SAND2015-4306C

# A Reaction Kinetics Approach to Polyurethane Foam Expansion and Polymerization


Rekha Rao, Lisa Mondy, Christine Roberts, Melissa Soehnel, Kevin Long, Victor Brunini, David Noble, Mathew Celina

*Sandia National Laboratories*

*Albuquerque, NM*

James Tinsley

*Honeywell Kansas City Plant*

*Kansas City, MO*


**31st Annual Meeting of the Polymer Processing Society**
**Jeju Island, Korea**
**June 7 - 11, 2015**


National Nuclear Security Administration

SAND2015-????C

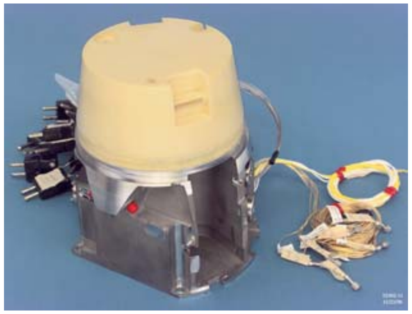
Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-AC04-94AL85000.

Sandia National Laboratories

# 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



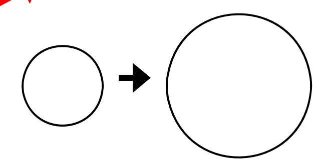
Mock component encapsulated with PMDI from "KCP Encapsulation Design Guide" (Mike Gerding, UUR)

# 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**



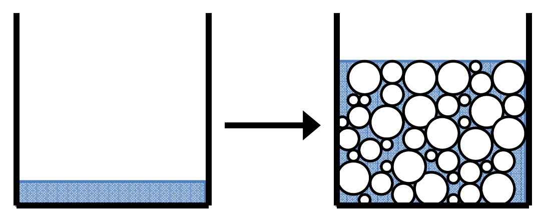
Exothermic Cure Reaction → Heat

**Accelerates Foaming Reaction**

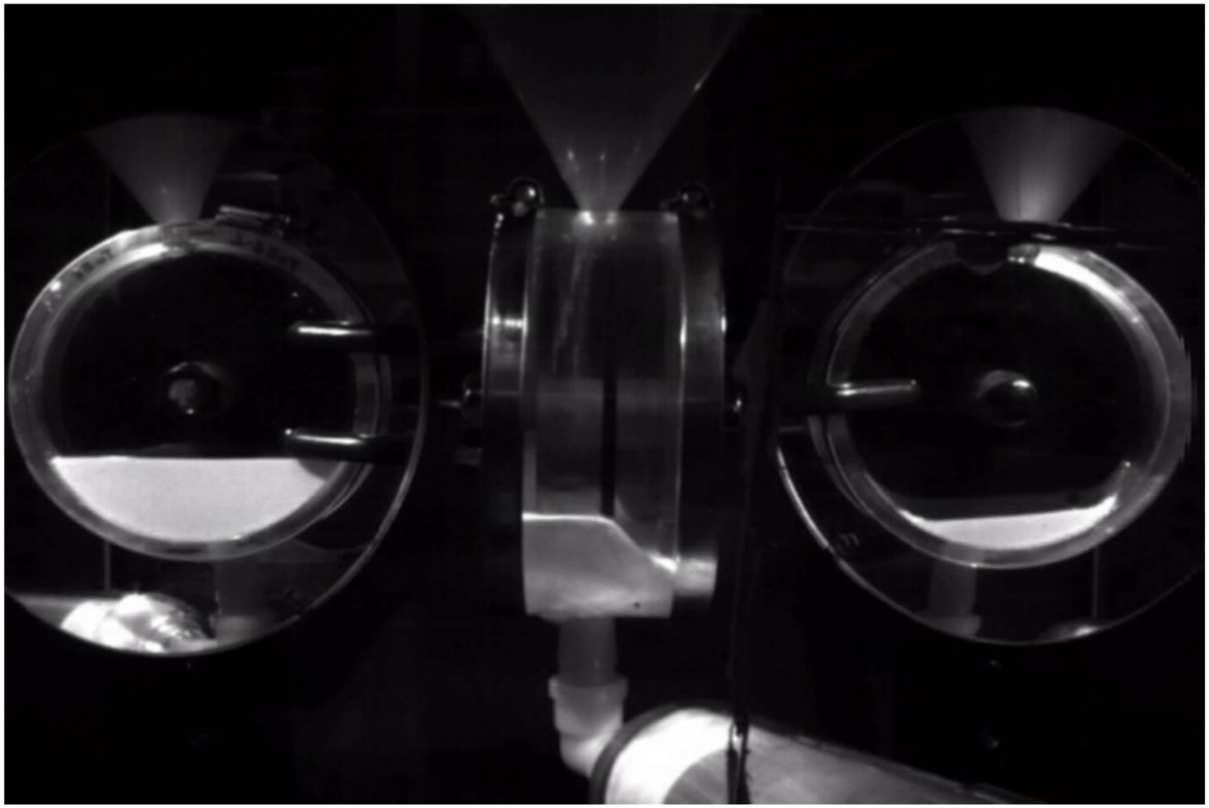
***r* ~ *k*(*T*)**

**A + BG → AB + G↑**

**Vaporize Volatile Components**



# Foam Filling is Complex



3 views of foam filling a complex mold with several plates spaced unevenly. Vent location is critical to keep from trapping air.

- Gas generation drives the foam expansion, changing the material from a viscous liquid to a multiphase material.
- Continuous phase is time- and temperature-dependent and eventually vitrifies to a solid.

**We are developing computational models to help us understand foam expansion, filling and curing. We want to predict material properties for the structural response as part of "cradle-to-grave" manufacturing/aging response.**

# 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

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

Thermal properties depend on gas volume fraction and polymer properties

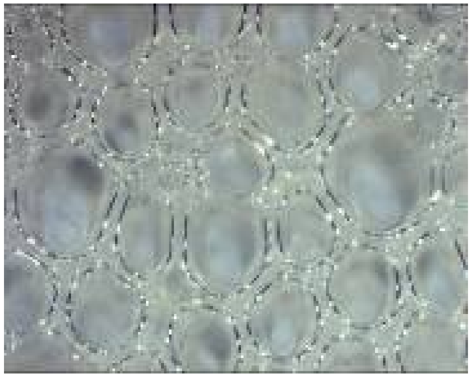
$$k = \frac{2}{3}\left(\frac{\rho}{\rho_l}\right)k_l + \left(1-\frac{\rho}{\rho_l}\right)k_v$$

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

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

$$\mu = \mu_0\exp\left(\frac{\varphi_v}{1-\varphi_v}\right) \qquad \mu_0 = \mu_0^0\exp\left(\frac{E_\mu}{RT}\right)\left(\frac{\xi_c{}^p - \xi^p}{\xi_c^p}\right)^{-q}$$

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



Foam is a collection of bubbles in curing polymer

# Reaction Kinetics Models

Extent of reaction equation for **polymerization**: condensation chemistry

- Polymerization extent determined with condensation chemistry. Includes the ability to vitrify, or arrest, the cure kinetics by introducing the glass transition $T_g$ based on the di Benedetto form:

$$\frac{\partial \xi}{\partial t} = \left(\frac{1}{(1+wa)^{\beta}}\right)\left(k_0 \exp\left(-\frac{E}{RT}\right)\right)\left(b+\xi^m\right)\left(1-\xi\right)^n \qquad \log_{10} a = \frac{-C_1\left(T-T_g\right)}{C_2+T-T_g} \qquad T_g = \frac{T_{g0}(1-\xi)+A\xi T_{g\infty}}{(1-\xi+A\xi)}$$

- *a* represents a time-shift factor (WLF form) between material and laboratory time. As *a*>>1, the reaction rate slows down due to loss of mobility.
- $\beta$ , $w$, $C_1$, $C_2$, $T_{g0}$, $T_{g\infty}$, $A$ are material parameters determined from data

Extent of reaction equations for **gas generation** as $H_2O$ and isocyanate react to give $CO_2$: calculate density from molar concentration of $CO_2$

$$\frac{dC_{H_2O}}{dt} = -Nk_{H_2O}C_{H_2O}{}^{n}$$

$$\frac{dC_{CO_2}}{dt} = +Nk_{H_2O}C_{H_2O}{}^{n}$$

$$k_{H_2O} = A_{H_2O}\exp(-E_{H_2O}/RT)$$

$$N = 0.5\left\{1+\tanh\left(\frac{t-t_{nucleation}}{t_{nucleation}}\right)\right\}$$

$$\rho_{gas} = \frac{PM_{CO_2}}{RT}$$

$$v = \frac{V_{gas}}{V_{liq}} = \frac{M_{CO_2}C_{CO_2}}{\rho_{gas}} \qquad \phi_v = \frac{v}{1+v}$$

$$\rho_{foam} = \rho_{gas}\phi_v + \rho_{liq}(1-\phi_v)$$

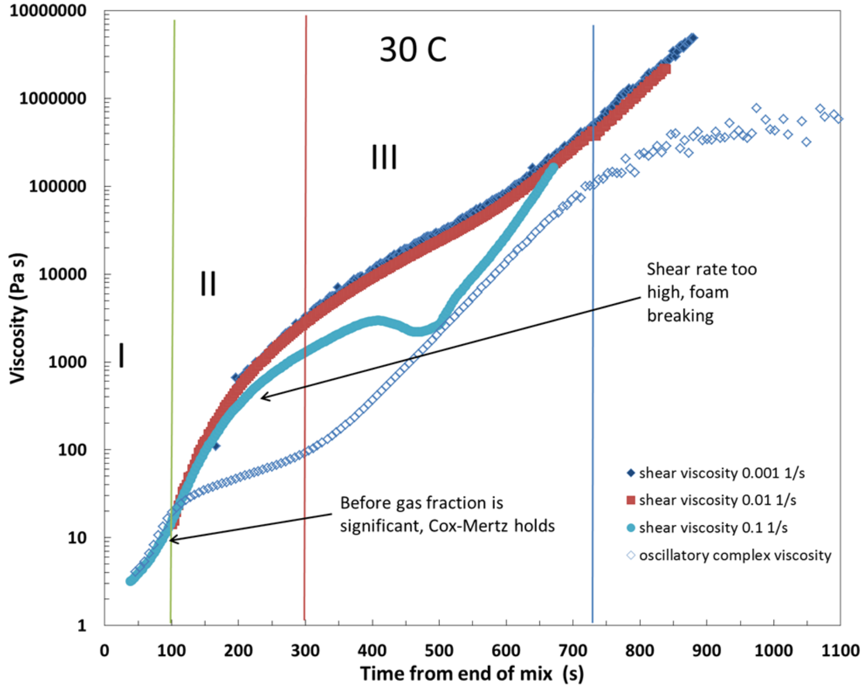
- Equations solved with the finite element method using a level set to determine the location of the free surface (Rao et al., IJNMF, 2012)
- Experiments to determine foaming and curing kinetics as well as parameters for model

- $N$ is a function to approximate the time it takes bubbles to form

# Summary of Experiments Needed for Model Parameters

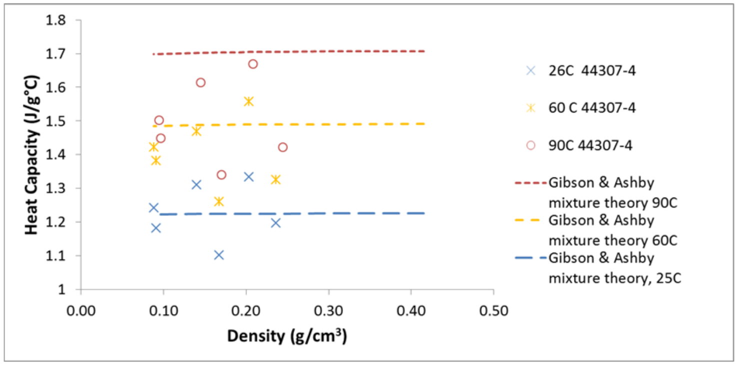
**Rheology** of both wet and dry (nonfoaming) PMDI

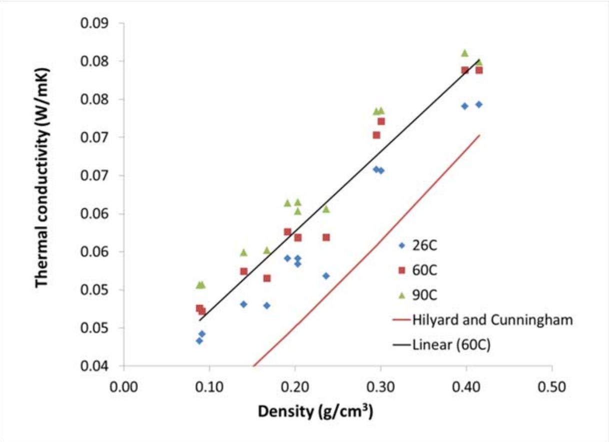
$$\mu_0 = \mu_0^0 \exp(\frac{E_\mu}{RT})(\frac{\xi_c^{\ p} - \xi^p}{\xi_c^{\ p}})^{-q}$$




- Measured both oscillatory and steady shear viscosities with time
- Isothermal
- Foam rheology evolves as gas fraction and polymerization increase
- Higher shear rates destroy the foam

**Heat of reaction and thermal properties** estimated from solid foam properties




- Differential scanning calorimetry (DSC) gives lumped heat of reaction
- Thermal properties as functions of temperature
- Thermal conductivity is a function of the gas fraction

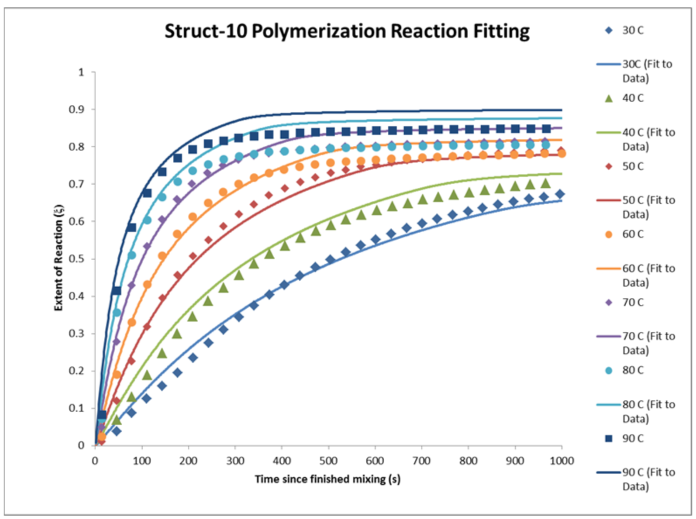
# Extent of Reaction for Polymerization

- Fit the rate and the extent of reaction to IR data to a standard equation form
- Fit $T_g$ to both rheology and DSC data: $T_g$ changes as cure progresses making this complex

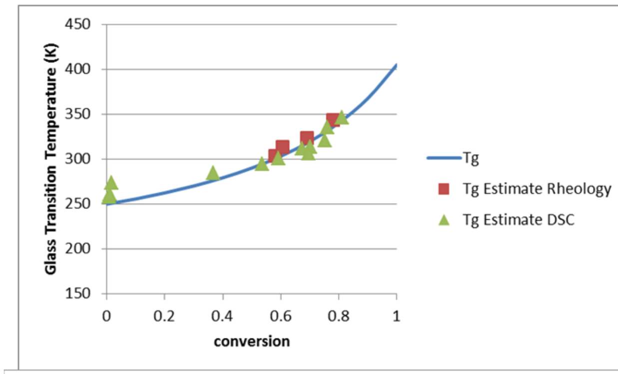
$$\frac{\partial \xi}{\partial t} = \left(\frac{1}{(1+wa)^{\beta}}\right)\left(k_0 \exp\left(-\frac{E}{RT}\right)\right)(b+\xi^m)(1-\xi)^n$$

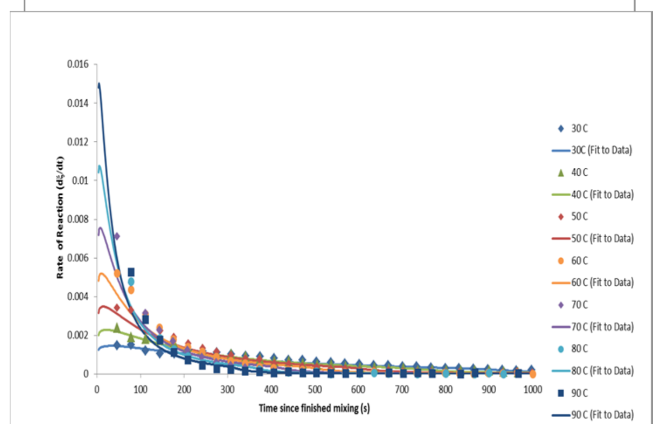
$$\log_{10} a = \frac{-C_1(T-T_g)}{C_2+T-T_g}$$

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




- New form captures arrest of reaction below the glass transition temperature ($T_g$ evolves with extent of reaction)




Rate and extent of reaction fit to data, where parameters of the model, including Tg are optimized for lower temperatures expected in the process. The apparent time-to-gel from rheology is correlated with extent to give a Tg with conversion. Similar analysis can be done with DSC and results are consistent.

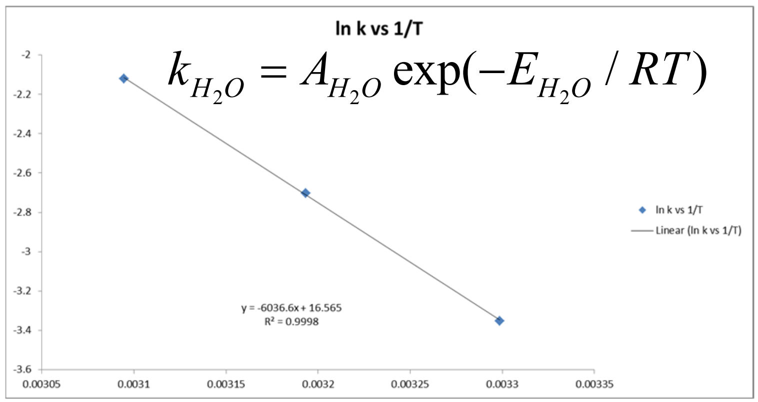
# Kinetics of $CO_2$ Generation

- Write gas generation kinetics in terms of moles/volume liquid and track both $H_2O$ and $CO_2$
- Fit semi-isothermal data for volume evolution with time to determine the rate of reaction and the exponent, n
- Bubble nucleation time estimated with a smooth function N
- Fit is better at lower temperatures (more isothermal experiment)

$$\frac{dC_{H_2O}}{dt} = -Nk_{H_2O}C_{H_2O}{}^{n}$$

$$\frac{dC_{CO_2}}{dt} = +Nk_{H_2O}C_{H_2O}{}^{n}$$

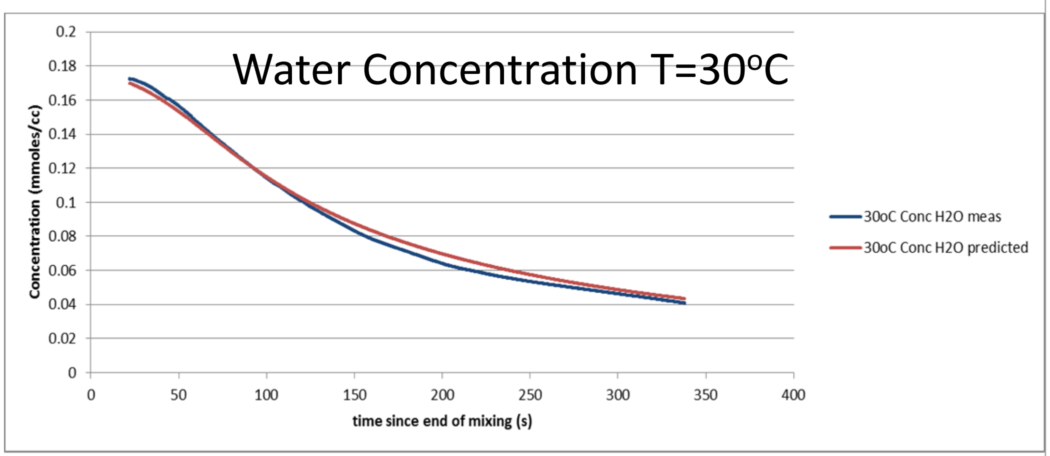
$$N = 0.5\left\{1 + \tanh\left(\frac{t - t_{nucleation}}{t_{nucleation}}\right)\right\}$$

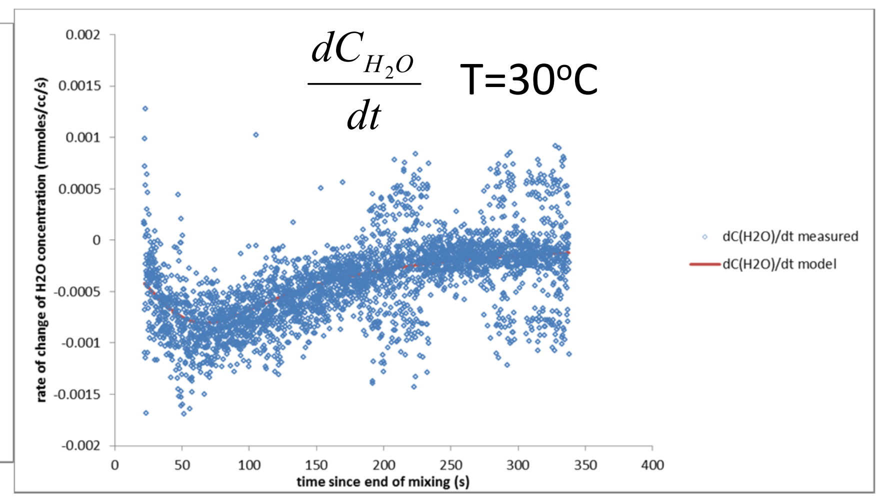



n=1.8

Ea/R=- 6036

$A_{H2O}$=1.56e7 cc/mmol s



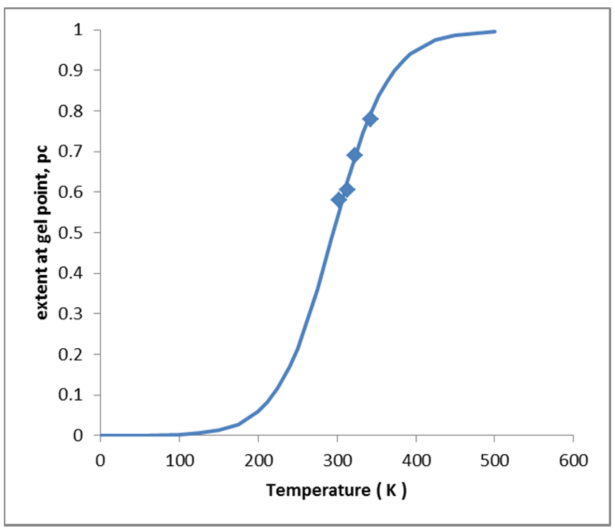
# Model Foam Viscosity μ as f(ξ,φ)

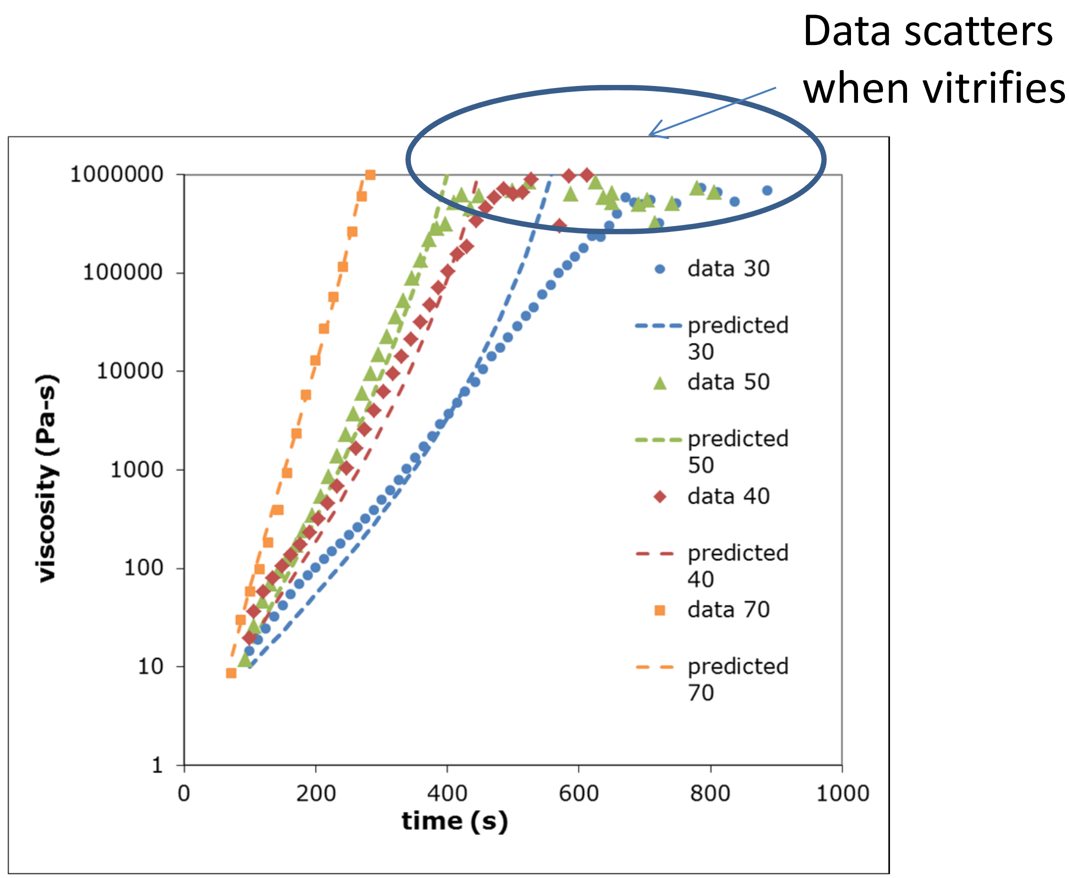
**Assume dominated by continuous phase viscosity only**

- Note this will underestimate foam viscosity at early times (μ ↑ as ϕ ↑)
- IR kinetics + dry formulation rheology (two sets of experiments) give an approximation of the curing continuous phase rheology
- Relate time of vitrification to ξ to find $\xi_c$ as f(T), consistent with cure kinetics equation

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

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



# 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:**

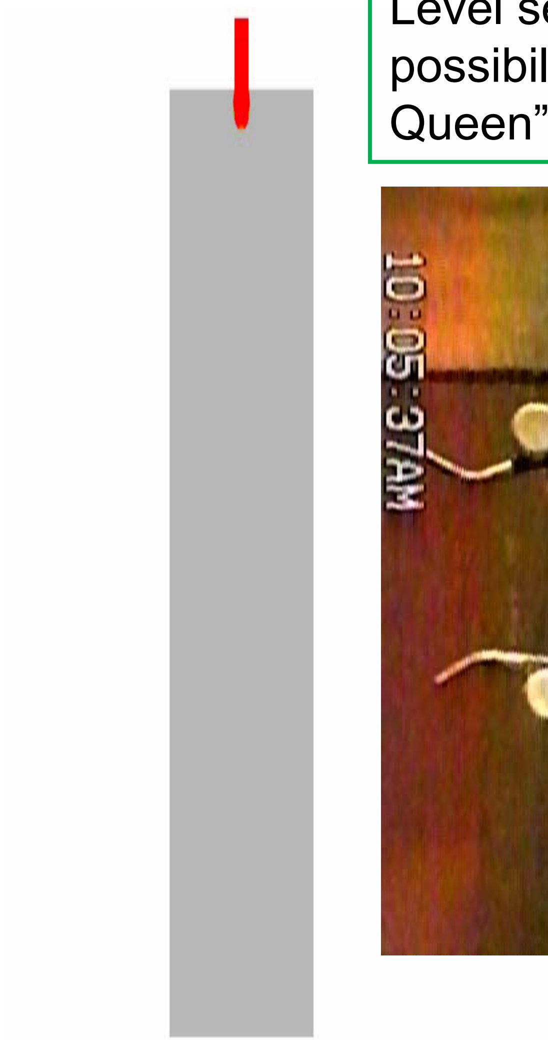
- Interface reconstructed from higher dimensional function
- Fixed mesh
- "Diffuse" interface physics
- Interface deformation theoretically unconstrained

**Examples:**

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

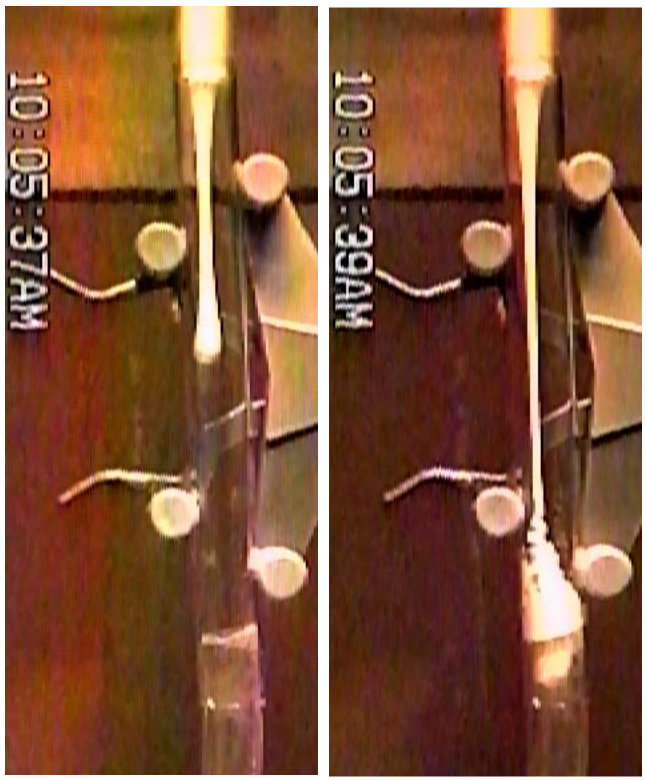
PA Sackinger, PR Schunk, RR Rao, "A Newton-Raphson pseudo-solid domain mapping technique for free and moving boundary problems: A finite element implementation," *J. Comp. Physics*, 125, 83, 1996.

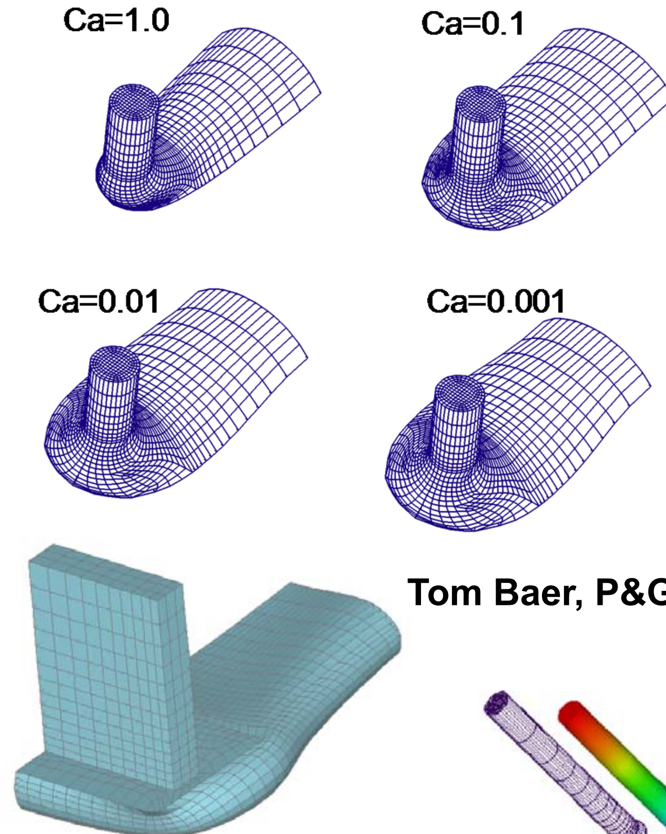
# Embedded Interface Methods Can Capture Topological Changes



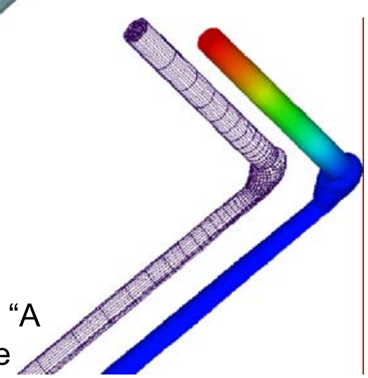
Scott Roberts, SNL

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




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.

# 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.

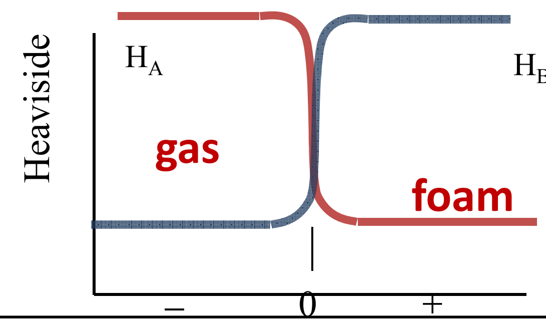
- Equations of motion, kinetics and energy balance averaged based on level set, ϕ

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

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

$$H_A + H_B = 1$$

Rao et al, IJNMF, 2012



# 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

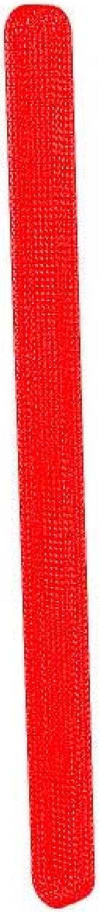
$$\underline{\underline{A}}\,\underline{x} = \underline{b}$$

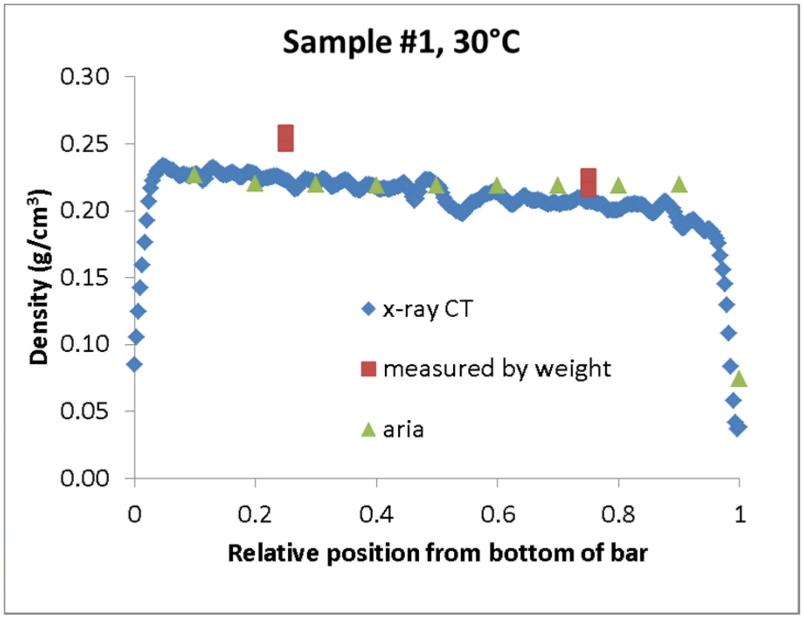
- Issues: Linear system solved with Krylov-Based iterative solvers => require stabilization Dohrman-Bochev Stabilization (2004)

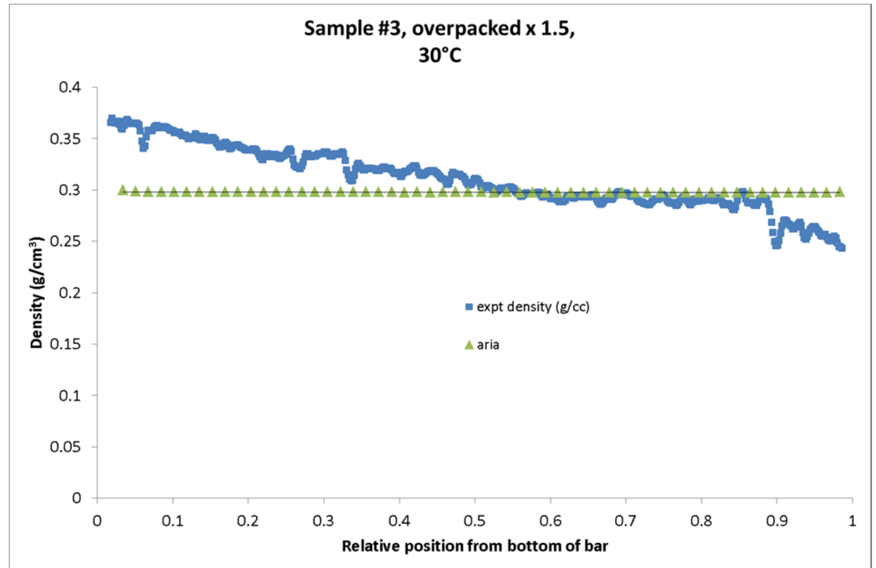
$$R_i^c = \int_D \phi^i [\nabla \cdot u] dV + \sum_{Elem} \tau_{pspp} (\phi^i - \pi\phi^i)(p - \pi p) dV$$

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

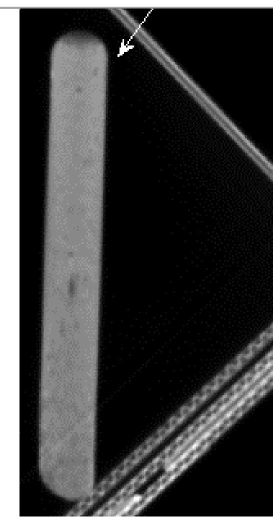
# Structural Foam Density Predictions





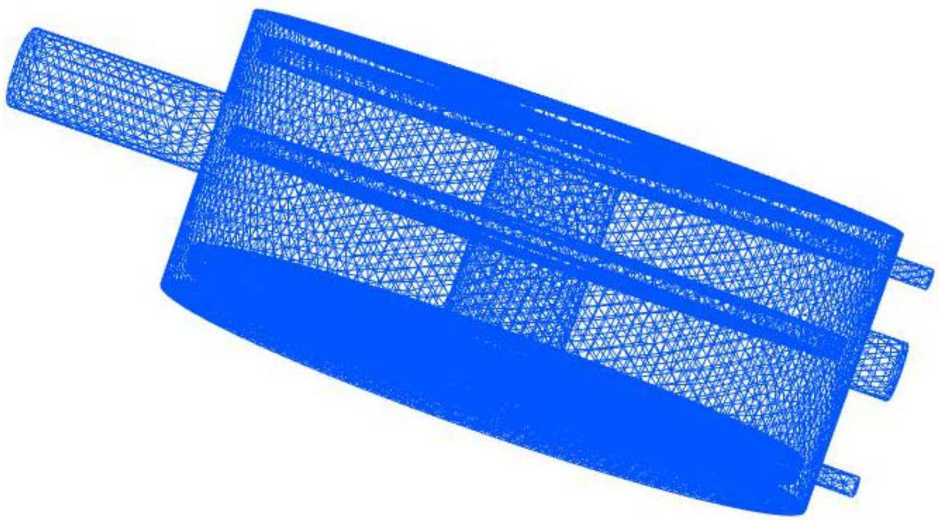

Density for PMDI-10 foam free rise at 30$^{o}$C : x-ray CT, weight measurement, and Sierra Aria run



X-ray CT of PMDI-10 foam free rise at 30$^{o}$C

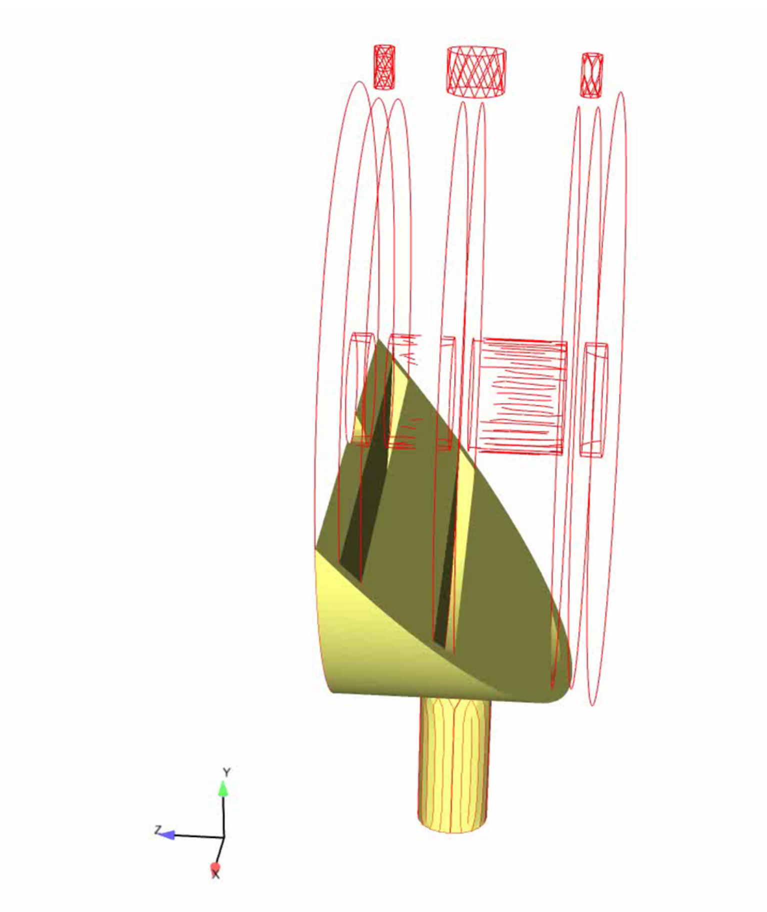
- Density predictions for free rise and over packed foam
- Model under predicts gradients, especially for over packed foam
- Is foam drainage and important phenomena?

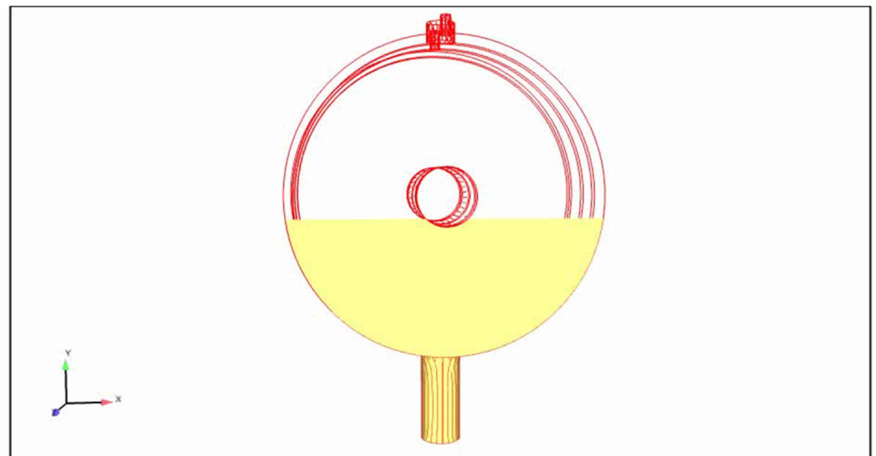
# Idealized Foam Encapsulation Part: Board Would Contain Electronics in Real Part

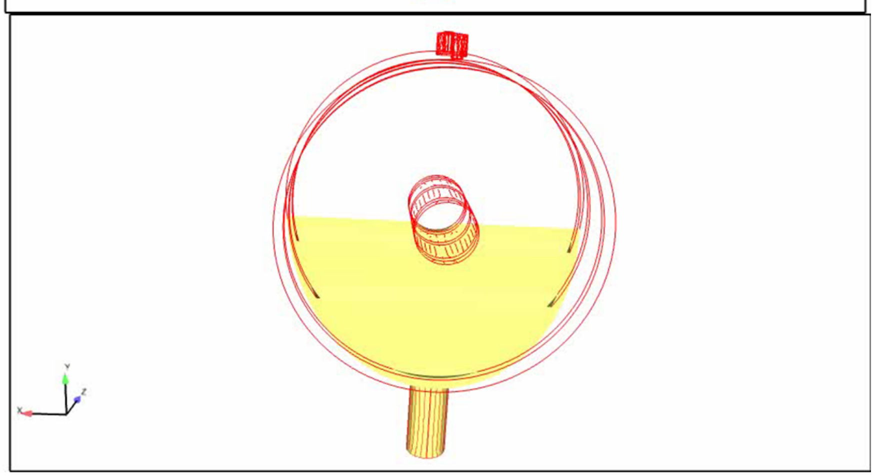


- Mold is preheated to ten degrees hotter than the foam
- Inflow is asymmetric and fills thinner area first
- Boards have different thicknesses of foam
- Three vents are used to improve filling
- Foam slips at the wall using a Navier slip condition with Beta = .001
- Gas slips ten times more than the foam

# Foam Filling Simulation of Complex Part with Plates

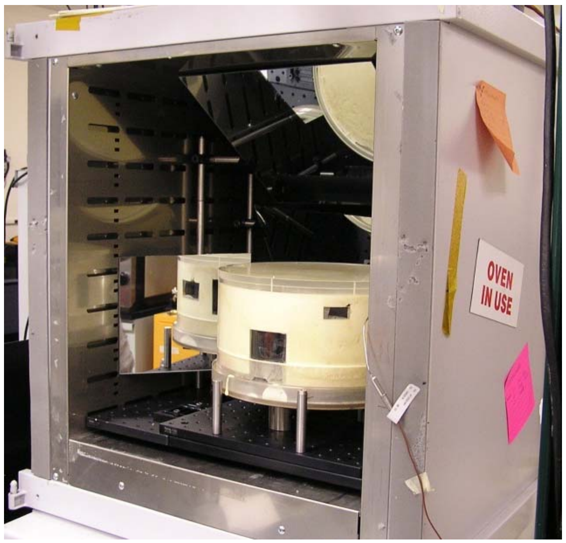


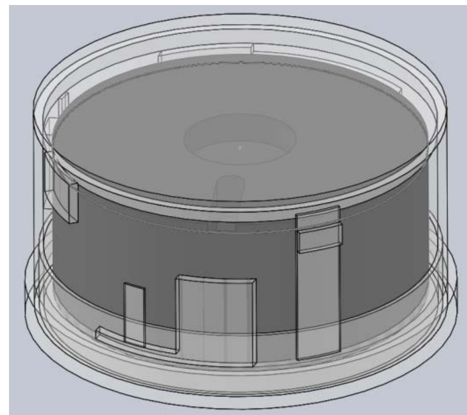


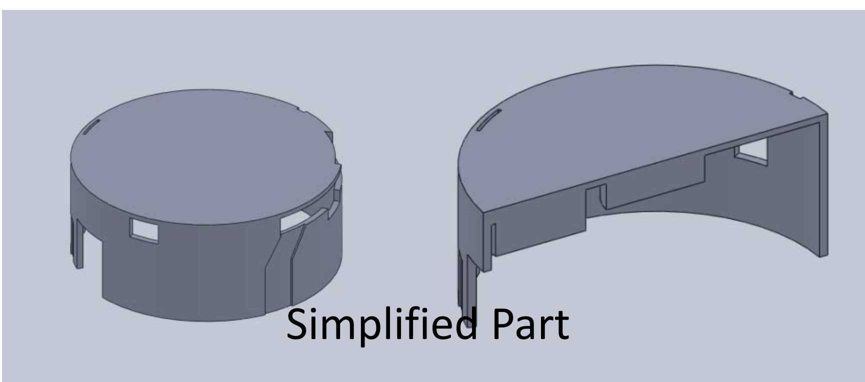


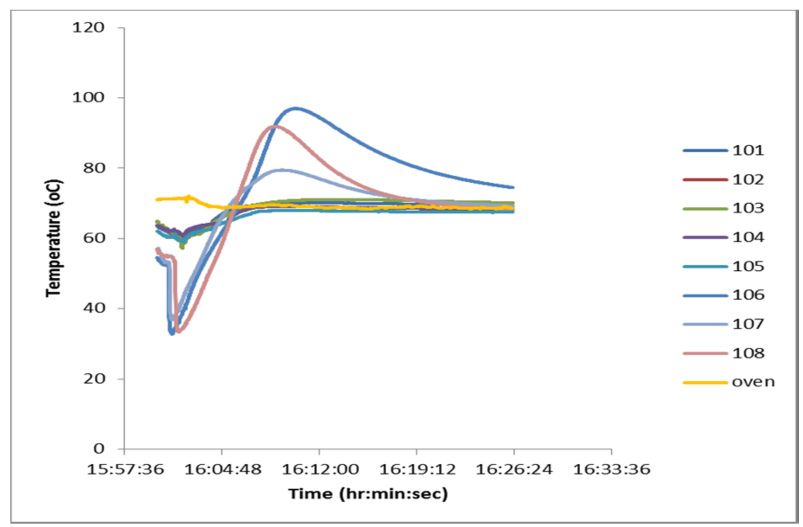
# Simplified Structural Support Mold Tests

- 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



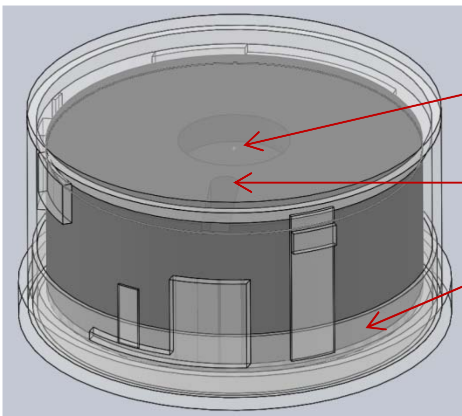





# Simplified Structural Support Mold Test 1

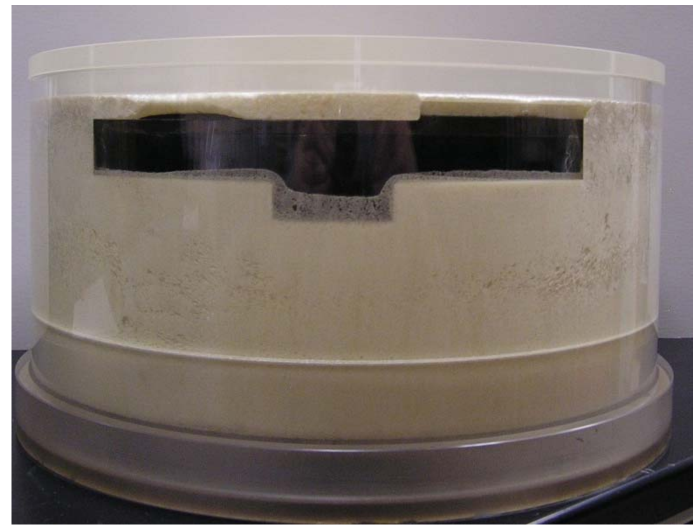
- First try filled using slower reacting encapsulation foam
- Used 10 pcf free rise encapsulation PMDI foam at a quantity to produce a 14 pcf part
- Pre-heated mold to 65C, room temp foam kits (typical for encapsulation)
- Scheme to fill around bottom reservoir and top cavities
- Temperature instrumented with four camera views



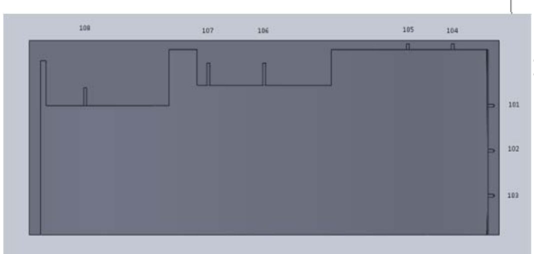
Cavity B (poured)

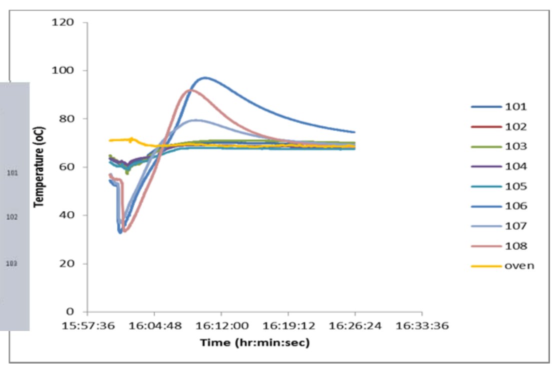
Cavity A (poured)

Bottom reservoir (syringe)



Last place to fill is above large feature on opposite side of mold from Cavity A

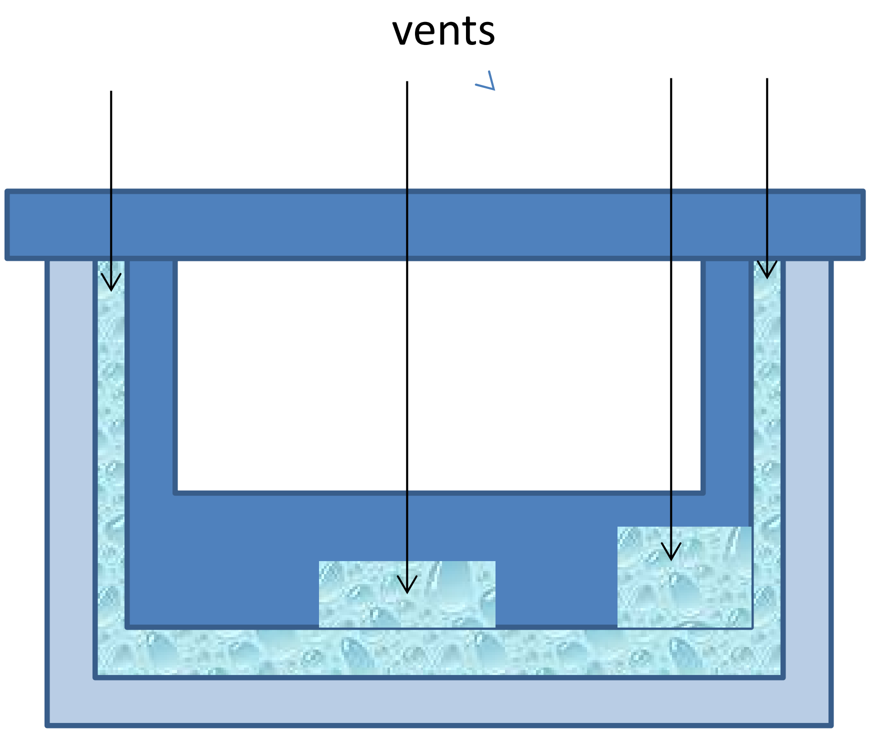


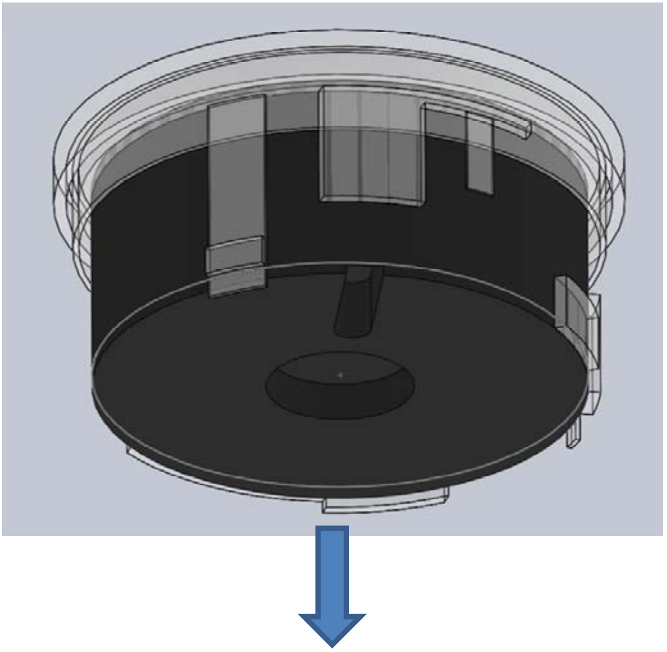



Temperature measurements provide model validation data

# Simplified Structural Support Mold Test 3

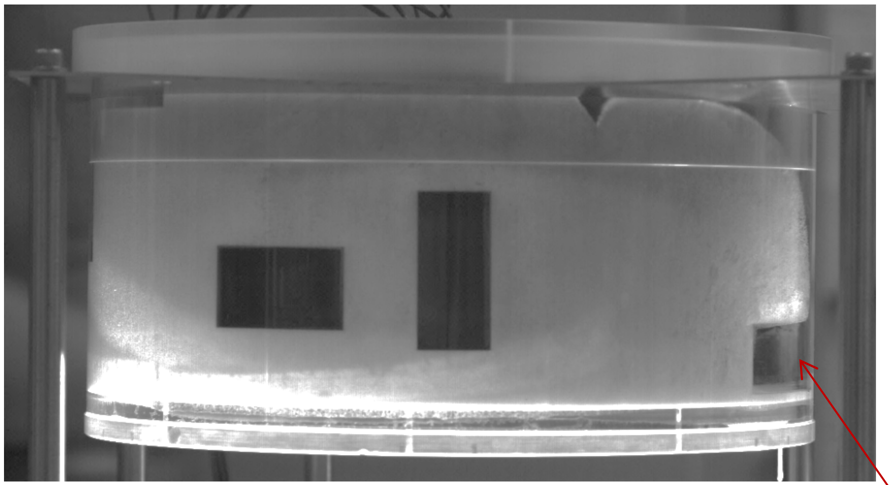
- Used 10 pcf free rise structural PMDI foam, filled to produce a 13 pcf part
- To speed up process and slow down foam reaction rates:
  - No preheats
  - Mixed 30 seconds instead of 1 minute
  - Pour all foam into one reservoir, the lid of the upside down part
- Temperature instrumented with four camera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

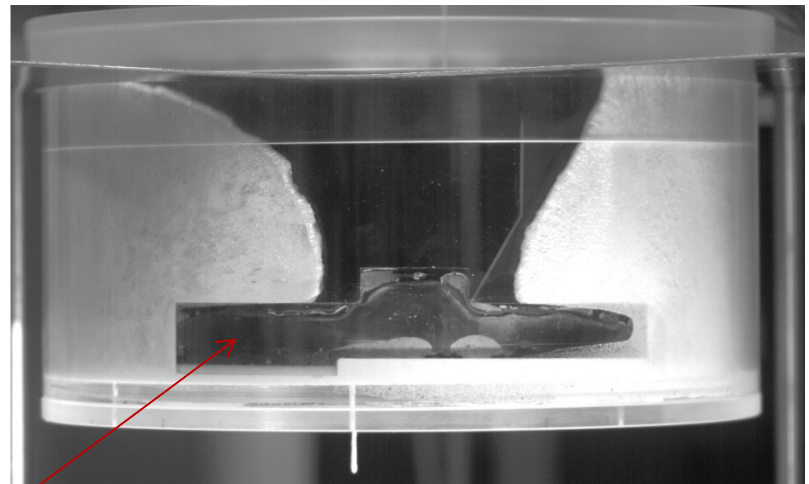


Push inside mold down into bowl that once was the lid

# Last Place to Fill Now on Other Side of Largest Feature

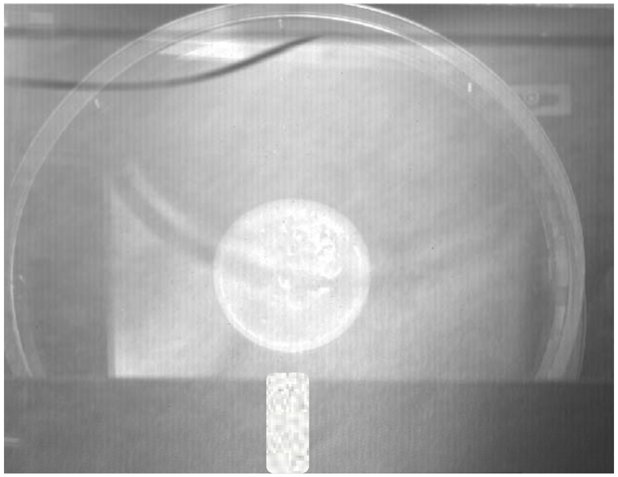




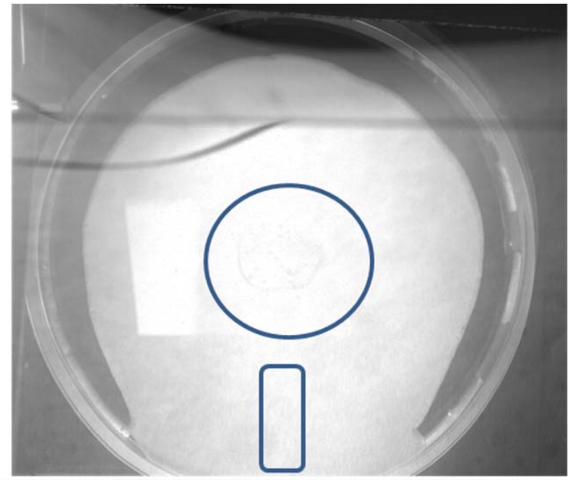
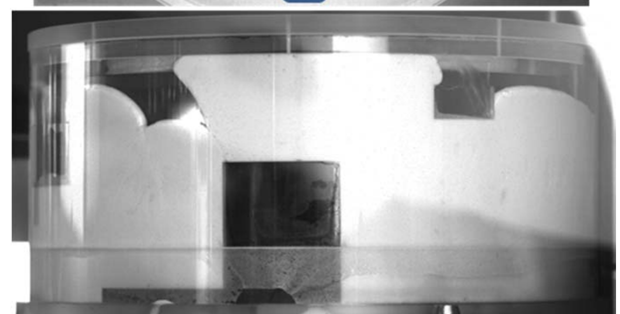
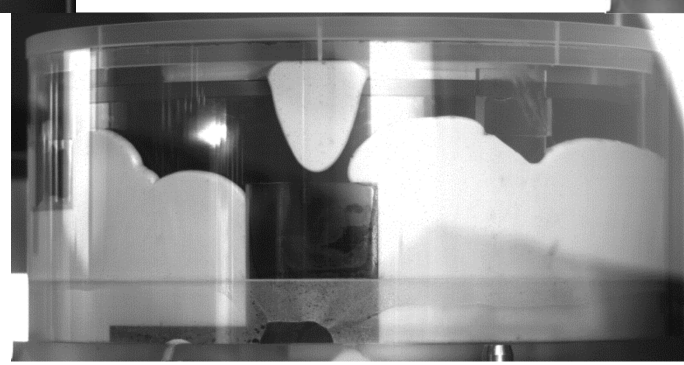
Largest feature

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

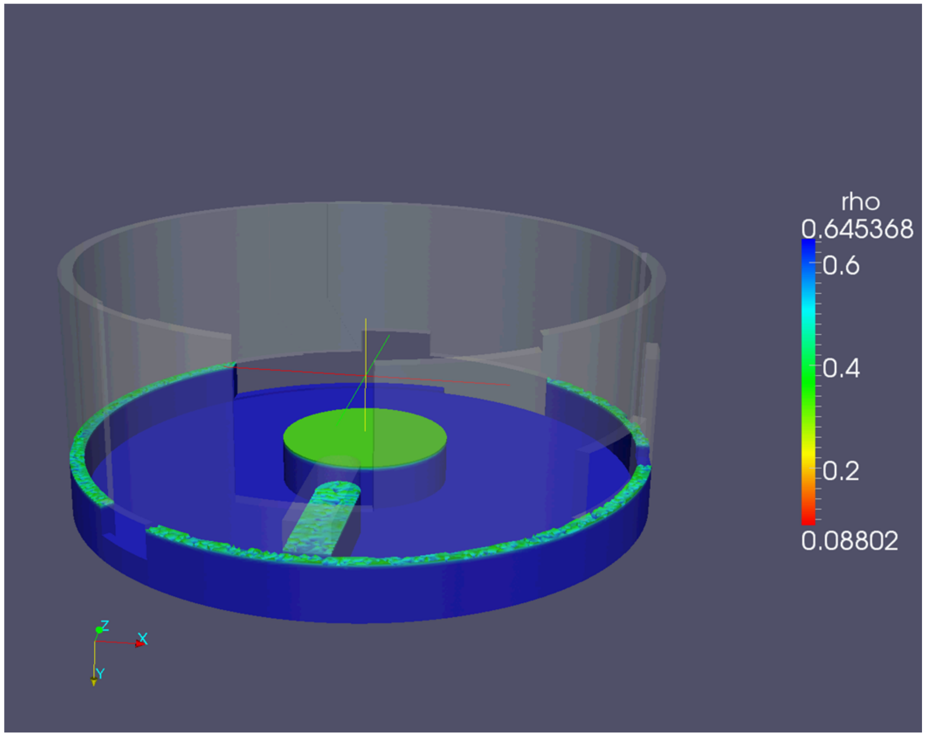
# Filling Method Creates Knit Lines

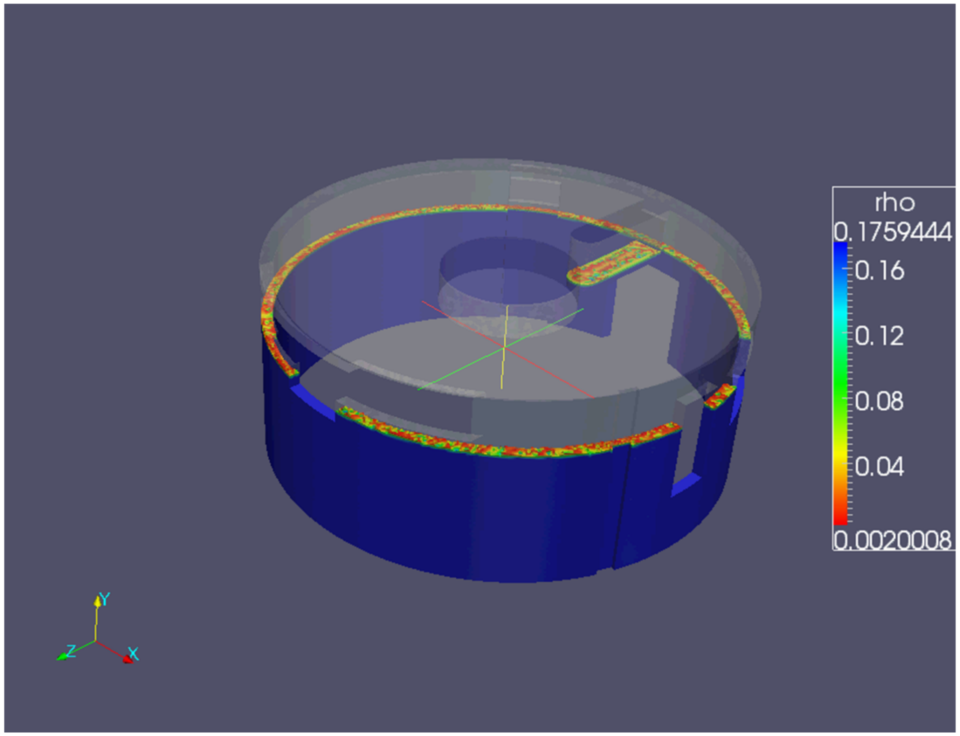



Foaming material is originally placed in top rectangular and cylindrical reservoirs and in bottom rim reservoir, to simulate legacy KC filling method

# Computational Modeling of Filling of Complex Mold

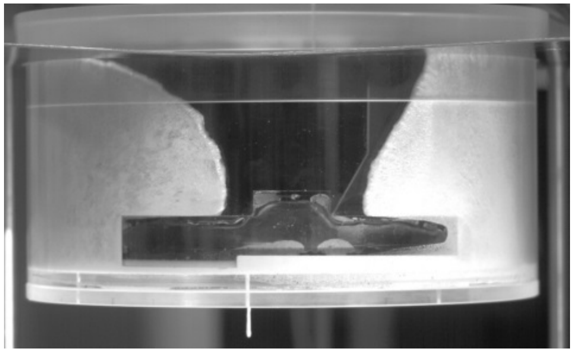


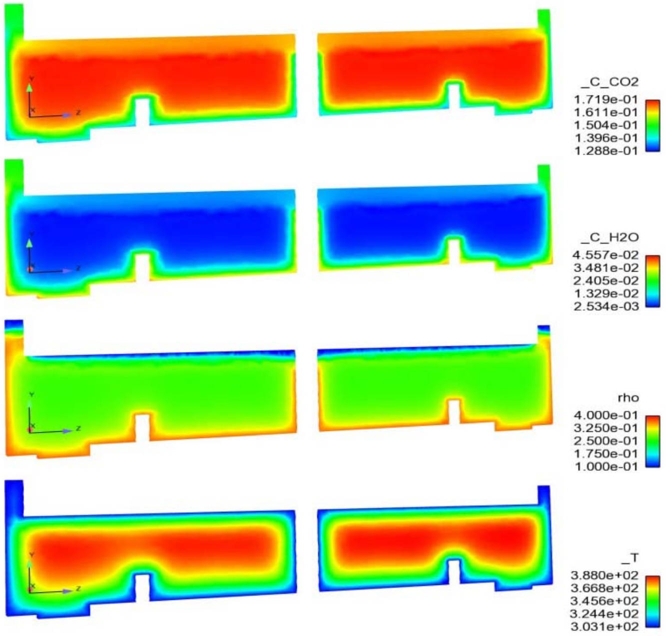



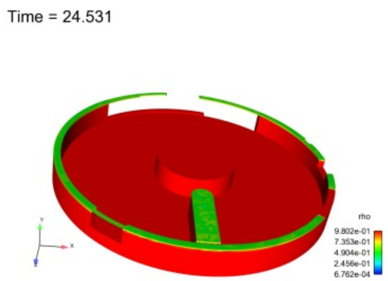
# Model Give More Physics than Just the Filling Locations

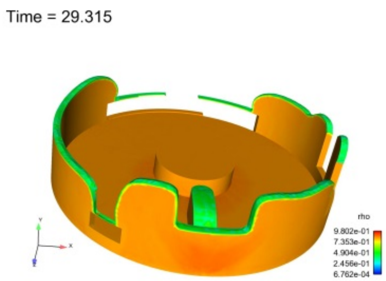
Models developed for foam filling and curing
=> density/cure

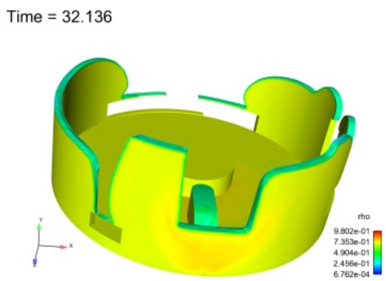
- The model allows us to look inside the mold
- New kinetics show water depletion and $CO_2$ variations
- Density variations are seen in the mold
- Foam exotherms significantly even and early times

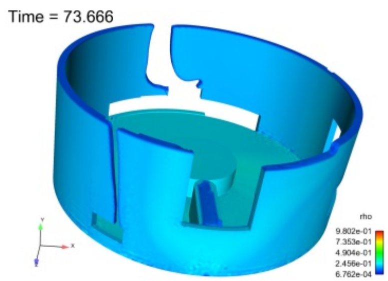




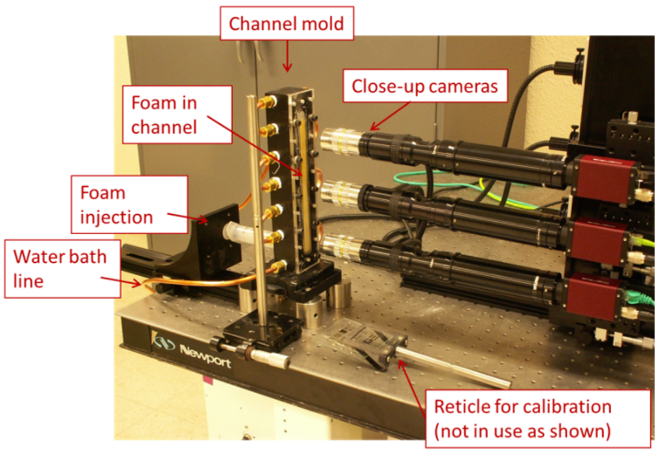



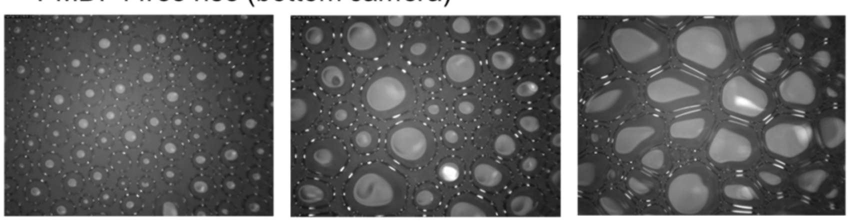



# Study of the Evolution of Bubble Size

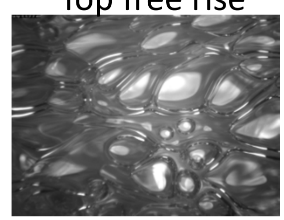



- Three cameras record bubbles at transparent wall (top, middle, and bottom of a column) as foam fills the column
- Light area in pictures below are where the wall is wetted by the bubble – edges are dark lines dashed with bright spots (makes difficult to automatically analyze)
- Image processing developed to analyze – checks by hand shows software good until late times when the bubbles distort severely
- Bubbles nominally about 200-300 microns in diameter
- Size and shape evolve in time, depend on temperature, foam density
- Over packing the foam helps keep the bubbles small and round
- Under packed foam often ends up with highly distorted bubbles near leading front

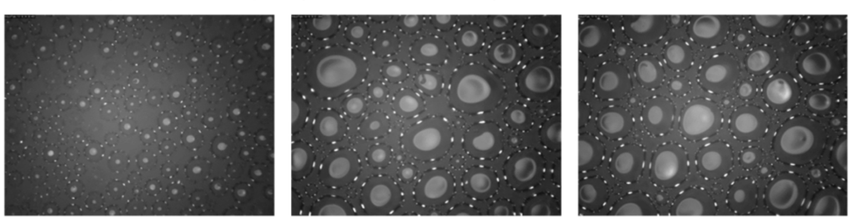
PMDI-4 free rise (bottom camera)



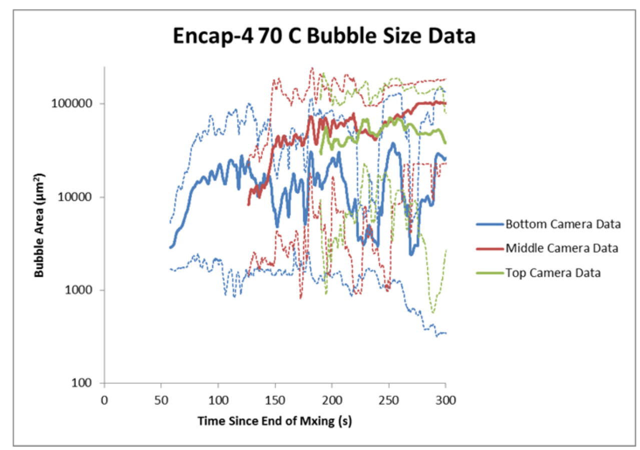
Top free rise



PMDI-4 packed to 8pcf (bottom camera)



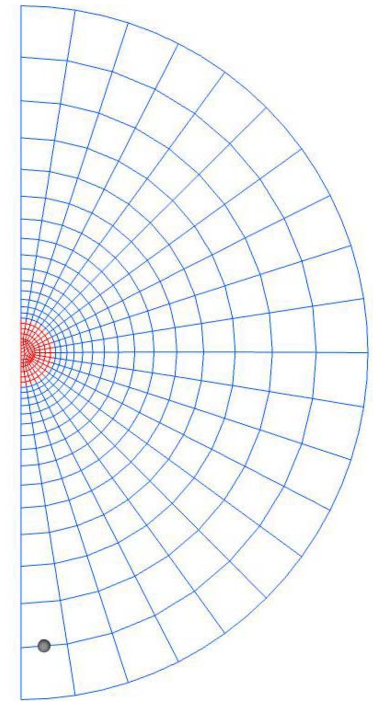
Time=79.5 s Time=152 s Time=266 s since end of mixing

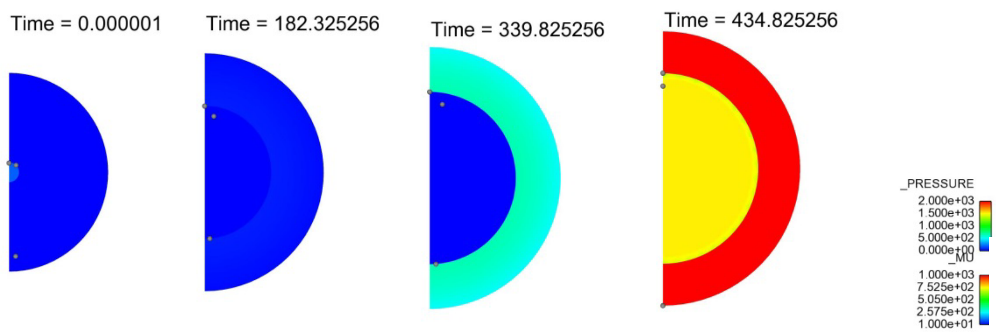


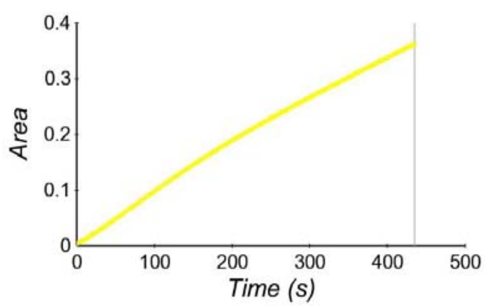

Results of image processing. Solid lines are mean value. Dotted lines indicate top and bottom 10% of values to indicate spread.

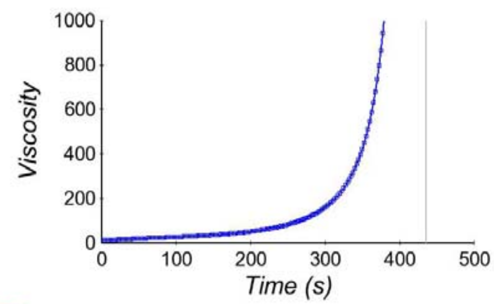
# Bubble Expansion in a Polymerizing Fluid

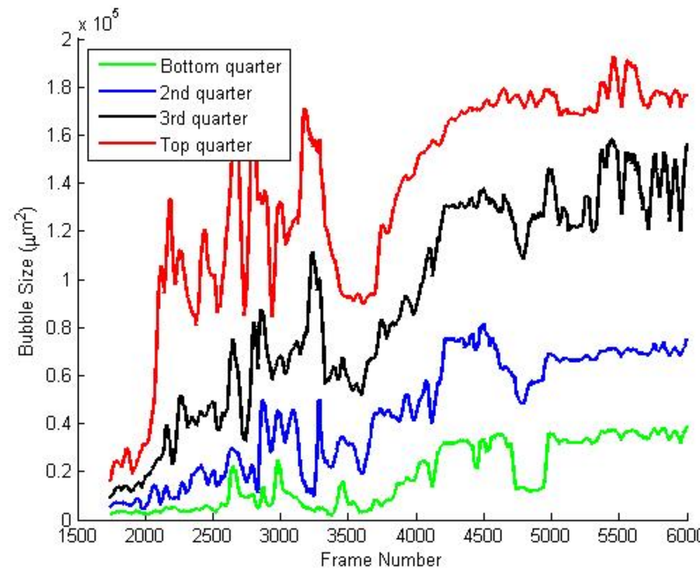
- Bubble grows as $CO_2$ enters the bubble
- Growth is halted abruptly once the polymer reaches the gel point and the viscosity diverges
- Post-gelation, bubble pressurization is observed
- ALE mesh is robust over shape change
- Data shows the correct trends when compared to experiment





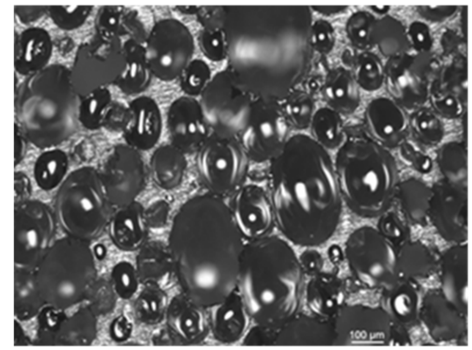
# Conclusions and Future Work

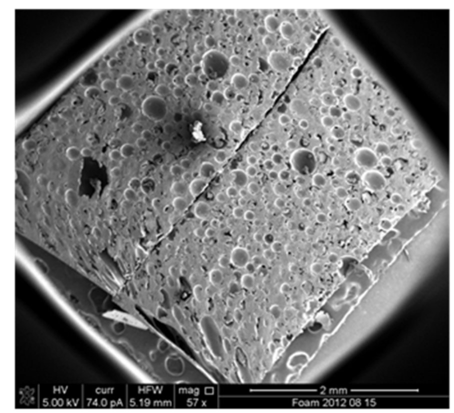
- **Current model is adequate for production calculation**
  - Determining metering, initial placement, voids, gate, and vent location
  - Investigate encapsulation of new geometries of interest
  - Current model is "first order." We are working to make the model more predictive
- **Next generation model need to include**
  - Equation of state for density approach for gas phase
  - Two-phase $CO_2$ generation model: solubilized $CO_2$ in the polymer and $CO_2$ gas in the bubbles
- **Include local bubble size and bubble-scale interactions**
  - Predict bubble size with Rayleigh-Plesset equation

$$\rho\left(\frac{3}{2}\dot{R}^2 + R\ddot{R}\right) = p_{gas} - p_{liq} - 2\frac{\sigma}{R} - 4\eta_{polymer}\frac{\dot{R}}{R}$$

  - From the bubble size and number density, predict foam density
  - Bubble-scale modeling to include gelation and gas pressure in density model to make it more predictive
  - Drainage/creaming term could help make density model more representative of experiments

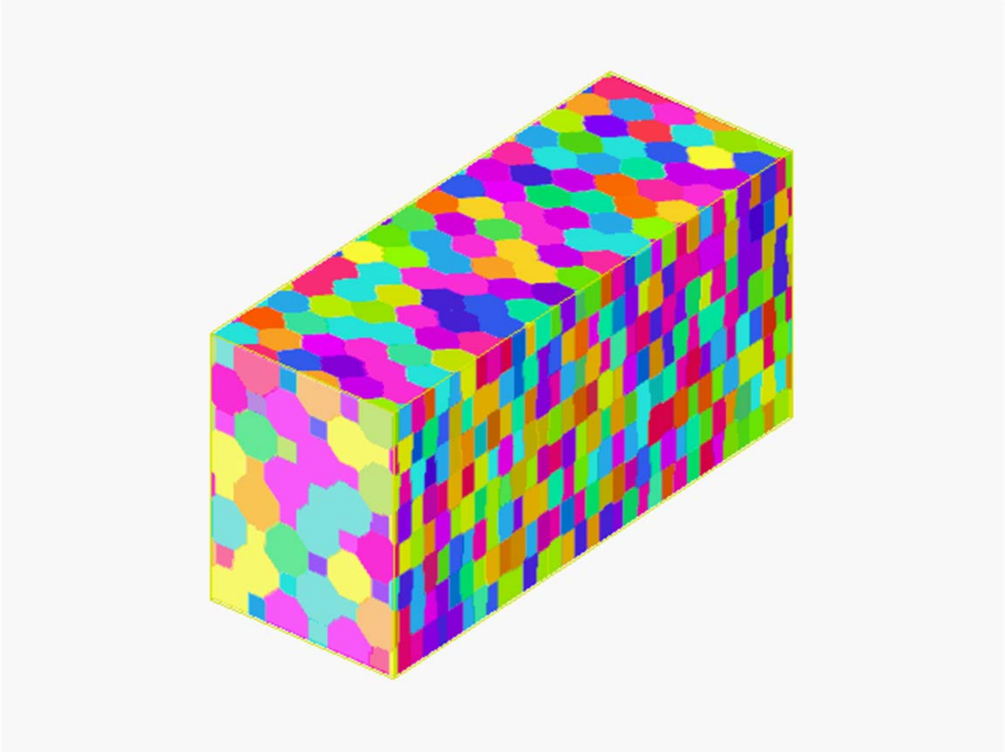
SEM of foam showing polydispersity



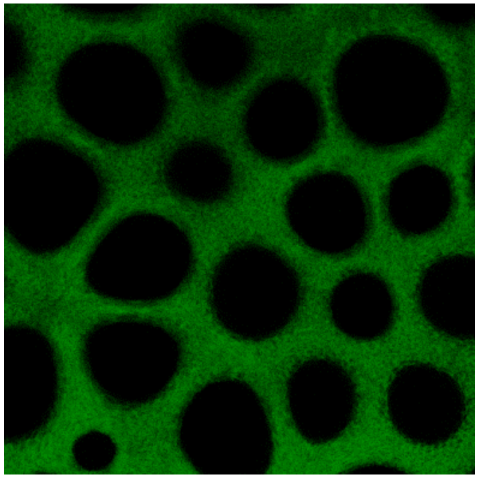


Bubble at walls are elongated and show coarsening

# Questions?



Pott's model of foam bubbles in shear flow (Veena Tikare, SNL)



Confocal image of foam showing bubble size and shape (Christine Roberts, SNL)