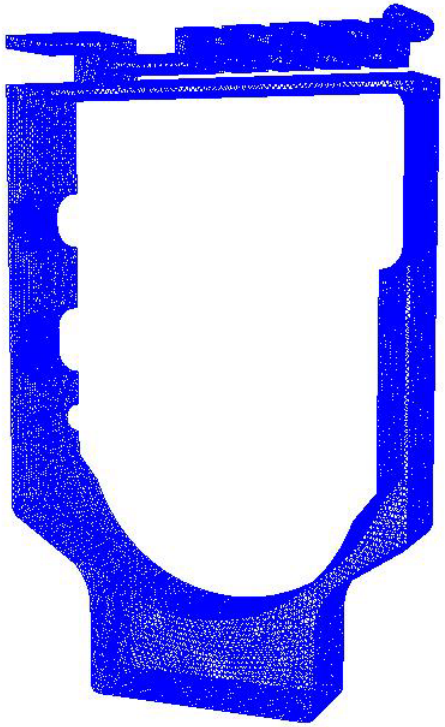
$k = 1/80$

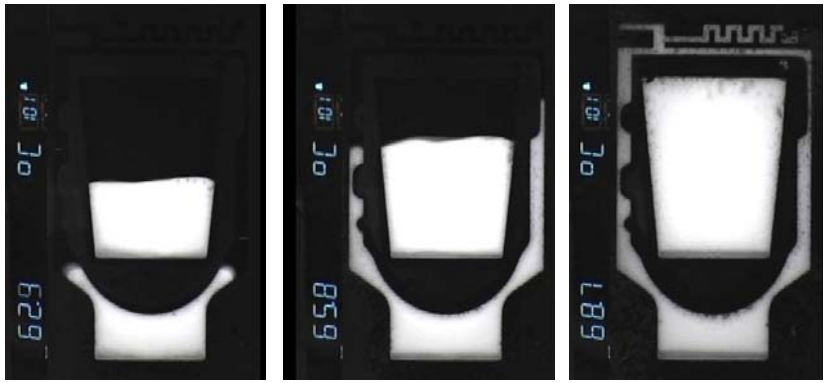
- Density is homogeneous spatially, but changes in time
- Numerically simple density model is empirical, but physics rich. Will be used for large component encapsulation simulations











Example frames. Center “free rise” cup also included in mold.

Note unblown foam at bottom and creaming of bubbles near top.

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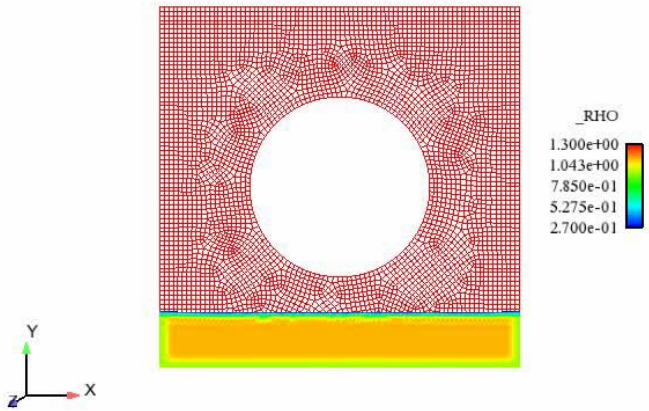
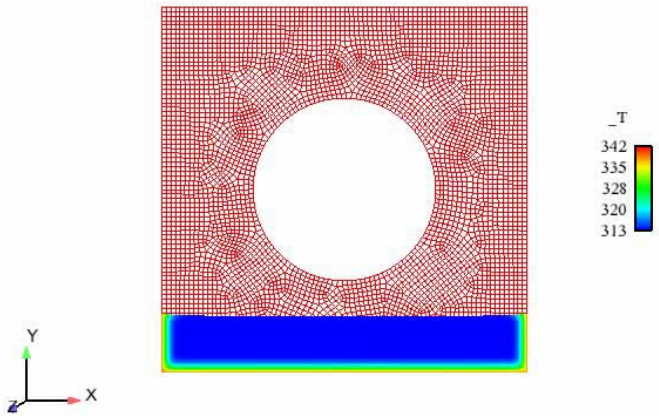
Variable Density as a Function of Fluorinert Concentration

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





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

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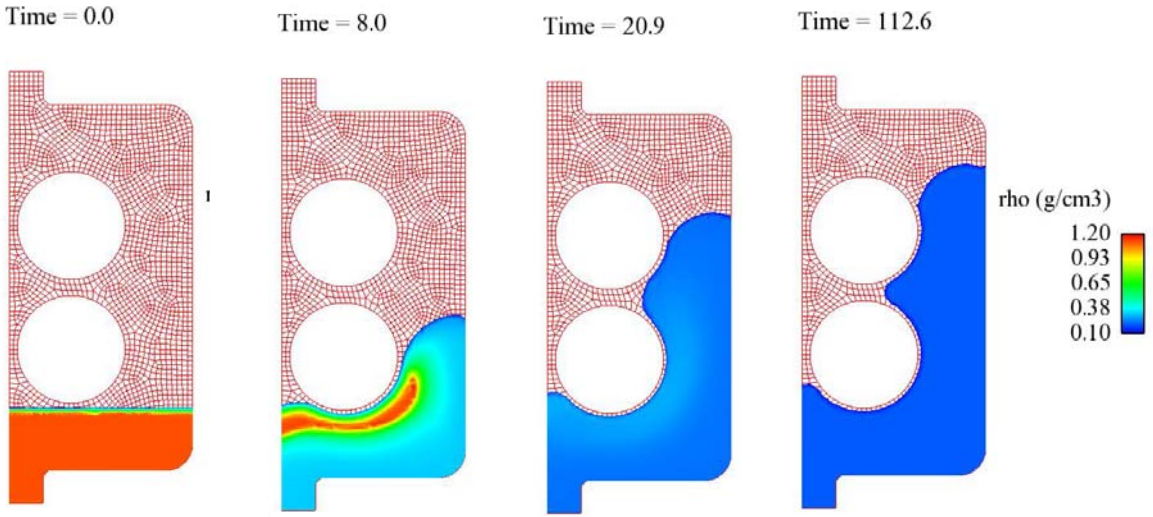
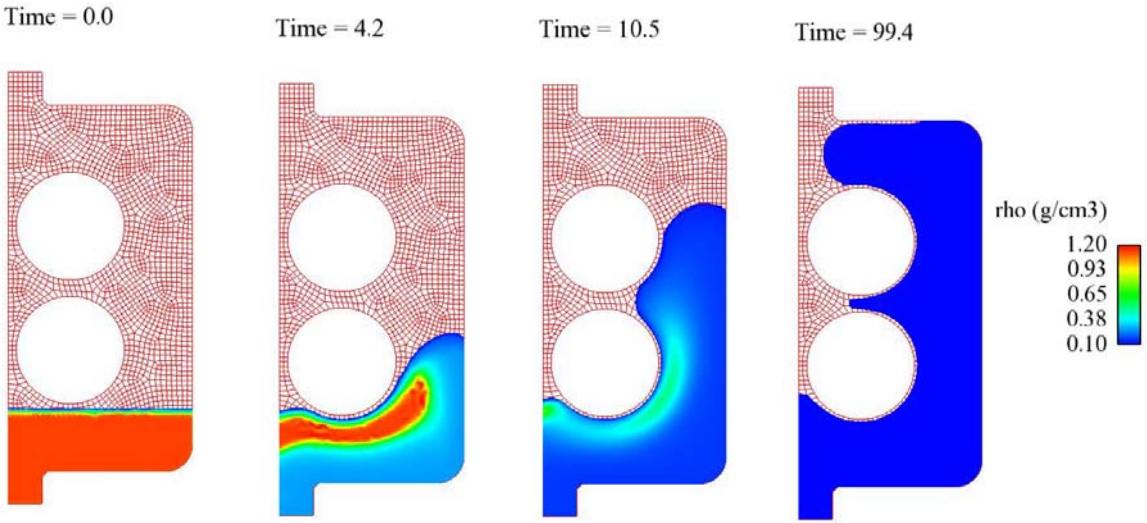
Modeling Can be Used to Aid in Material Selection and Metering



- 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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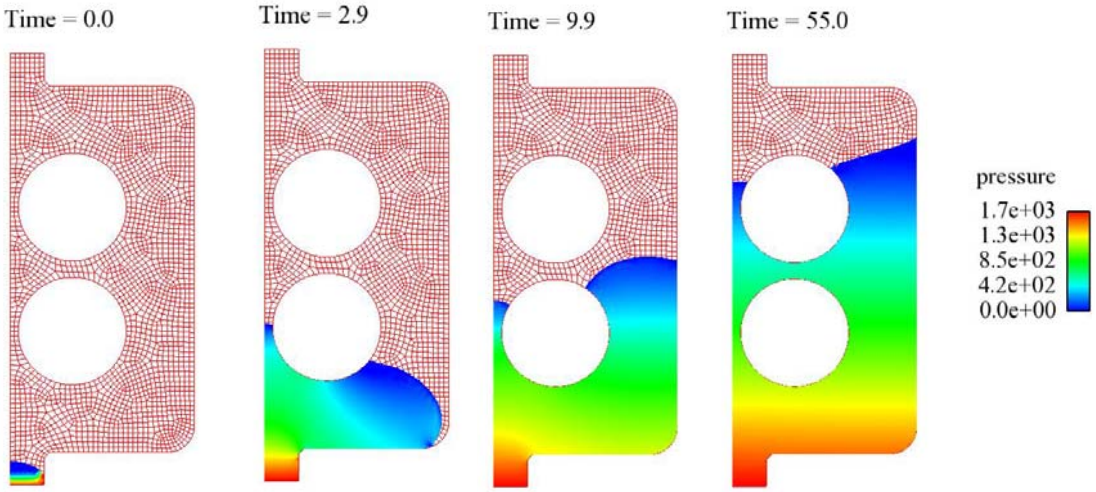
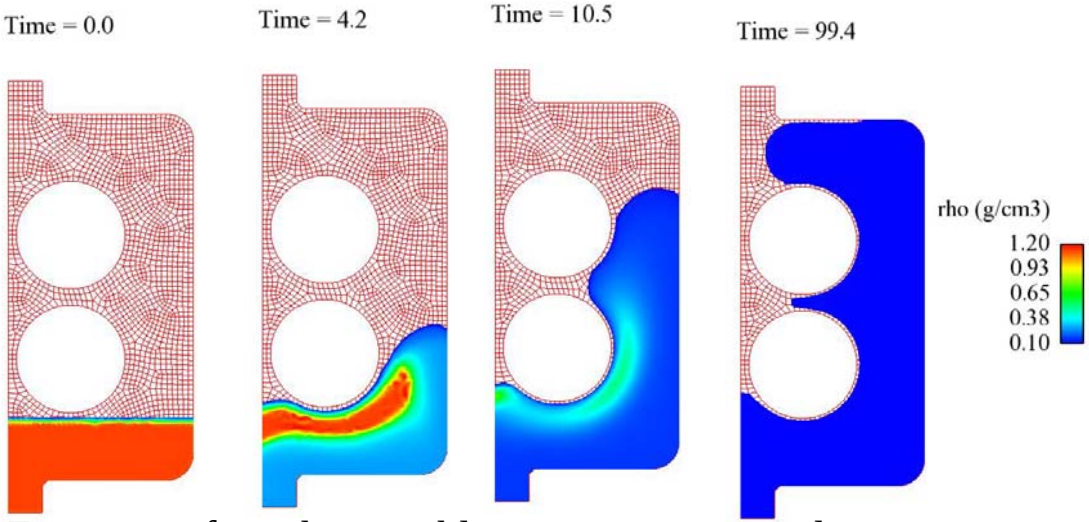
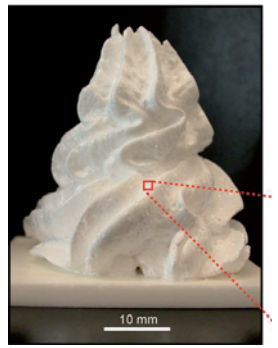
Pressure Driven Flow Profiles Different From Free Rise Foam



Pressure driven flow leaves smaller voids than free rising foam



Free rising foam has trouble entering interstitial spaces



Ultrastable aqueous foam stabilized with nanoparticles

Injection of syntactic foam into mold

Modeling inspired new project to develop nonaqueous ultrastable foam to be injected molded for component encapsulation

Conclusions and Future Work

- **Foams are complex, poorly understood, materials**
- **Experimental discovery and multiscale modeling used to develop continuum model for blown foams**
  - **NMR and confocal microscopy for droplet size, settling/flotation etc**
  - **Single bubble experiments confirm primary nucleation mechanism**
  - **Multiple experiments yield viscosity model**
  - **PIV will be used to develop boundary conditions**
- **Coupled physics requires modeling**
  - **Current models show 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-scale modeling of nucleation mechanism will give source term taking into account nucleation rate**
- **Preliminary modeling shows value in process design**

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