SAND2016-8010C

THE FLUID MECHANICS OF POLYURETHANE FOAM EXPANSION AND POLYMERIZATION

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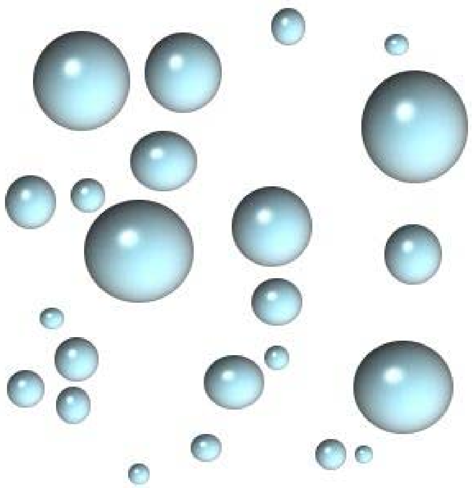
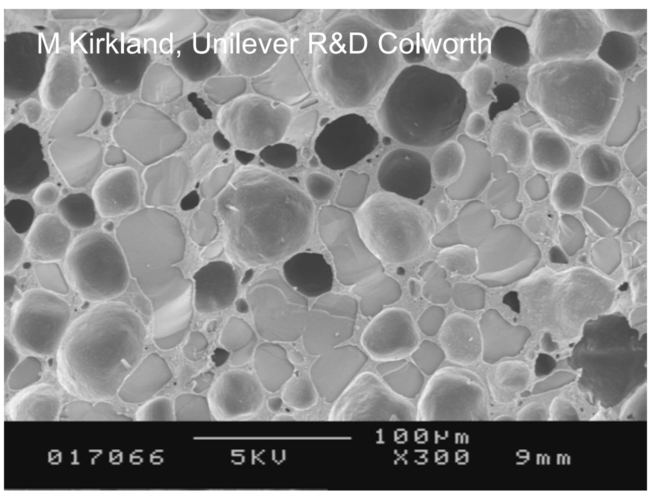
What is a Foam?

- 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

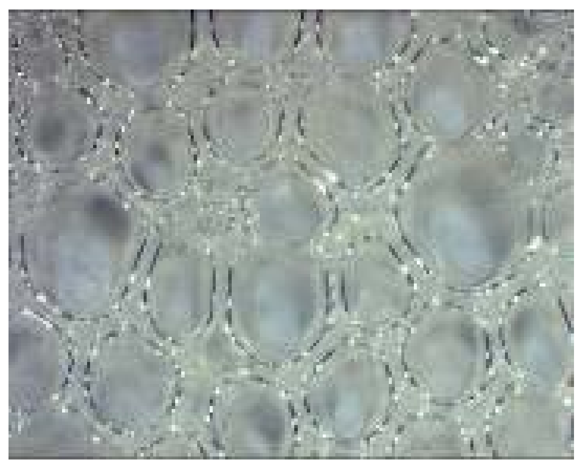


Bubbles

Whipped cream



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



Epoxy foam is a collection of bubbles in polymer

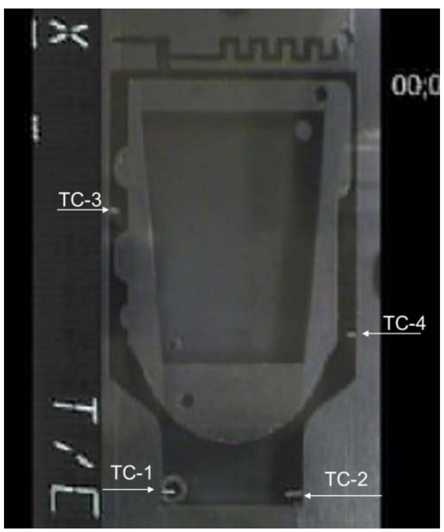
Foams need enough bubbles to jam, *e.g.* bubbles are touching or it is just a bubbly liquid

Introduction

Overarching Goal: **Cradle-to-grave model for foaming, vitrification, cure, aging**
Focus on moderate density PMDI foams

Injection, foaming and initial curing at lower T

Oven time at higher T to make sure it is fully cured



Remove from mold – predict cure and thermal stresses

Predict shape and size over years

Introduction

Stage I

Fluid

Pre-Gel
(0-10^3 seconds)

Chemistry results in both gas production (foaming) and matrix polymerization (curing)

Foaming liquid rises to fill the mold until polymer matrix gelation

Heat, pressure generated

Gelation

Stage II

Soft-Solid

Post-Gel Cure
(10^3– 10^4 seconds)

Variations in temperature cause variations in density and extent of cure

Solid polymer matrix locks in density gradients

Further gas production causes bubble pressurization with minimal volume increase

Vitrification

Stage III

Solid

Vitrified and Released
(10^4 + seconds)

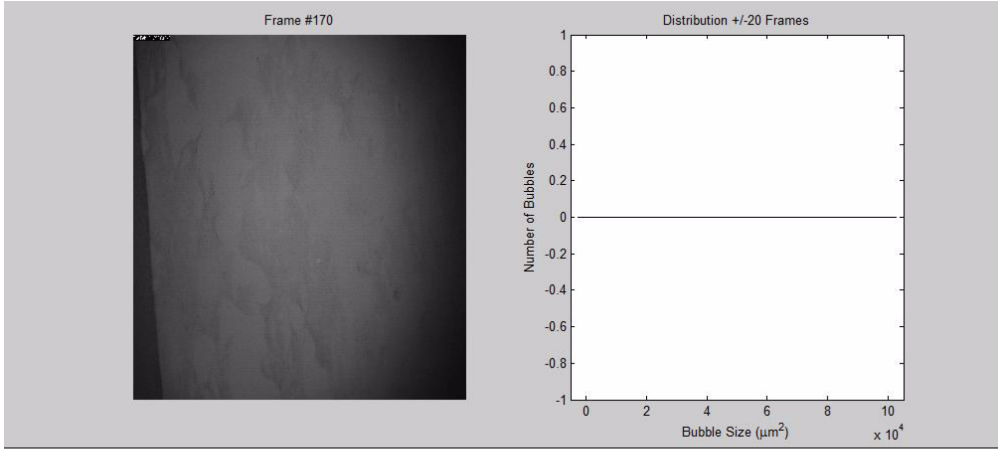
Residual stresses, density, and properties vary spatially

Both long and short term shape change is possible as different parts of the foam relax at different rates

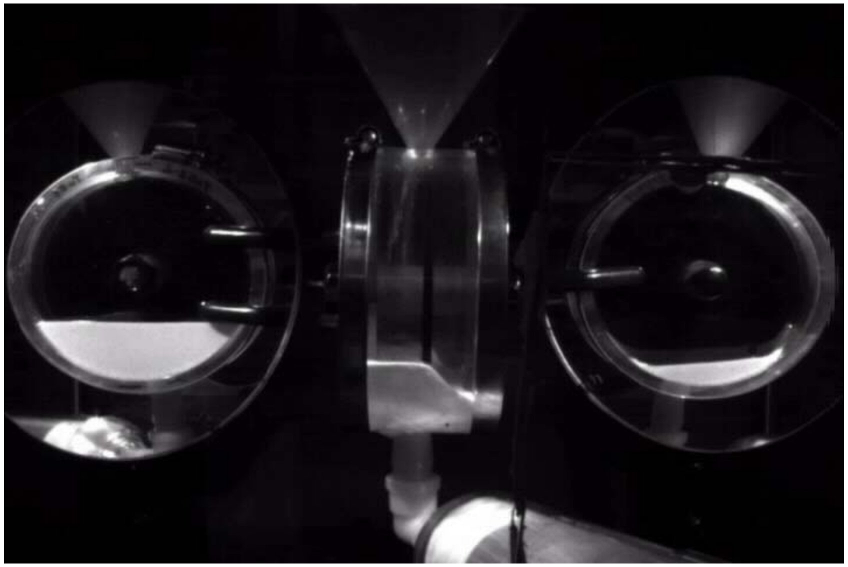
Boundary conditions strongly influence residual stresses

- Processing parameters at earlier stages will affect quality of part at later stages

Foam Filling is Complex



Foam front moving past camera, with bubble sizes at transparent wall determined with image processing.



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

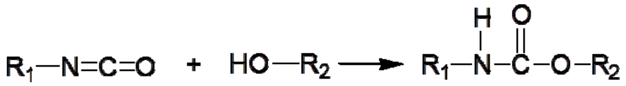
- PMDI is used as an encapsulant for electronic components and lightweight structural parts, to mitigate against shock and vibration.
- **We would like to develop a computational model to help us understand foam expansion for manufacturing applications and how inhomogeneities effect the structural response of the final part, including long term shape stability.**
- 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.

Polyurethane (PMDI): Model Development

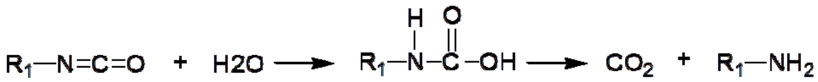
- We use a variety of physically and chemically blown foams. PMDI is used as an encapsulant for electronic components, to mitigate against shock and vibration, and to make light-weight structural parts.
- We would like to develop a computational model to help us understand foam expansion for manufacturing 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 polymerization. IR does not provide a clear signal for the foaming reaction: Tracked with volume generation.

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

Two key reactions: Isocyanate reaction with polyols and water

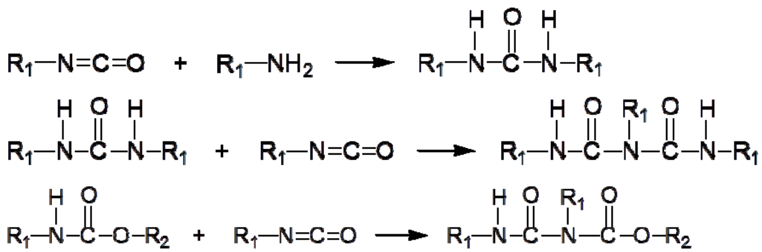


Urethane formation, crosslinking



Foaming reaction yields CO_2 and amine

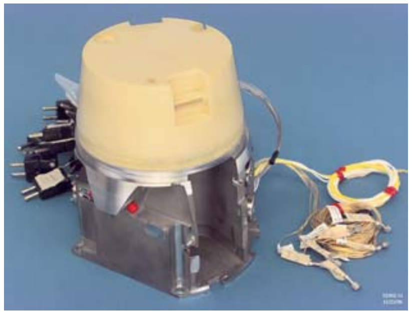
Various follow up reactions: Isocyanate reaction with amine, urea and urethane



Urea formation

Biuret formation

Allophanate formation



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

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
- Our kinetics are unique because our formulation is different from literature polyurethanes

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

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

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

Equations 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

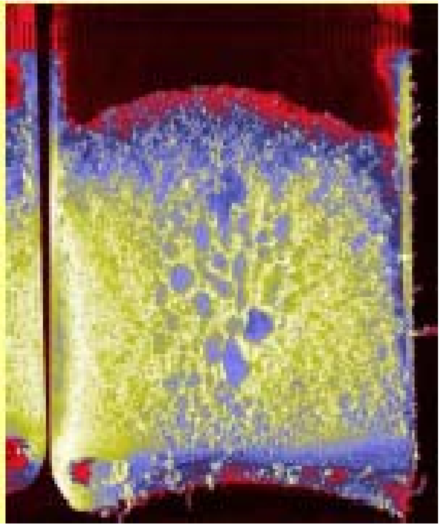
$$\frac{\partial \xi}{\partial t} = \left(\frac{1}{(1+wa)^{\beta}} \right) \left(k_0 \exp\left(-\frac{E}{RT} \right) \right) \left(b + \xi^m \right) (1-\xi)^n$$

Molar concentration equations for water and carbon dioxide

$$\frac{dC_{H_2O}}{dt} = -k_{H_2O} C_{H_2O}^n \qquad C_{H_2O} = \frac{\rho_{foam} x_{H_2O}}{M_{H_2O}}$$

$$\frac{dC_{CO_2}}{dt} = +k_{H_2O} C_{H_2O}^n \qquad C_{CO_2} = \frac{\rho_{foam} x_{CO_2}}{M_{CO_2}}$$

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



NMR imaging shows coarse microstructure (Altobelli, 2006)

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

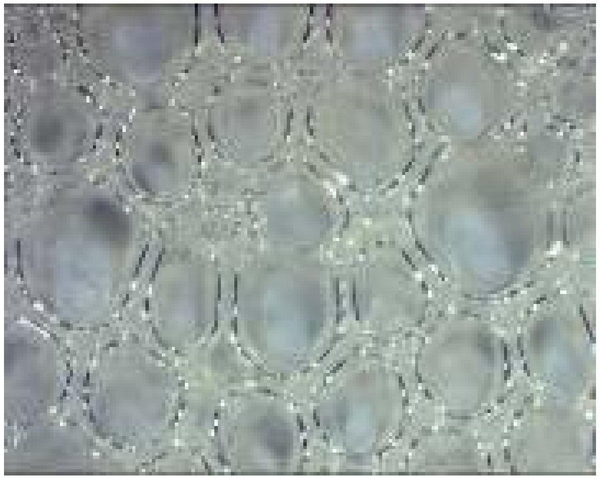
Foaming reaction predicts moles of gas from which we can calculate density

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

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

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

Compressibility built into this model via the ideal gas law for gas density



Foam is a collection of bubbles in curing polymer

Thermal properties depend on gas volume fraction and polymer properties

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

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

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

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

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

- 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)

M. Mooney, *J. Colloid Sci.*, **6**, 162-170 (1951).

Gibson, L. J.; M. F. Ashby. Cambridge University Press, Cambridge, UK, 1990

Extent of Reaction for Polymerization

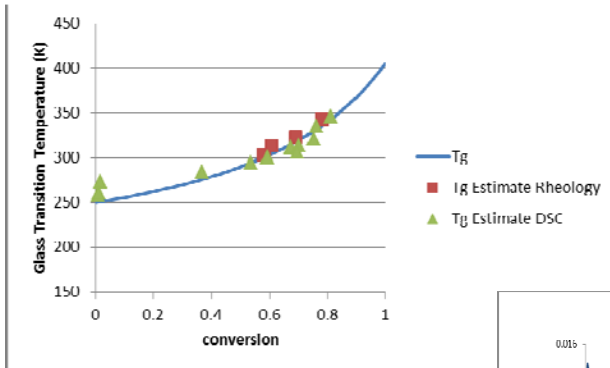
- Fit the rate and the extent of reaction to IR data to a standard equation form
- Fit T_g to both rheology and DSC data: T_g changes as cure progresses making this complex

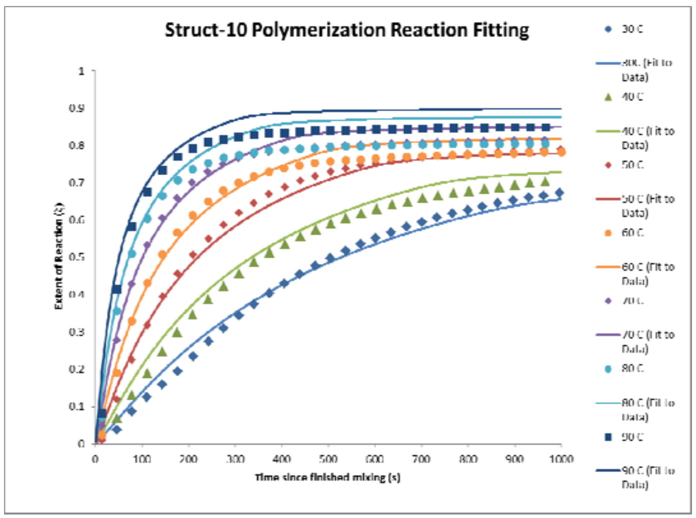
$$\frac{\partial \xi}{\partial t} = \left(\frac{1}{(1+wa)^{\beta}}\right)\left(k_0 \exp\left(-\frac{E}{RT}\right)\right)\left(b+\xi^{m}\right)\left(1-\xi\right)^{n}$$

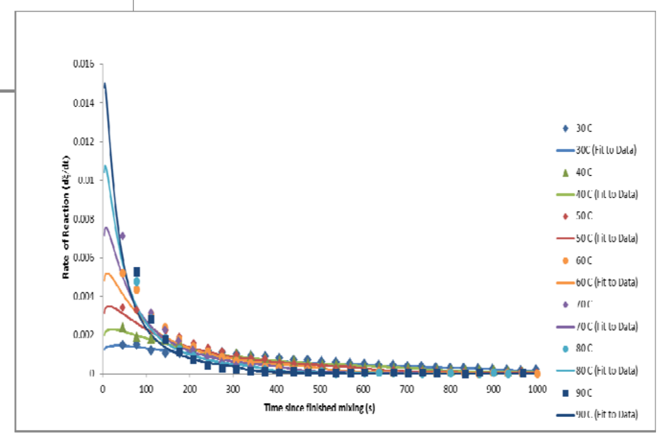
$$\log_{10} a = \frac{-C_1\left(T-T_g\right)}{C_2+T-T_g}$$

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

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







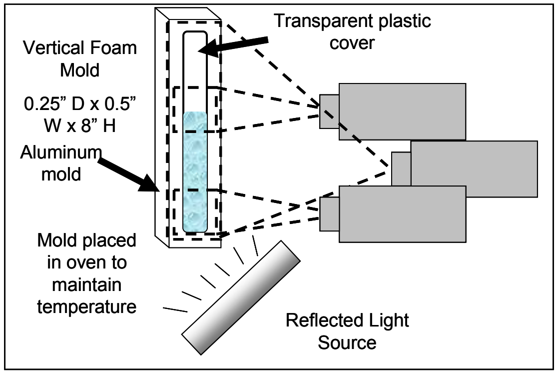
Rate and extent of reaction fit to data, where parameters of the model, including Tg are optimized for lower temperatures expected in the process. The apparent time-to-gel from rheology is correlated with extent to give a Tg with conversion. Similar analysis can be done with DSC and results are consistent.

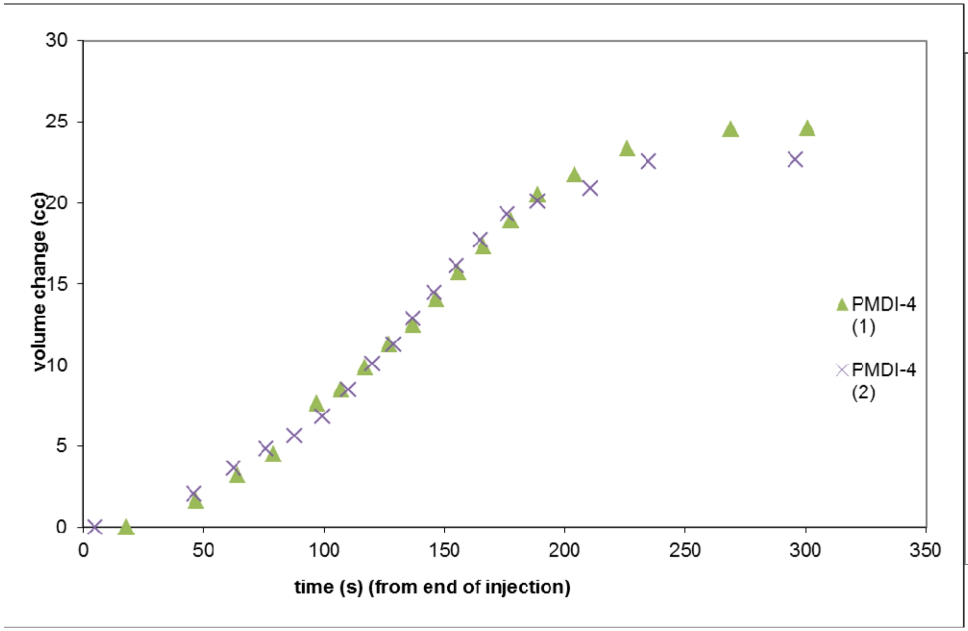
Kamal, M. R., and S. Sourour, *Poly. Eng. Sci* (1973)

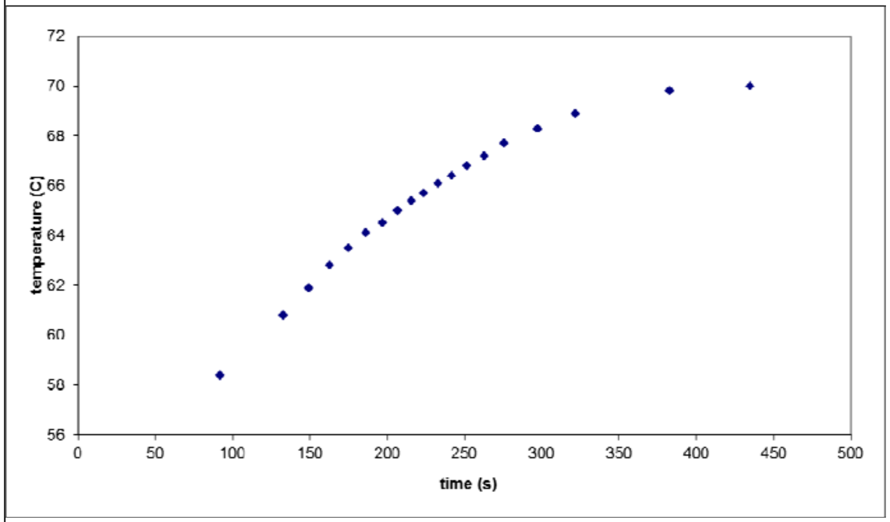
A.T. Di Benedetto, *J. Polymer Sci., Phys.*, **25,** 1949 (1987).

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.

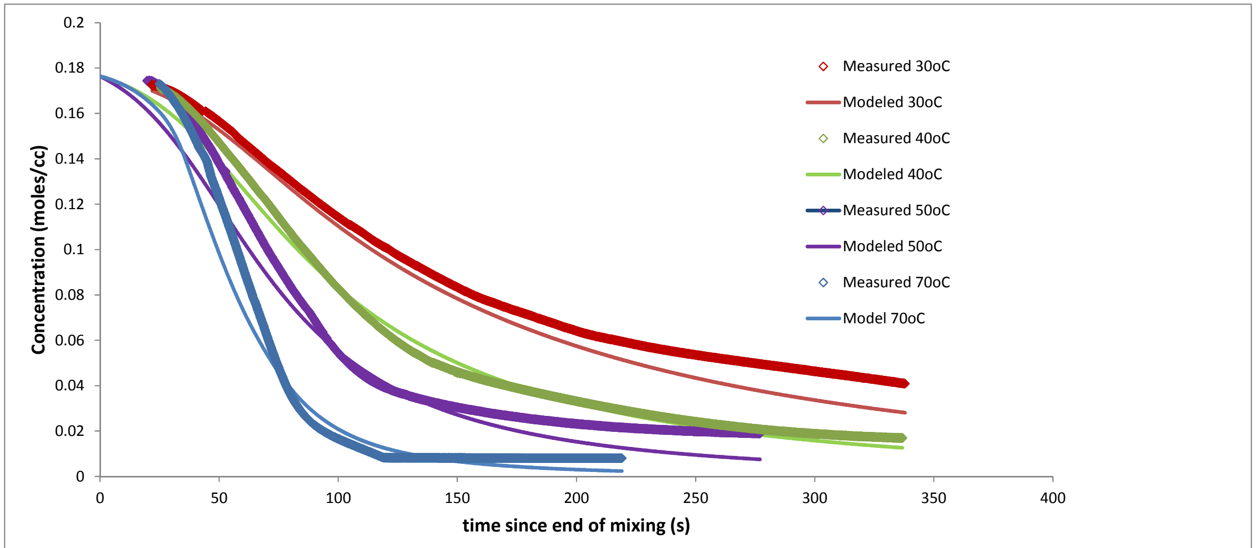


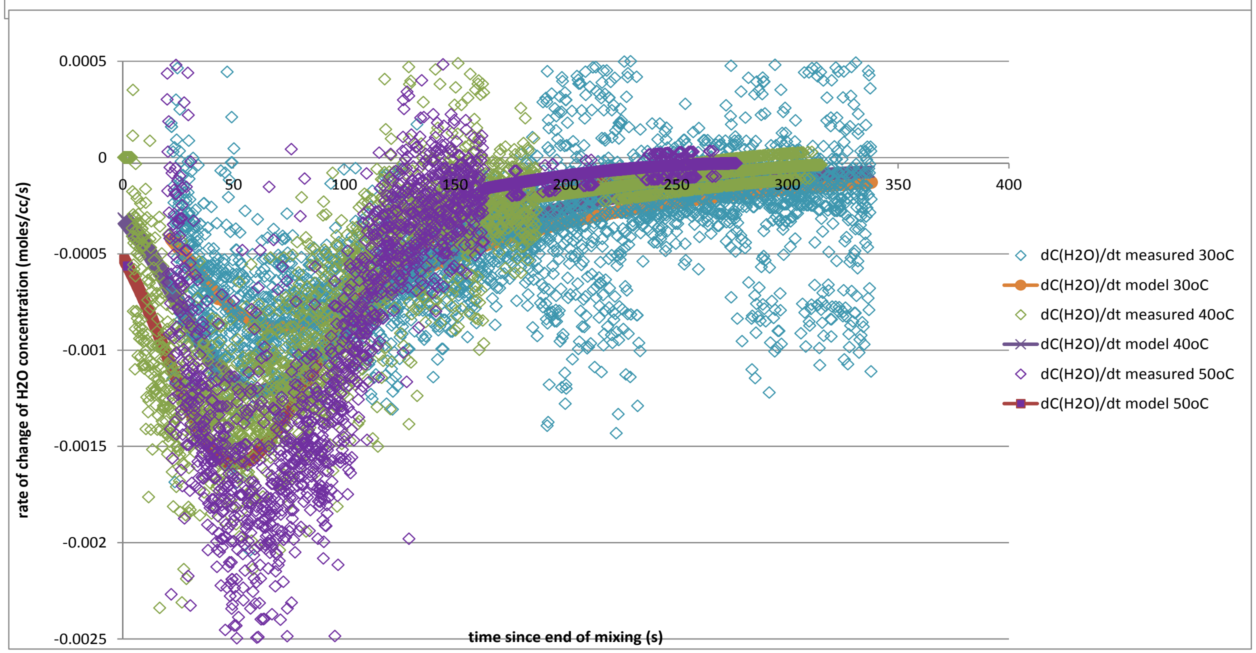




Kinetics of CO_2 Generation

- Fit the concentration of water and its rate of disappearance simultaneously





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

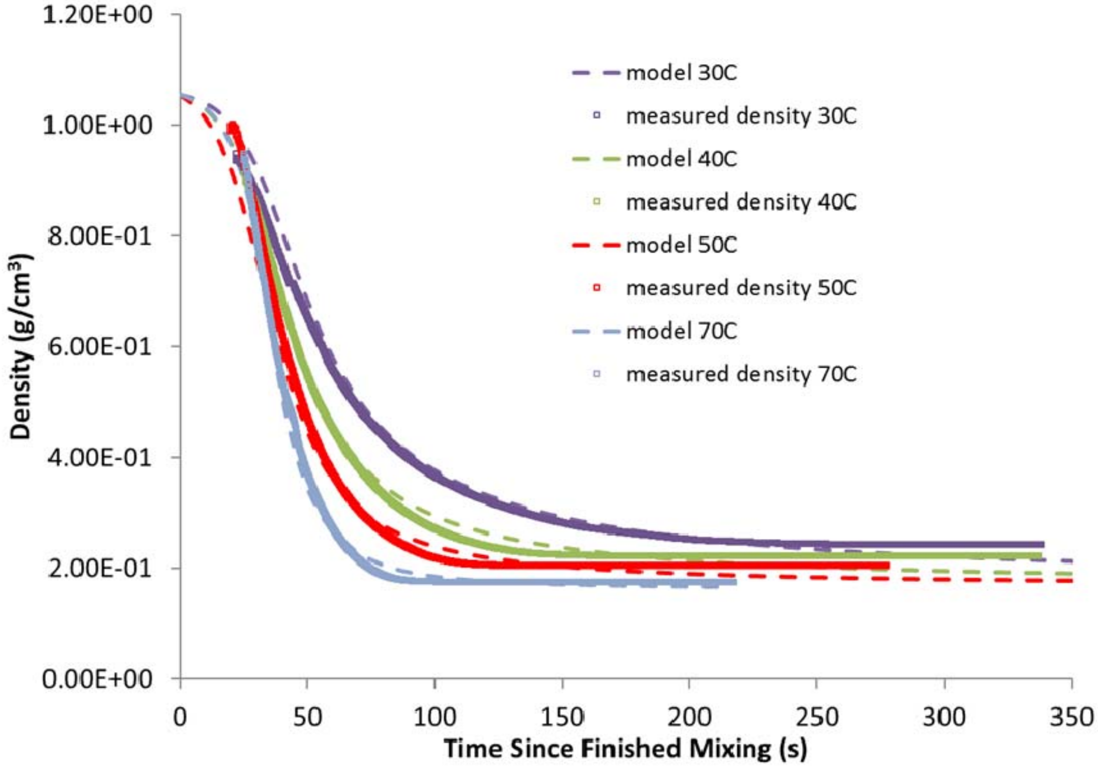
$$\frac{dC_{CO_2}}{dt} = +Nk_{H_2O}C_{H_2O}{}^{n}$$

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

- Apparent water concentration shows a change in slope
- Model must capture this
- Physically it relates to the solubility of the carbon dioxide in the polymer
- Must super saturate before nucleation and growth

Kinetics of CO_2 Generation

Predictions of density using a nucleation time of 40s and a time scale of 20s compared to measured density with time in the channel for various temperatures.



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

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

- Experiments give us average density
- Hard to determine evolving density gradients
- Measure density gradients from post-test experiments

Rao et al., "Polyurethane kinetics, for foaming and polymerization" submitted , *AICHE Journal*., June 2016

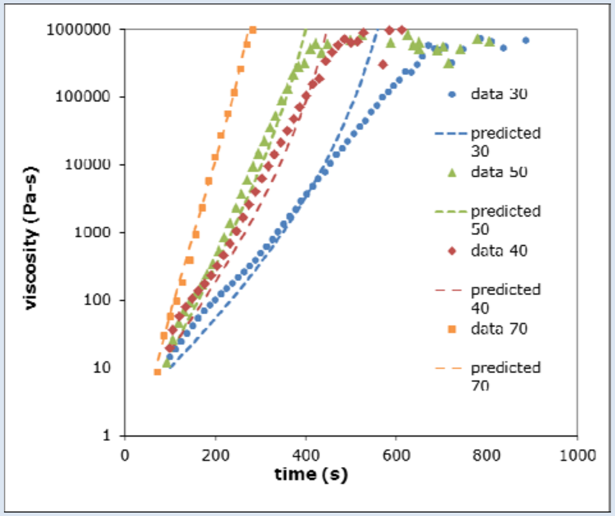
Model Foam Viscosity as f(ξ,ϕ)

Start with continuous phase viscosity only

- IR kinetics + dry formulation rheology (two sets of experiments) give an approximation of the curing continuous phase rheology
- Relate time of gel point to ξ to find ξ_c.

$$\mu_{polymer} = \mu_0^0 \left(\frac{\xi_c - \xi}{\xi_c} \right)^{-6} \qquad \xi_c = 0.86$$

$$\mu_0^0 = 600 e^{-1549/RT} \text{ Pa-s}$$

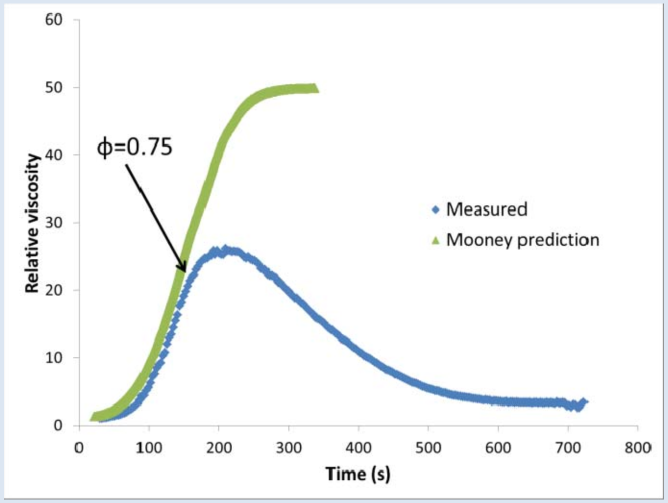


Relate foam viscosity to continuous phase viscosity

- Foam rise + wet formulation rheology (two sets of experiments) give an approximation of the rheology as a function of gas fraction
- Mooney prediction (for $\varphi_{gas} < 0.5$)

$$\mu_{\varphi} = \mu_{polymer} \exp\left(\frac{\varphi_g}{1 - \varphi_g} \right)$$

- For $\varphi_{gas} > 0.75$ estimate $\mu_{foam} = \mu_{cure} *f(\xi)$



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 $\phi(x,y,z) = 0$ should stay on this contour indefinitely
  - Does not preserve $\phi(x,y,z)$ as a distance function
  - Introduces renormalization step.

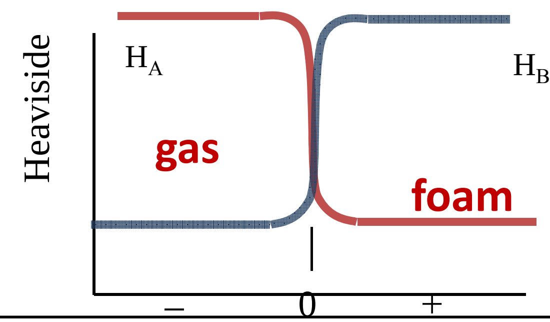
- Equations of motion, kinetics and energy balance averaged based on level set, ϕ

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

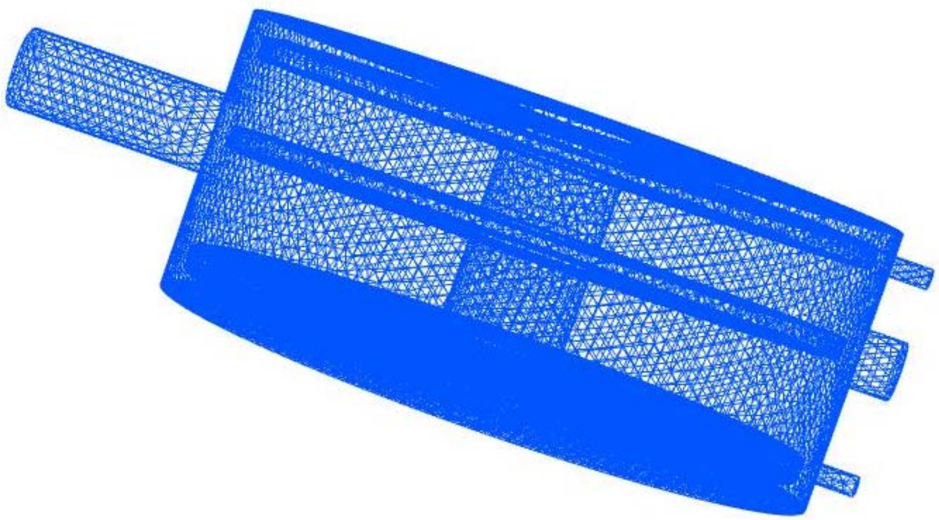
$$H_A \frac{D\rho_A}{Dt} + H_B \frac{D\rho_B}{Dt} + (H_A \rho_A + H_B \rho_B) \nabla \cdot u = 0$$

$$H_A + H_B = 1$$

Rao et al, IJNMF, 2012



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

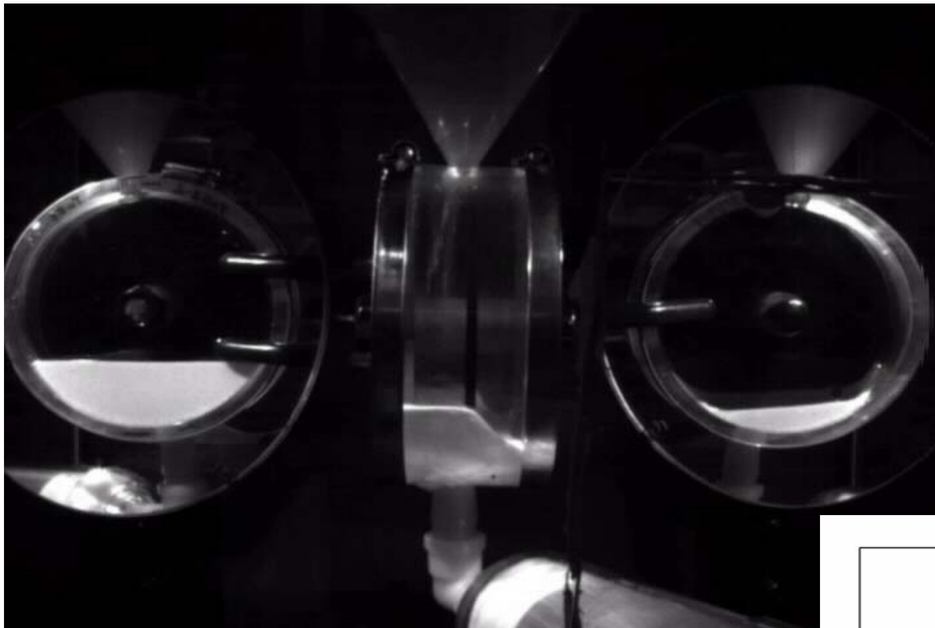


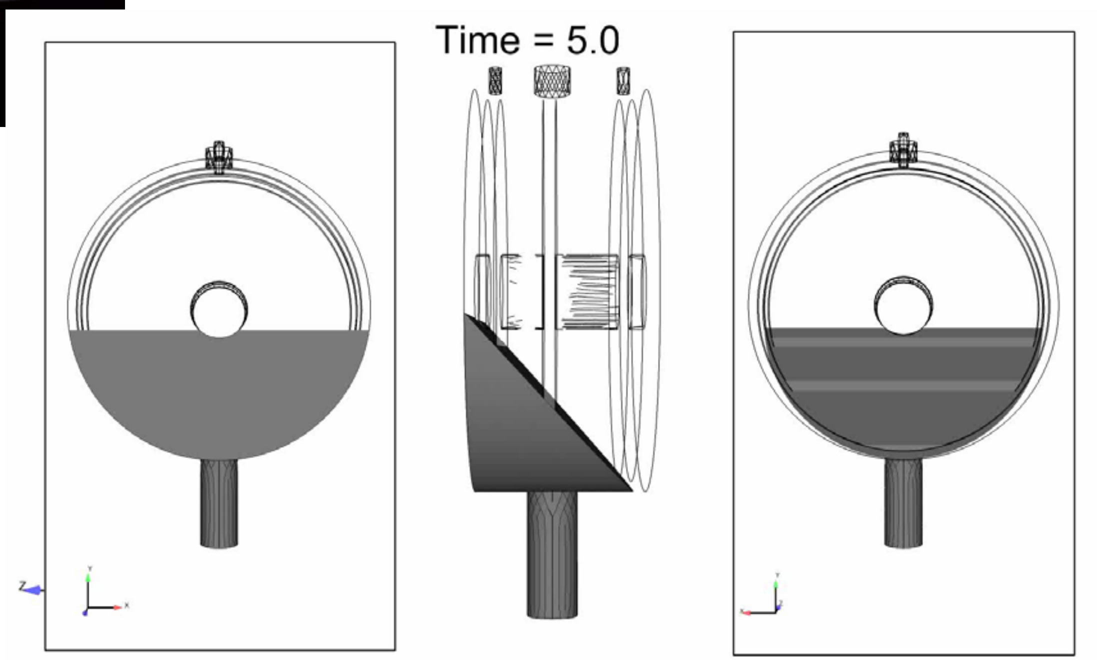
- Mold is preheated to ten degrees hotter than the foam
- Inflow is asymmetric and fills thinner area first
- Boards have different thicknesses of foam
- Three vents are used to improve filling
- Foam slips at the wall using a Navier slip condition with Beta = .001
- Gas slips ten times more than the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

$$n \cdot \underline{\underline{\tau}} \cdot n = \frac{1}{\beta}(v - v_s) \cdot n$$

$$\beta = (\beta_{gas} - \beta_{foam})H(\phi) + \beta_{foam}$$

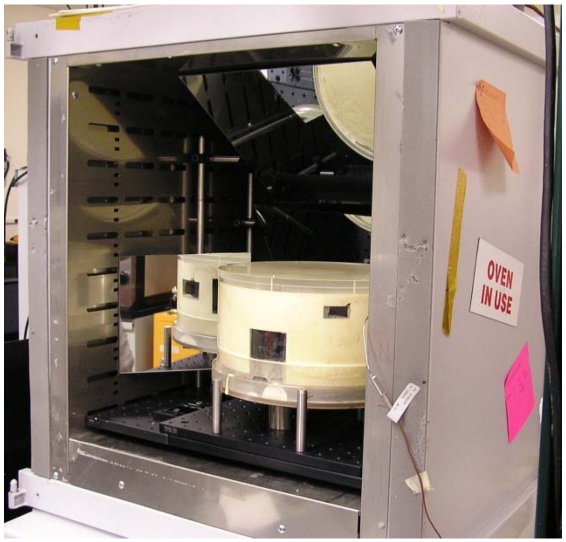
Foam Filling Simulation of Complex Part with Plates

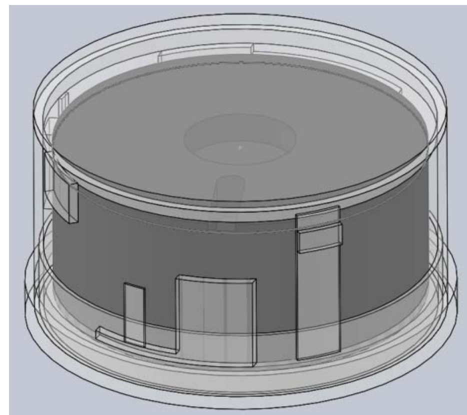


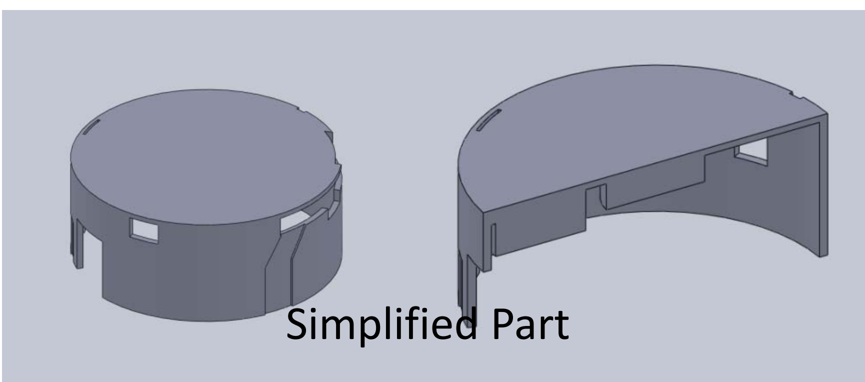


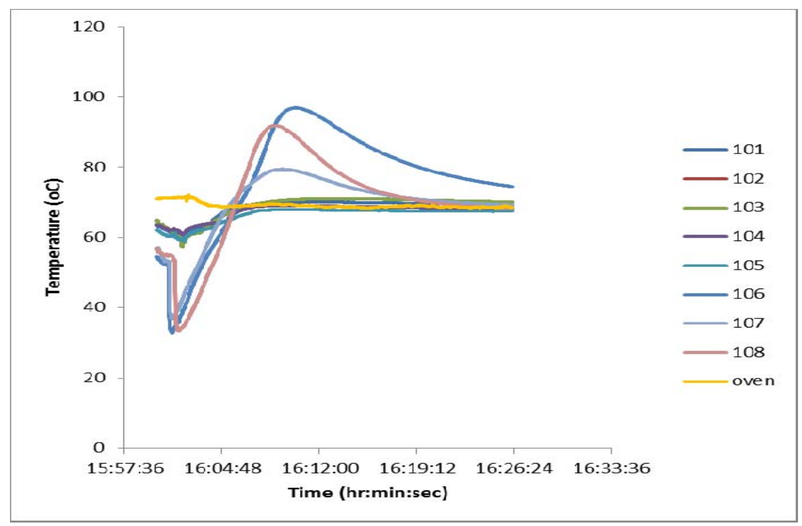
Simplified Structural Support Mold Tests

- 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

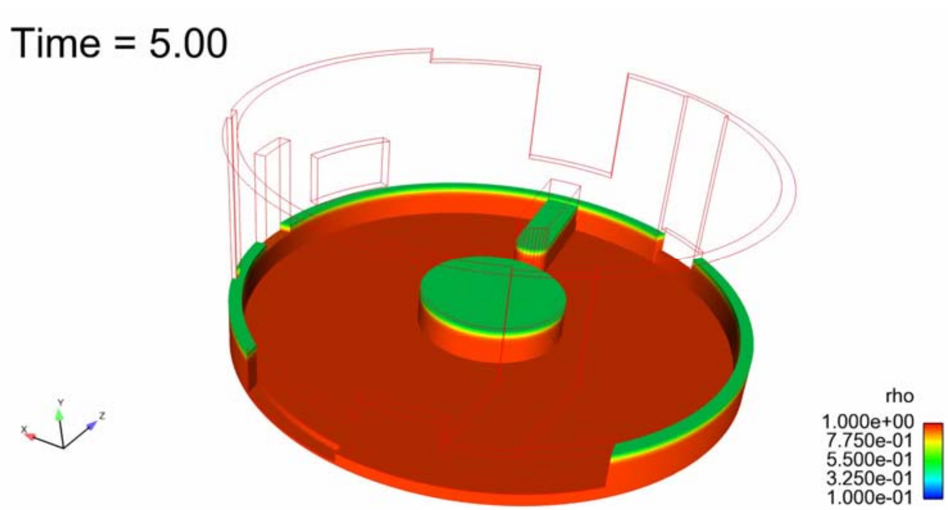


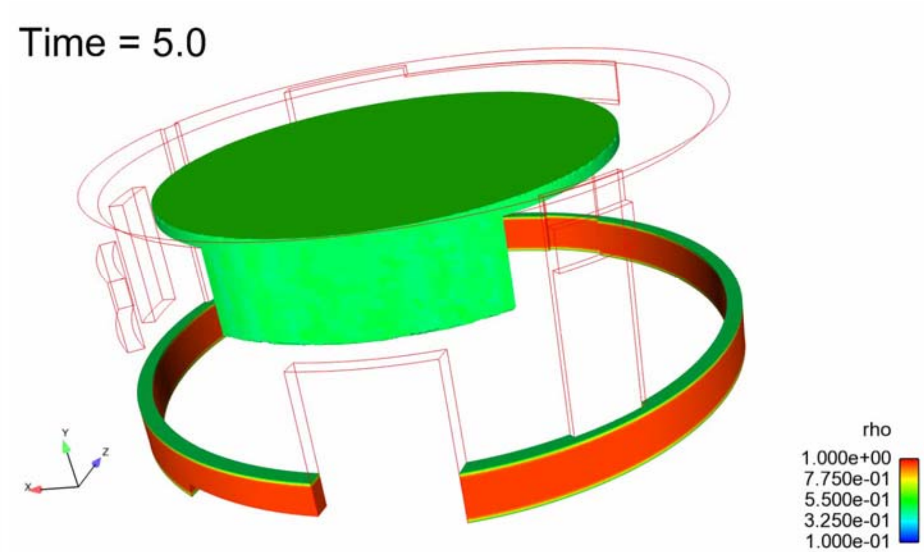




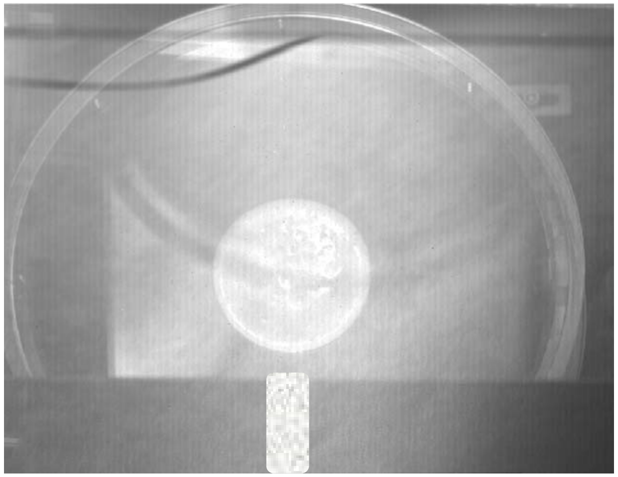


Computational Modeling of Foam Expansion Can Help Design a Mold Filling Process

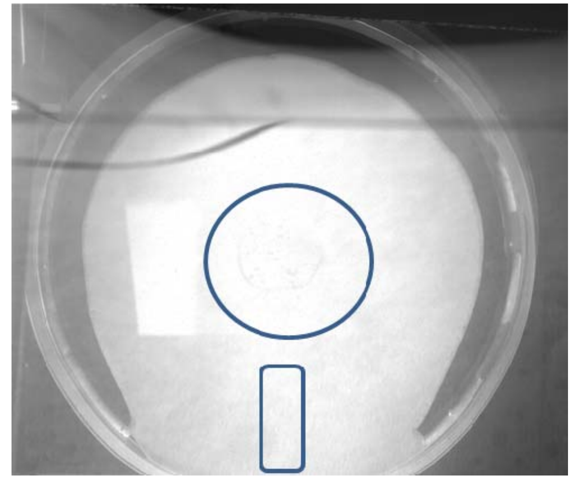


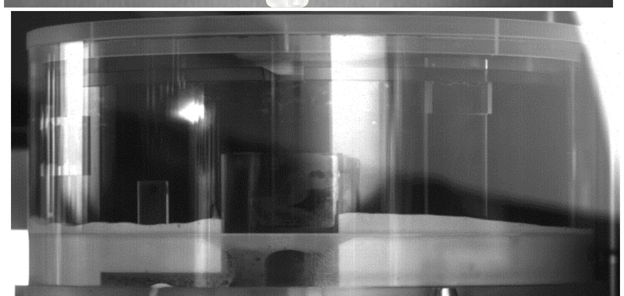


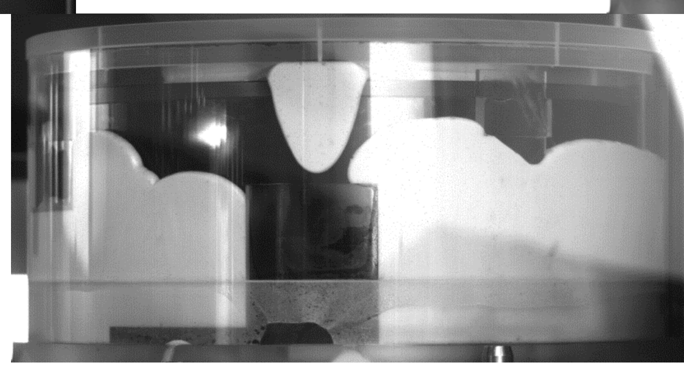
Filling Method Creates Knit Lines



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







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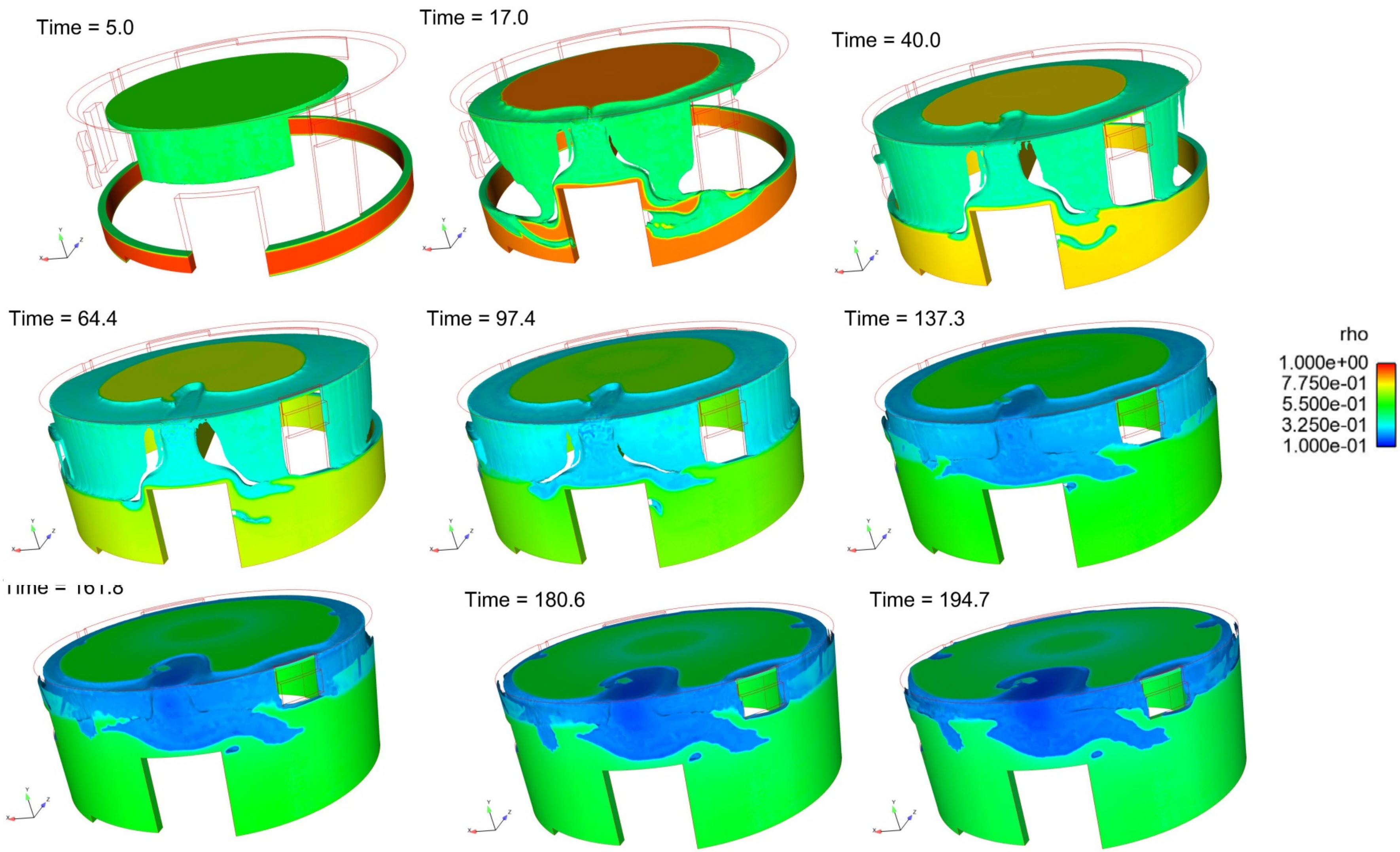
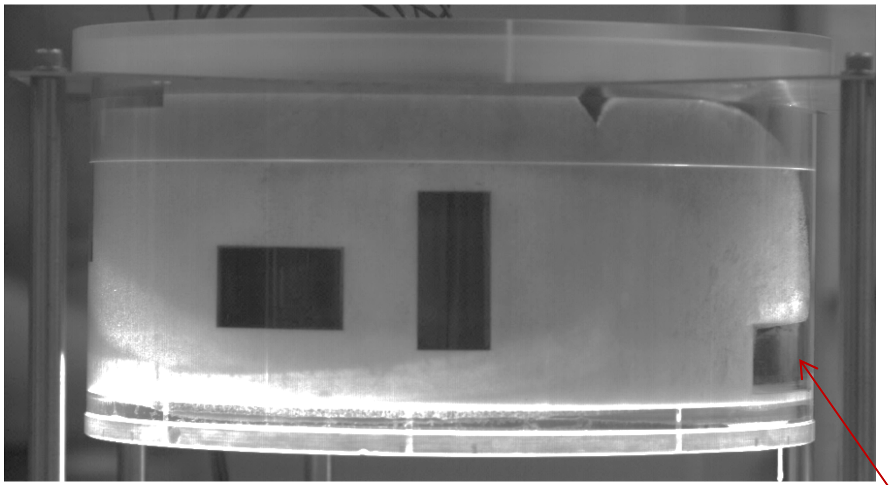
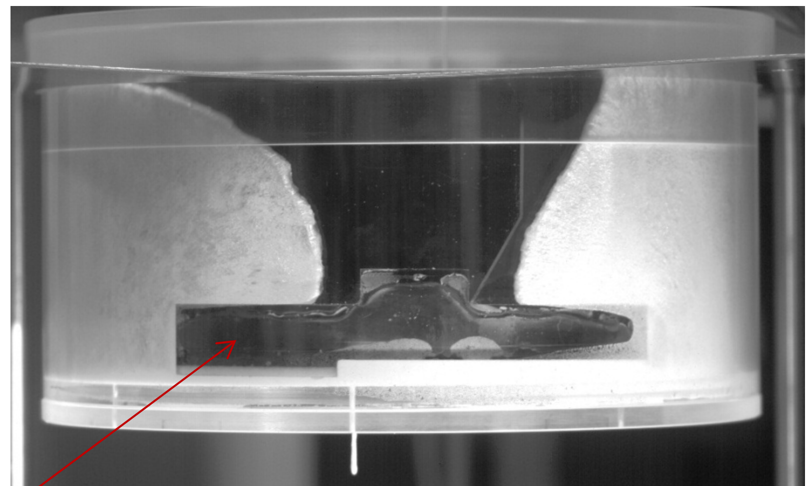


Last Place to Fill Now on Other Side of Largest Feature

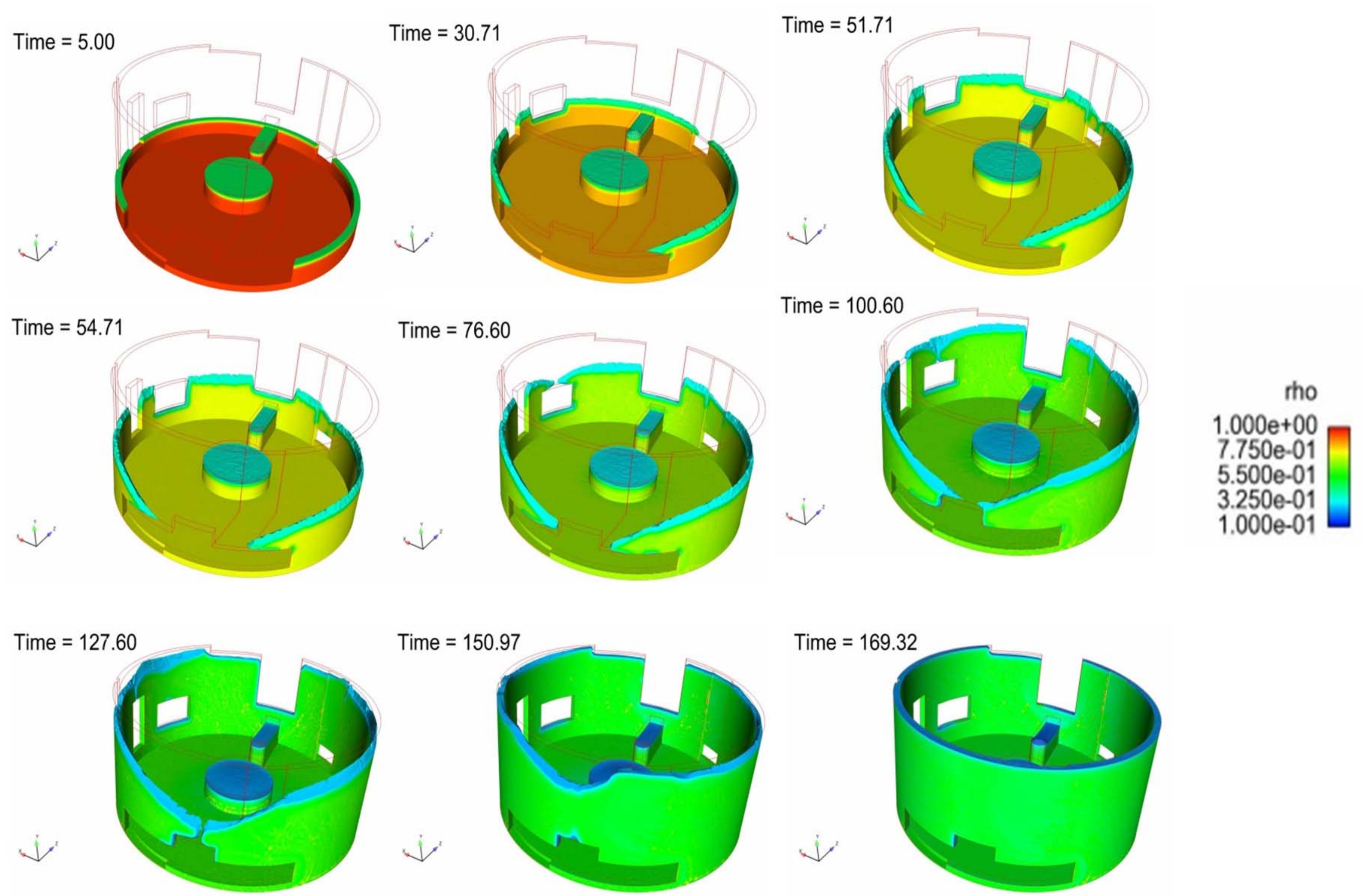




Largest feature

Short shot: less foam than encapsulation test 1, to see where last places to fill would occur. Reaction proceeded faster gelling foam before could finish rising.

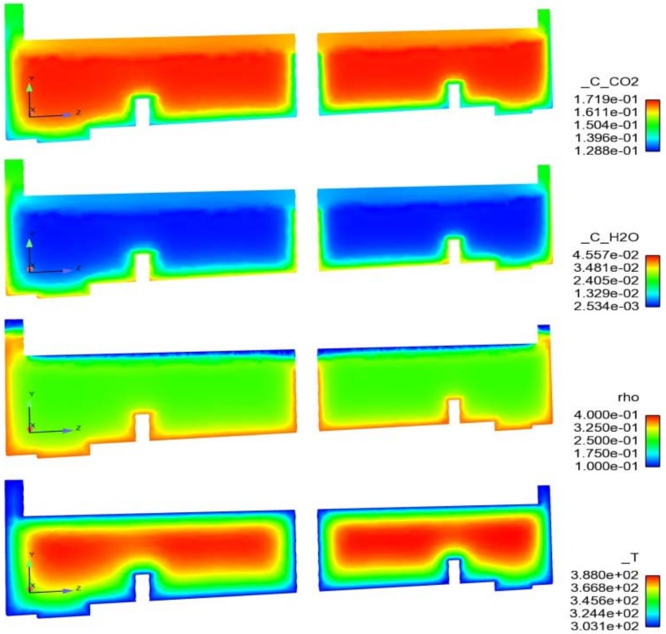
Computational Modeling of Foam Expansion Can Help Design a Mold Filling Process

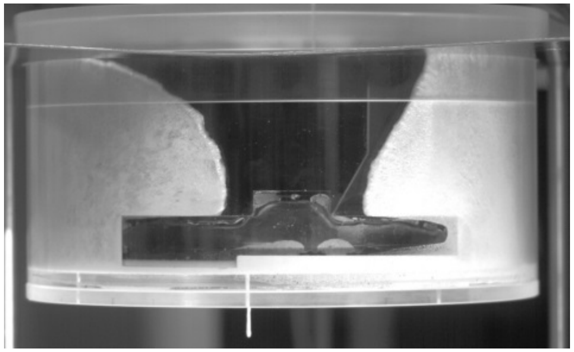


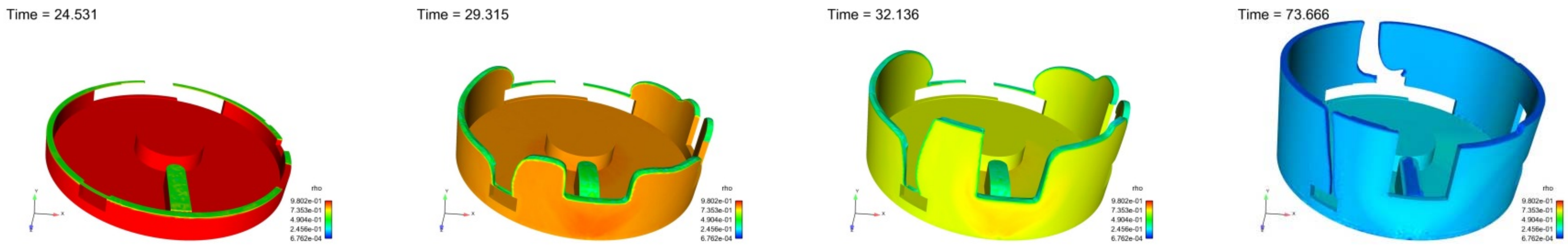
Model Give More Physics than Just the Filling Locations

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

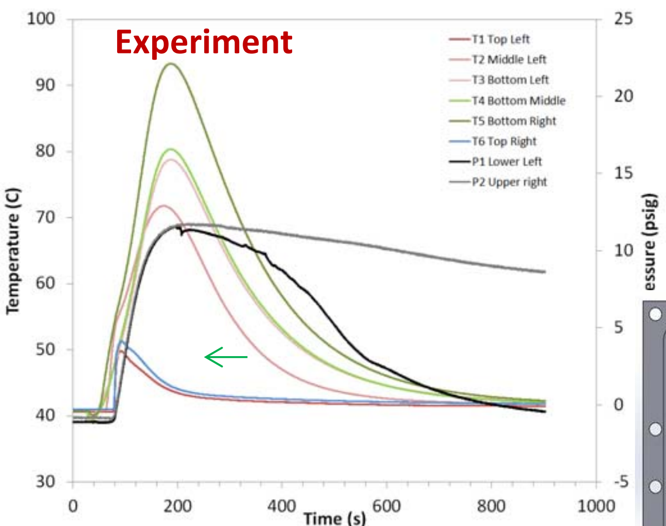


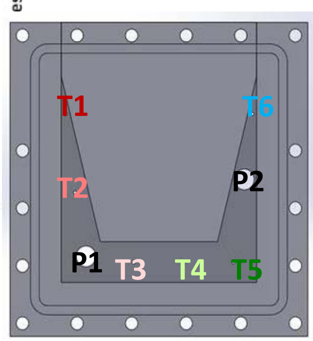


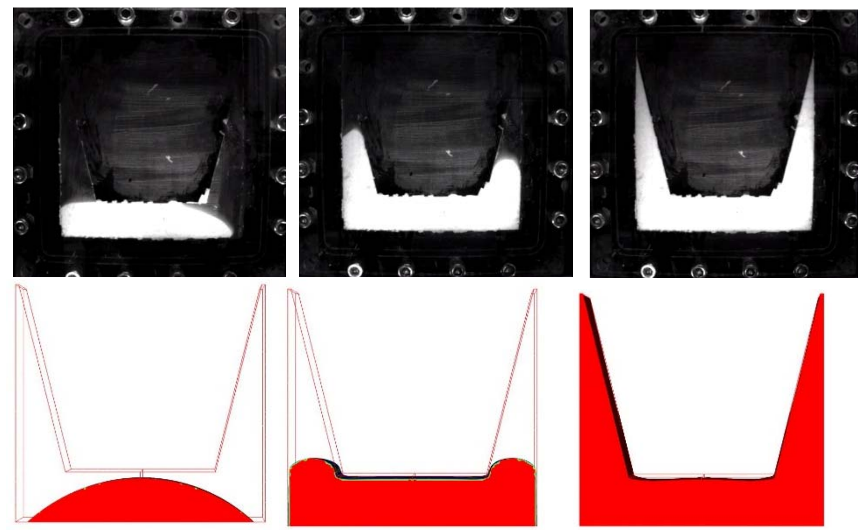


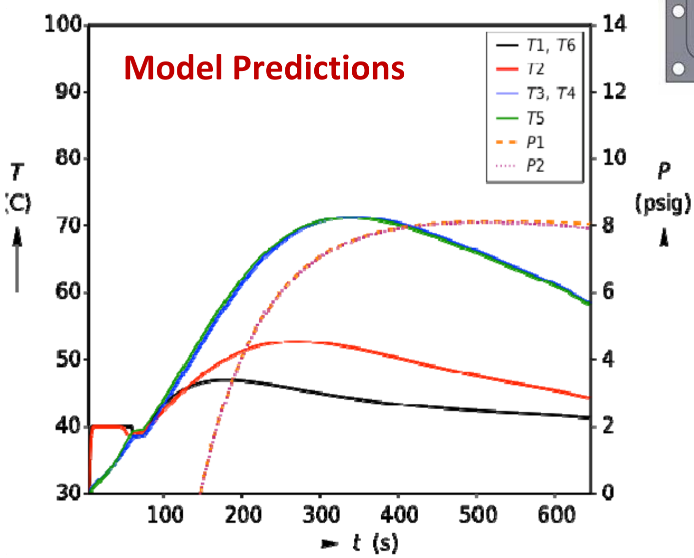
Foaming U-shaped Staple Mold

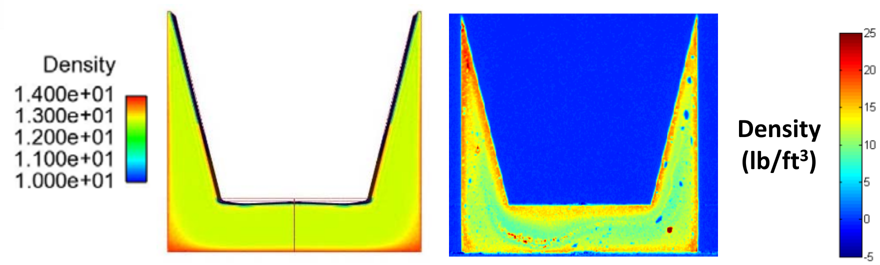
- Over many repeats, temperature, pressure, and flow profile are remarkably repeatable
- Imperfectly symmetric fill common
- Pressure rises as foam expands, relaxes at lower corner and stays positive at P2.







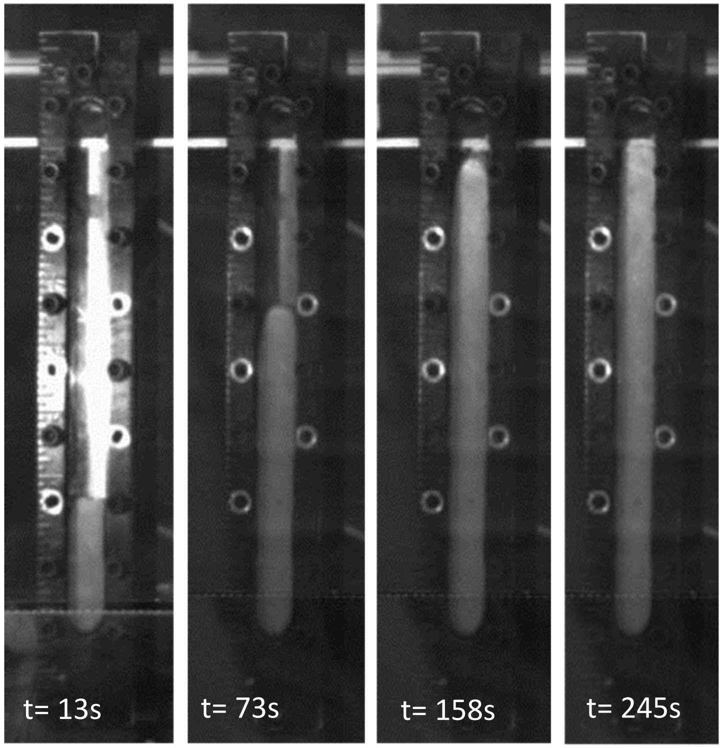




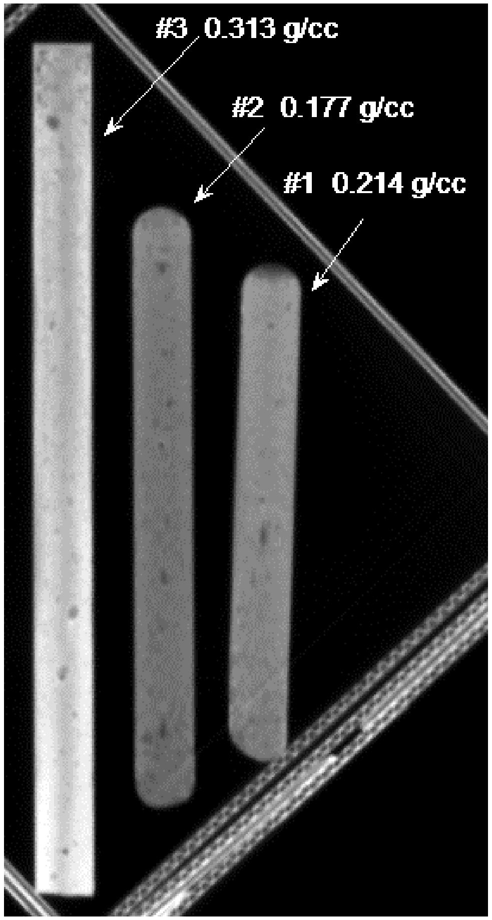
Model

X-ray CT Data (Thompson, 2016)

Density Study for Structural Foam PMDI-10



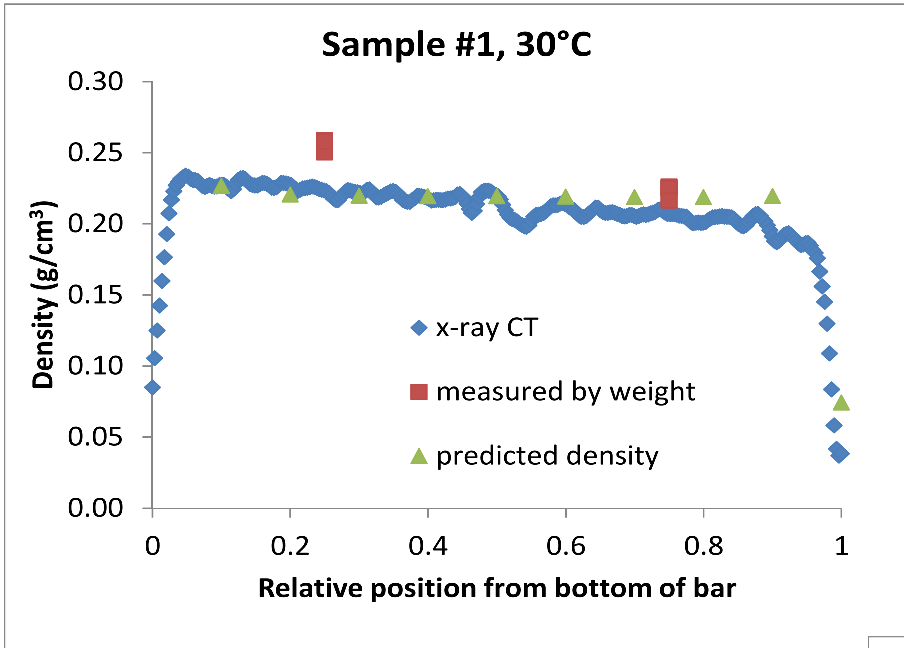
Foam expanding in a mold at 30°C. Time shown on frames is after the end of mixing the resin and the curative together for 45 seconds.

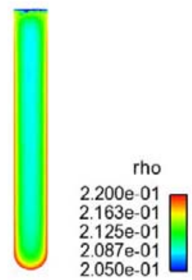


X-ray image of PMDI-10 foam bars: 1) free rise at 30°C, 2) free rise at 50°C, 3) over packed (1.5) at 30°C

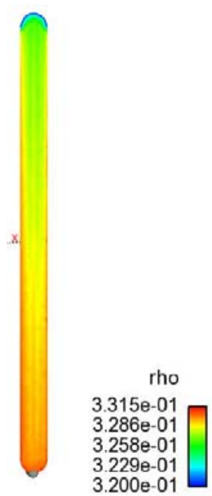
- Can the model predict the effects of over packing seen experimentally?
- Over-packed sample shows higher density and greater density variation
- 17% for free rise and 31% for over-packed foam bars

Density Study for Structural Foam PMDI-10

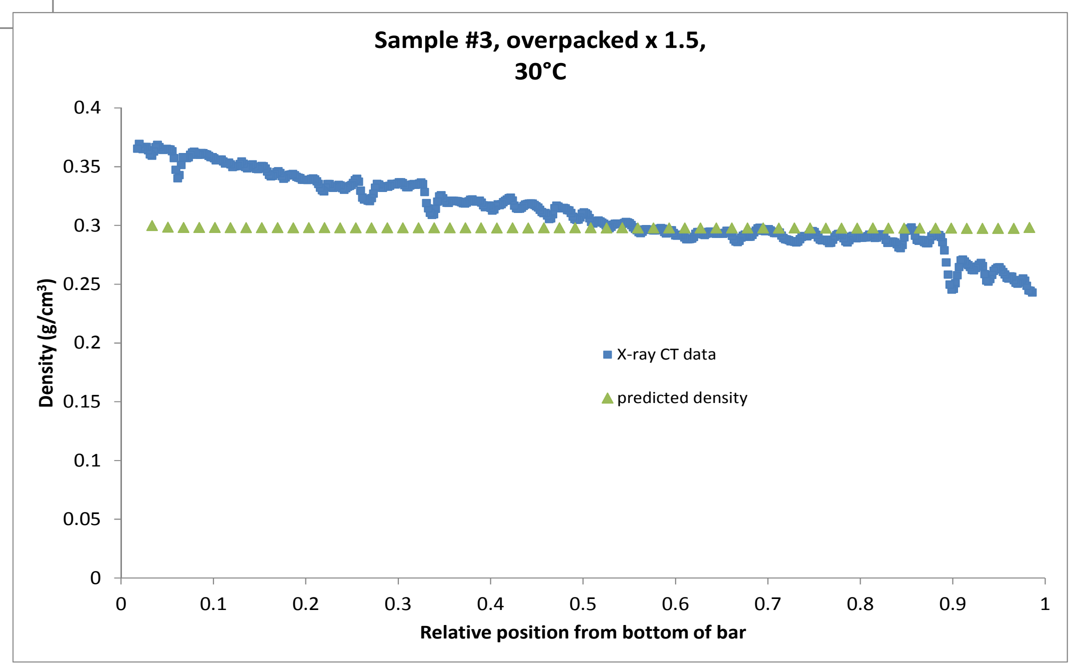




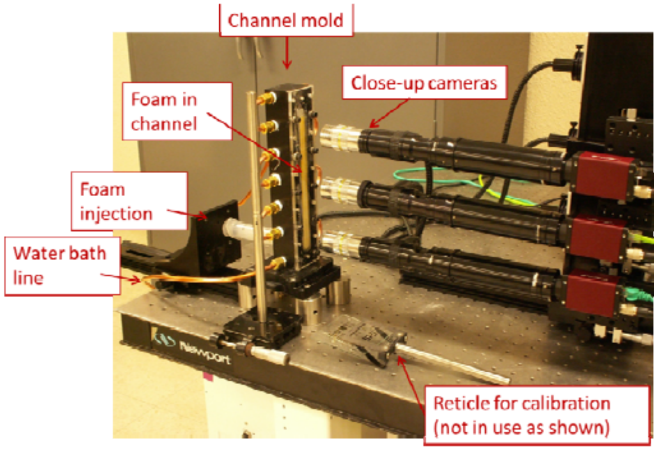
- Free rise foam density gradients. Plots are shown at the centerline of the foam cylinder
- Cylinder is under filled to give the free rise density



- Over packed (1.5) foam density gradients. Plots are shown at the centerline of the foam cylinder
- Self-closing vent lets air out, but keeps foam in for pressurization

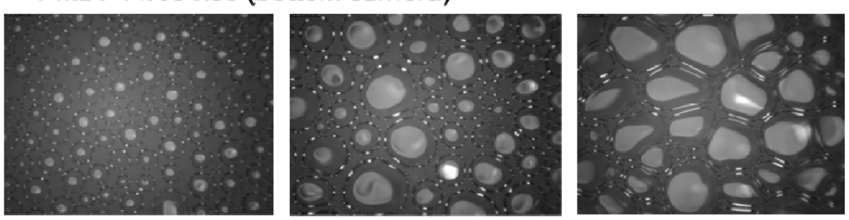


Study of the Evolution of Bubble Size

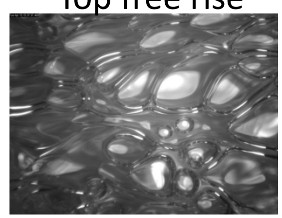


- Three cameras record bubbles at transparent wall (top, middle, and bottom of a column) as foam fills the column
- Light area in pictures below are where the wall is wetted by the bubble – edges are dark lines dashed with bright spots (makes difficult to automatically analyze)
- Image processing developed 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

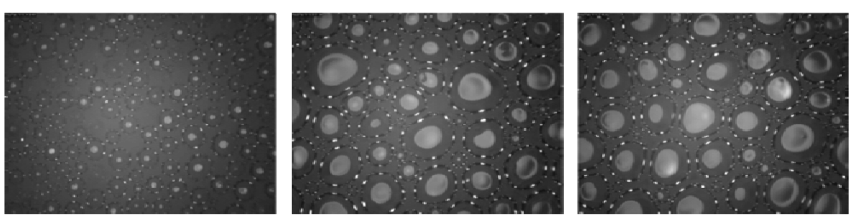
PMDI-4 free rise (bottom camera)



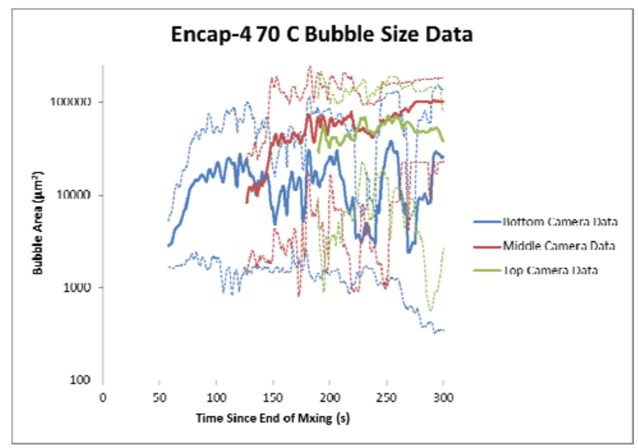
Top free rise



PMDI-4 packed to 8pcf (bottom camera)

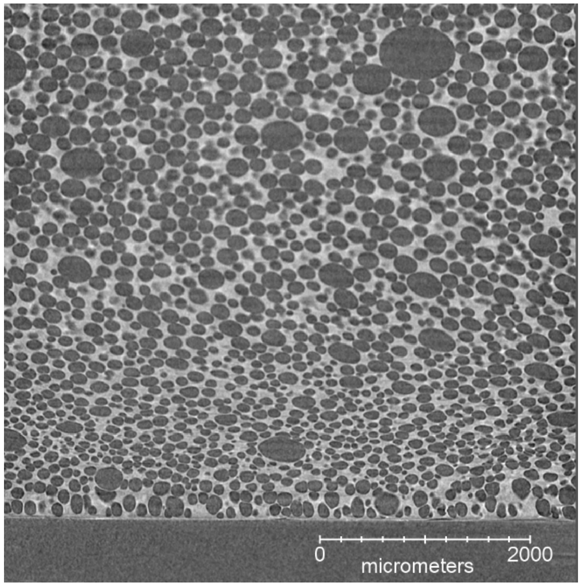


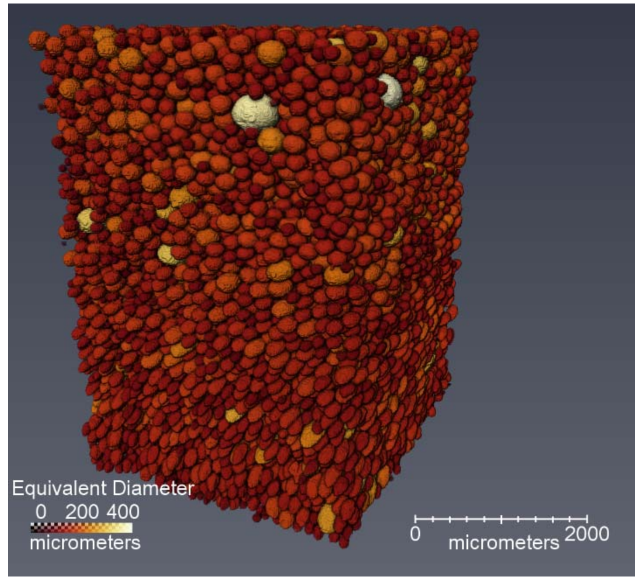
Time=79.5 s Time=152 s Time=266 s since end of mixing



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

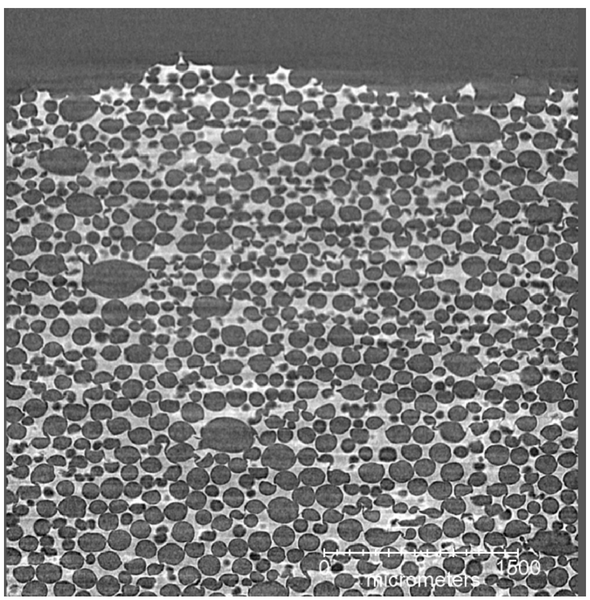
CT Microstructure of Bubbles from Large Complex Mold

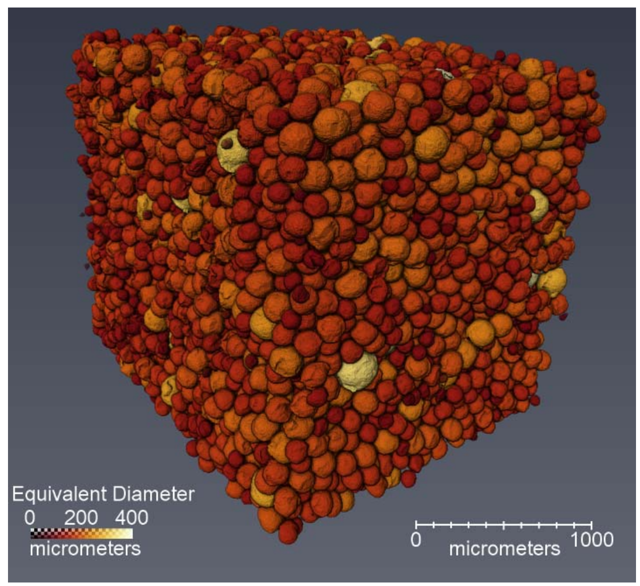




Sample 1 top

Foam microstructure
- Polydisperse bubble sizes
- Shear near boundaries cause elongated ellipsoidal bubbles

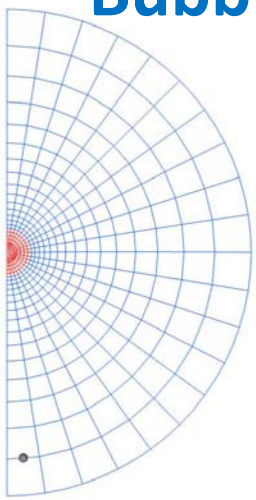




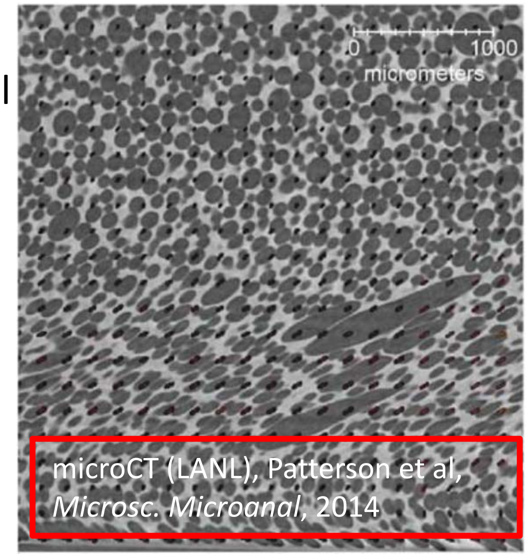
Sample 1 bottom

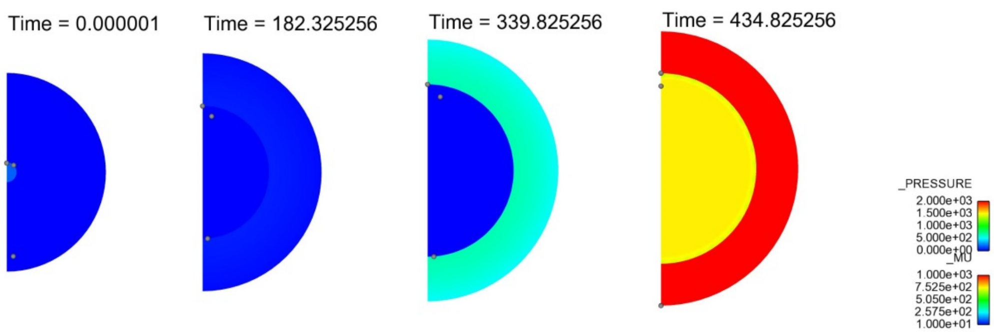
Brian M. Patterson, LANL, July 2016

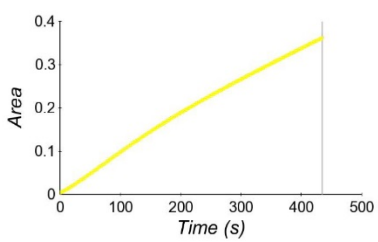
Bubble Expansion in a Polymerizing Fluid

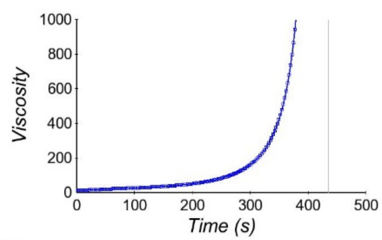


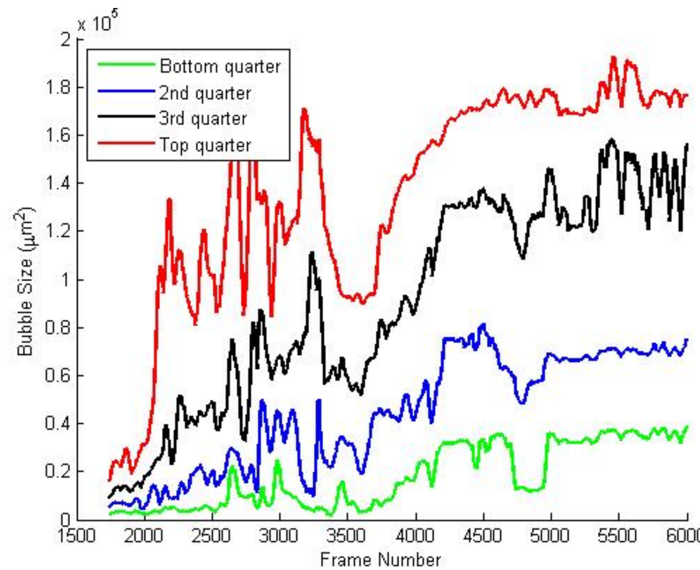
- Bubble grows as CO_2 enters the bubble (VLE model)
- Growth is halted abruptly once the polymer reaches the gel point and the viscosity diverges
- Post-gelation, bubble pressurization is observed
- ALE mesh is robust over shape change
- Data shows the correct trends when compared to experiment











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

ASC PE&M

Including Bubble-Scale Effects

$$\frac{\partial C_{H_2O}}{\partial t} + \nabla \bullet \vec{v} C_{H_2O} = D_{H_2O} \nabla^2 C_{H_2O} - (1-\varphi) k_{H_2O} C^n_{H_2O}$$

Existing equation with minor mods

$$\frac{\partial C_{CO_2}}{\partial t} + \nabla \bullet \vec{v} C_{CO_2} = D_{CO_2} \nabla^2 C_{CO_2} + (1-\varphi) k_{H_2O} C^n_{H_2O} - S_{pg}$$

Existing equation with mods including source

$$\frac{\partial C^g_{CO_2}}{\partial t} + \nabla \bullet \vec{v} C^g_{CO_2} = S_{pg}$$

New equation similar to liquid

$$\frac{\partial \rho_{gas}}{\partial t} + \vec{v} \bullet \nabla \rho_{gas} = -\rho_{gas} S_v + M_{CO_2} S_{pg}$$

New equation for bubble gas density

$$\frac{\partial n}{\partial t} = \nabla \bullet (\vec{v} n)$$

New equation for bubble number density

$$\varphi(t) = \frac{\rho_{foam} Y_g}{\rho_{gas}} = \frac{M_{CO_2} C^g_{CO_2}}{\rho_{gas}} \qquad \rho_f = (\rho_{gas} - \rho_{liq})\varphi(t) + \rho_{liq}$$

$$R_{av} = [\frac{3}{4\pi} \frac{\varphi}{n}]^{1/3}, \quad S_{av} = [\frac{3}{4\pi} \frac{1}{n}]^{1/3}$$

$$\Delta r = \frac{(S^4_{av} - R^4_{av}) - R_{av}(S^3_{av} - R^3_{av})}{S^3_{av} - R^3_{av}}$$

$$\eta_{polymer} = \eta^0_0 \exp(\frac{E_\mu}{RT})(\frac{\xi^p_c - \xi^p}{\xi^p_c})^{-q}$$

Source terms from bubble scale:

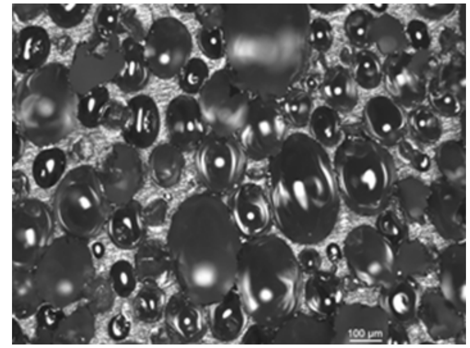
$$S_v = \frac{1}{4\eta_{polymer}}((\rho_{gas} \Re T / M_{CO_2} - p) - \frac{2\sigma}{R_{av}})$$

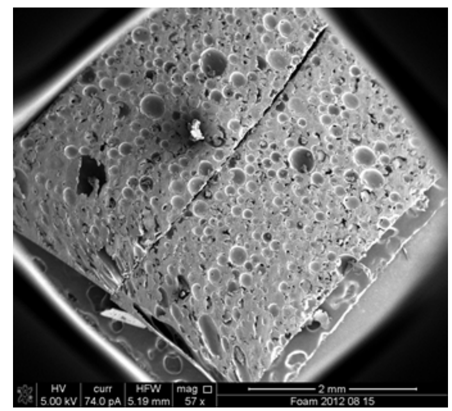
$$S_{pg} = 3\frac{\varphi}{R_{av}} D_{CO_2} \frac{C_{CO_2} - K_H \rho_{gas} \Re T / M_{CO_2}}{\Delta r}$$

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
  - 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

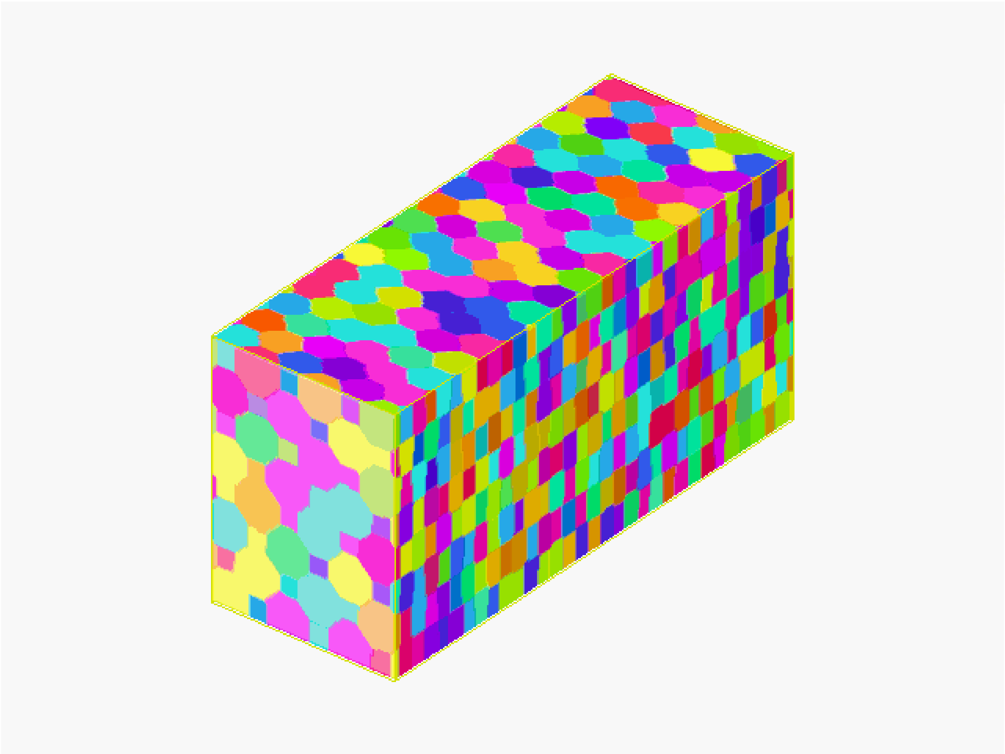
SEM of foam showing polydispersity



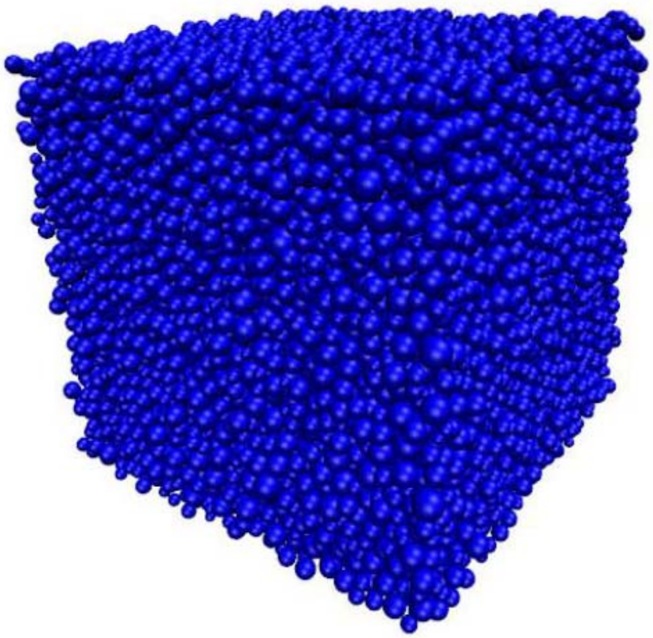


Bubble at walls are elongated and show coarsening

Questions?



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



Polydisperse bubble microstructure generated with LAMMPS and Aria/CDFEM (Dan Bolintineanu , SNL)