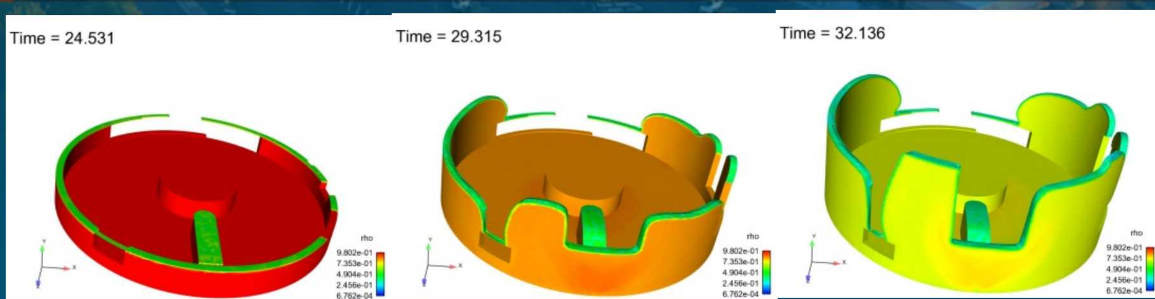
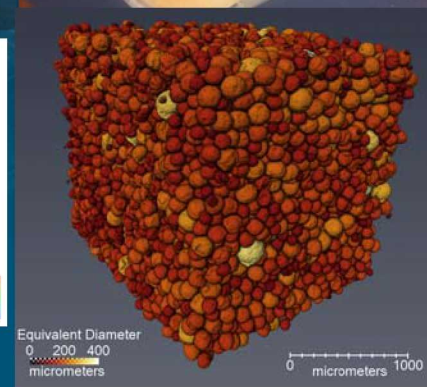
SAND2018-12917PE

MODELS OF POLYURETHANE FOAM FORMATION

3M
St. Paul, Minnesota
November 13th, 2018





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SAND2018-????

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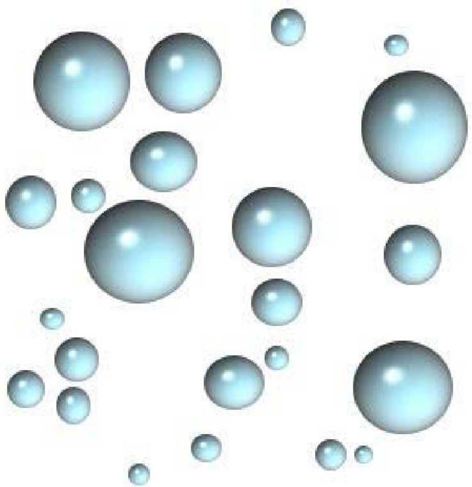
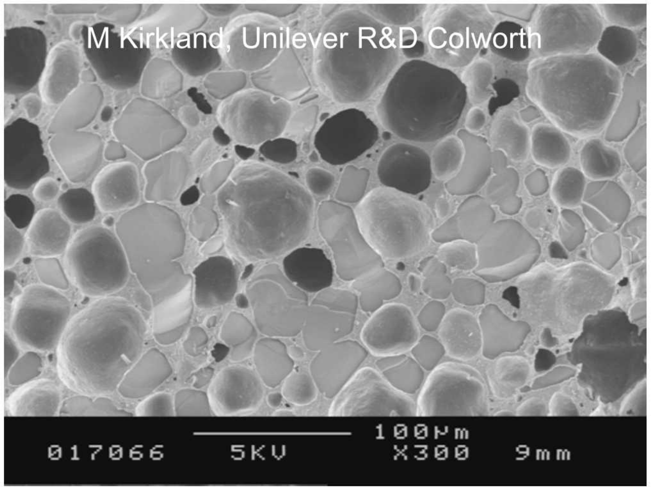
What is a Foam?



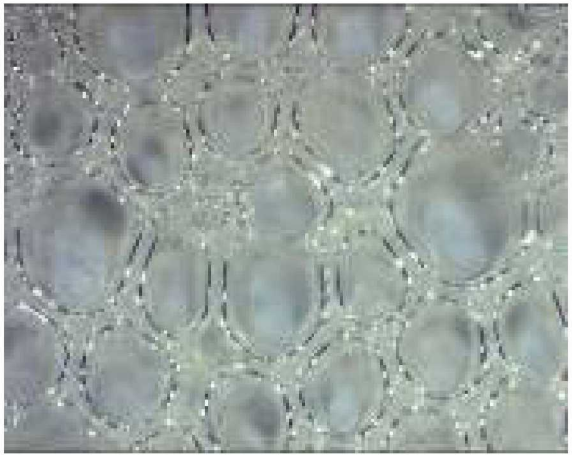
Bubbles

Whipped cream

- 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



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

Some Foam Projects at Sandia

Explosion Suppression

no foam

foam

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

Decontamination

Courtesy of J.B. Kelley

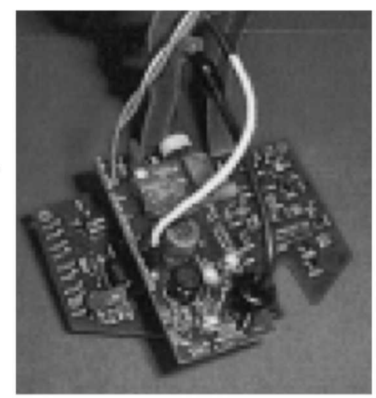
Encapsulation

Intruders/Unruly Crowds

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

Electronics—removable foam

reversible chemistry → **90°C**



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

Jamie Kropka (SNL)

Sandia National Laboratories

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

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)

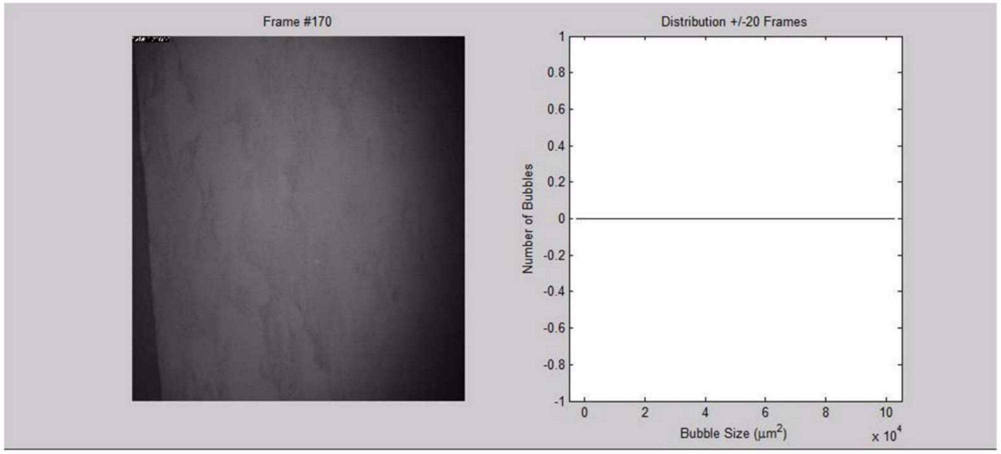
Residual stresses, density, and properties vary spatially

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

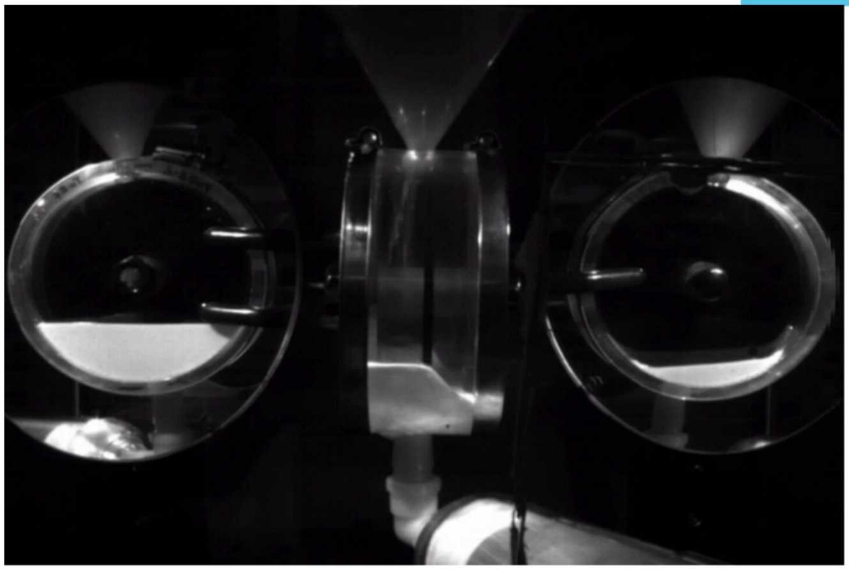
Boundary conditions strongly influence residual stresses

- 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.

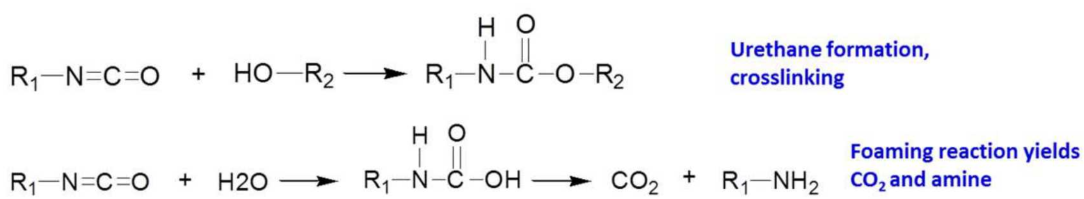
We would like to develop a computational model to help us understand foam expansion for manufacturing applications.

Polyurethane is a chemically blown foam having two primary, competing simultaneous reactions: CO_2 production and polymerization. Separating these reactions can be difficult.

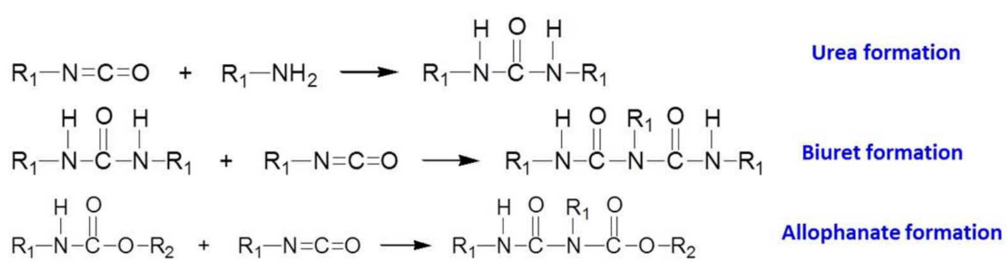
We use IR spectroscopy to track polymerization. IR does not provide a clear signal for the foaming reaction: Tracked with volume generation.

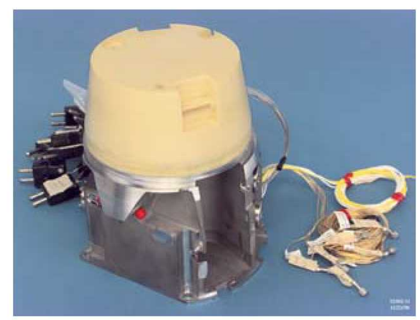
PU has a short pot-life: models can help reduce defects and improve filling process

Two key reactions: Isocyanate reaction with polyols and water



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





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

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

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

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

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

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

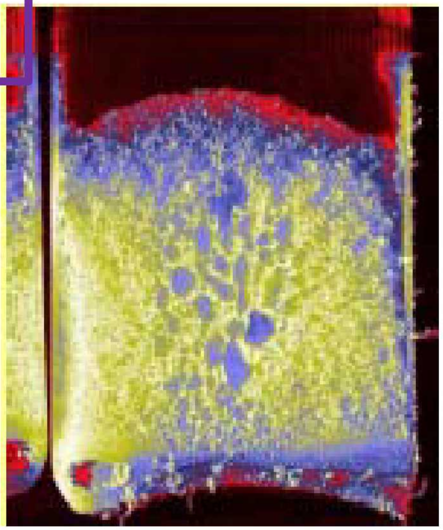
Extent of reaction equation for polymerization: condensation chemistry

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

Molar concentration equations for water and carbon dioxide

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

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



NMR imaging shows coarse microstructure (Altobelli, 2006)

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

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

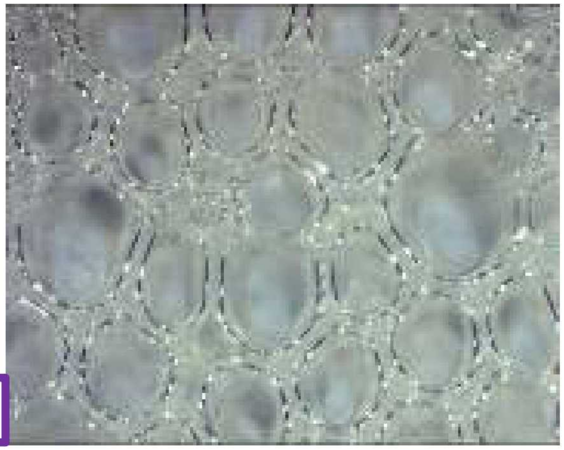
Foaming reaction predicts moles of gas from which we can calculate density

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

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

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

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



Thermal properties depend on gas volume fraction and polymer properties

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

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

Foam is a collection of bubbles in curing polymer

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

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

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

- 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

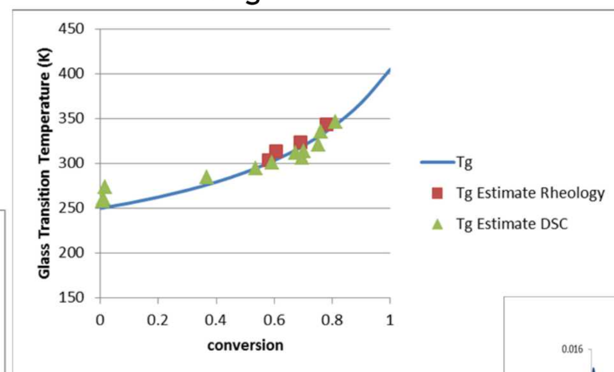
- Fit the rate and the extent of reaction to IR data to a standard equation form
- Fit T_g to both rheology and DSC data: T_g changes as cure progresses making this complex

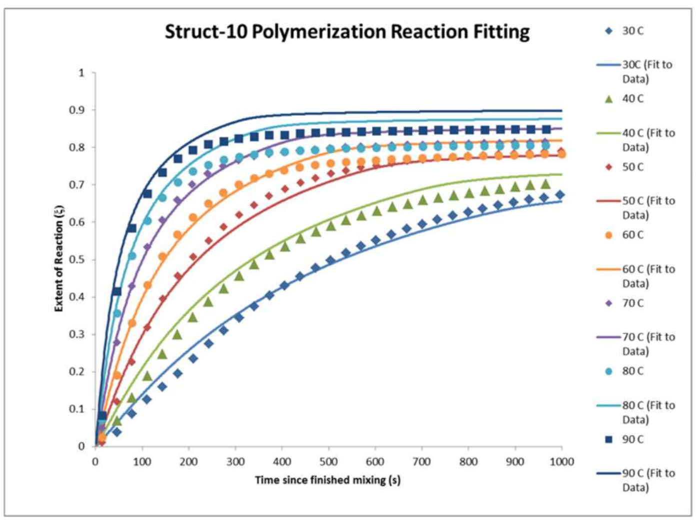
$$\frac{\partial \xi}{\partial t} = \left(\frac{1}{(1+wa)^{\beta}}\right)\left(k_0 \exp\left(-\frac{E}{RT}\right)\right)\left(b+\xi^m\right)(1-\xi)^n$$

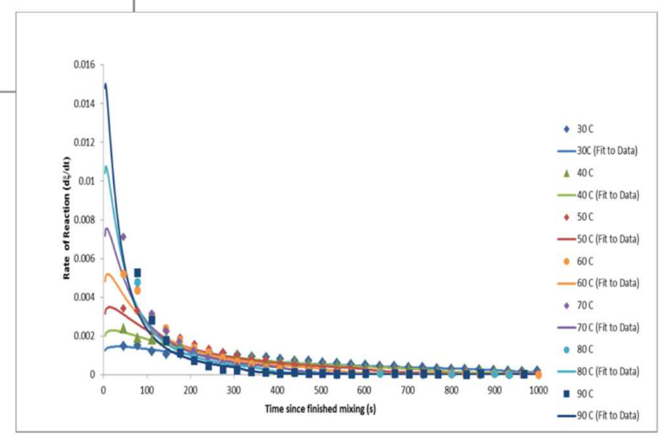
$$\log_{10} a = \frac{-C_1(T-T_g)}{C_2+T-T_g}$$

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

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







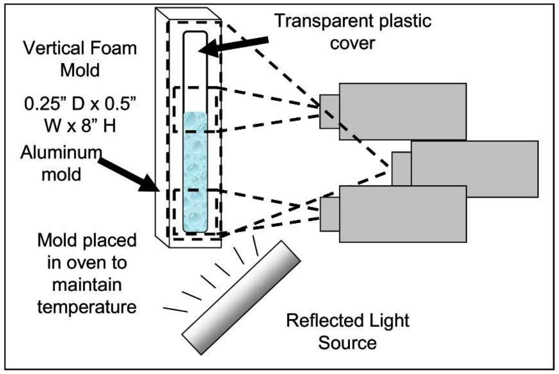
Rate and extent of reaction fit to data, where parameters of the model, including Tg are optimized for lower temperatures expected in the process. The apparent time-to-gel from rheology is correlated with extent to give a Tg with conversion. Similar analysis can be done with DSC and results are consistent.

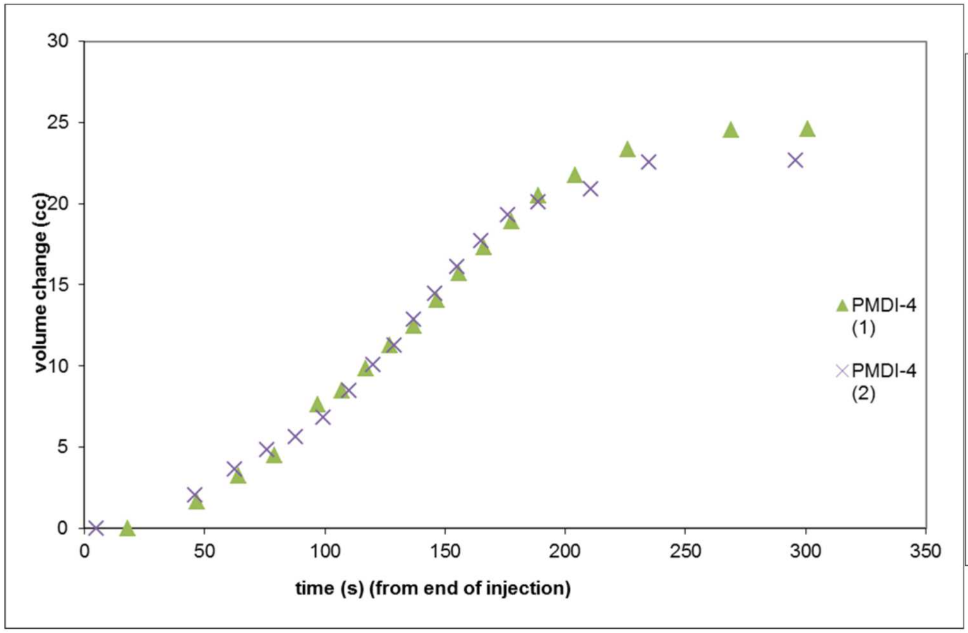
Kamal, M. R., and S. Sourour, *Poly. Eng. Sci* (1973)

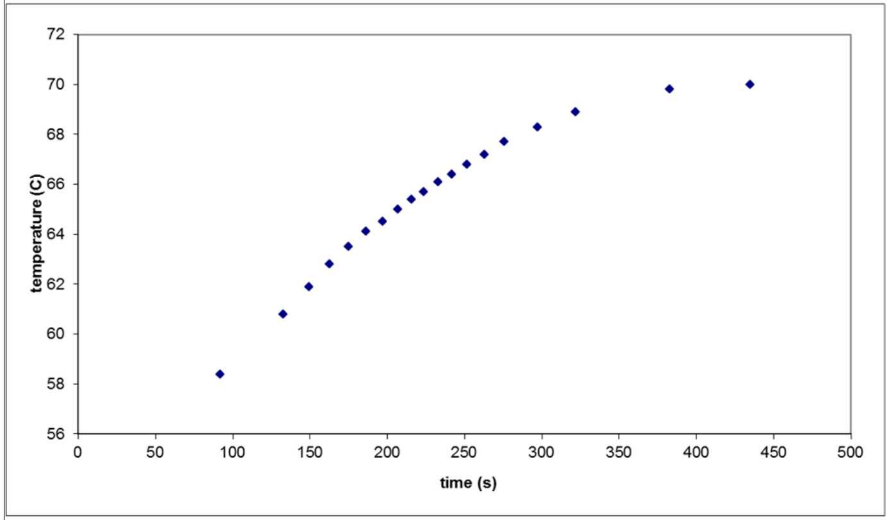
A.T. Di Benedetto, *J. Polymer Sci., Phys.*, **25,** 1949

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.

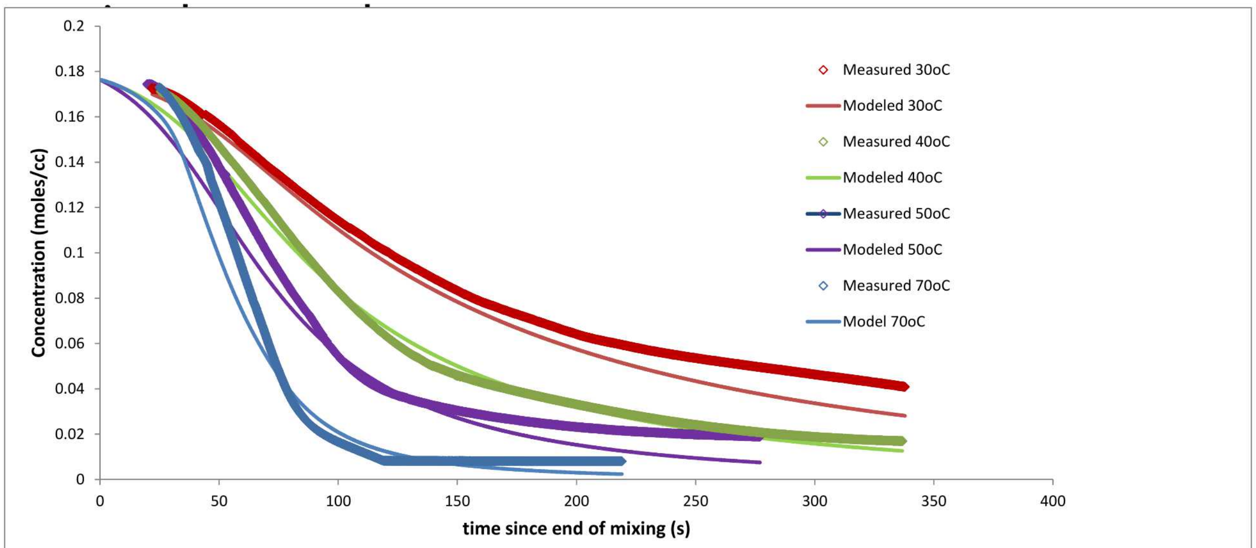


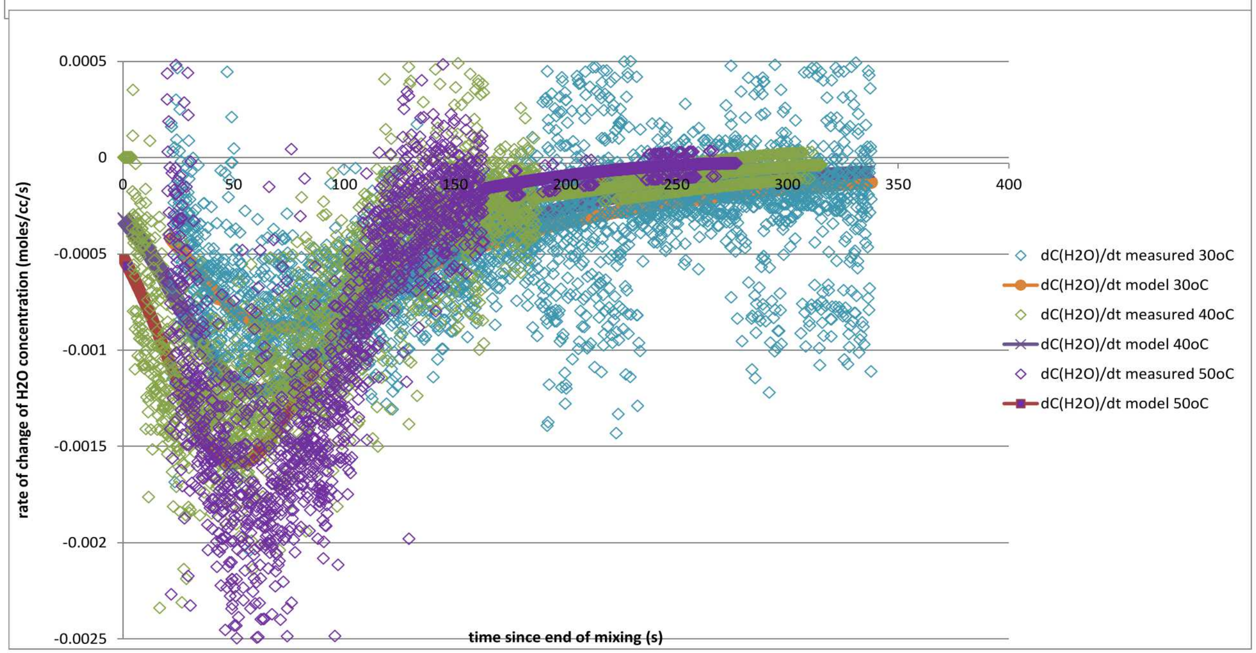




Kinetics of CO_2 Generation

- Fit the concentration of water and its rate of disappearance





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

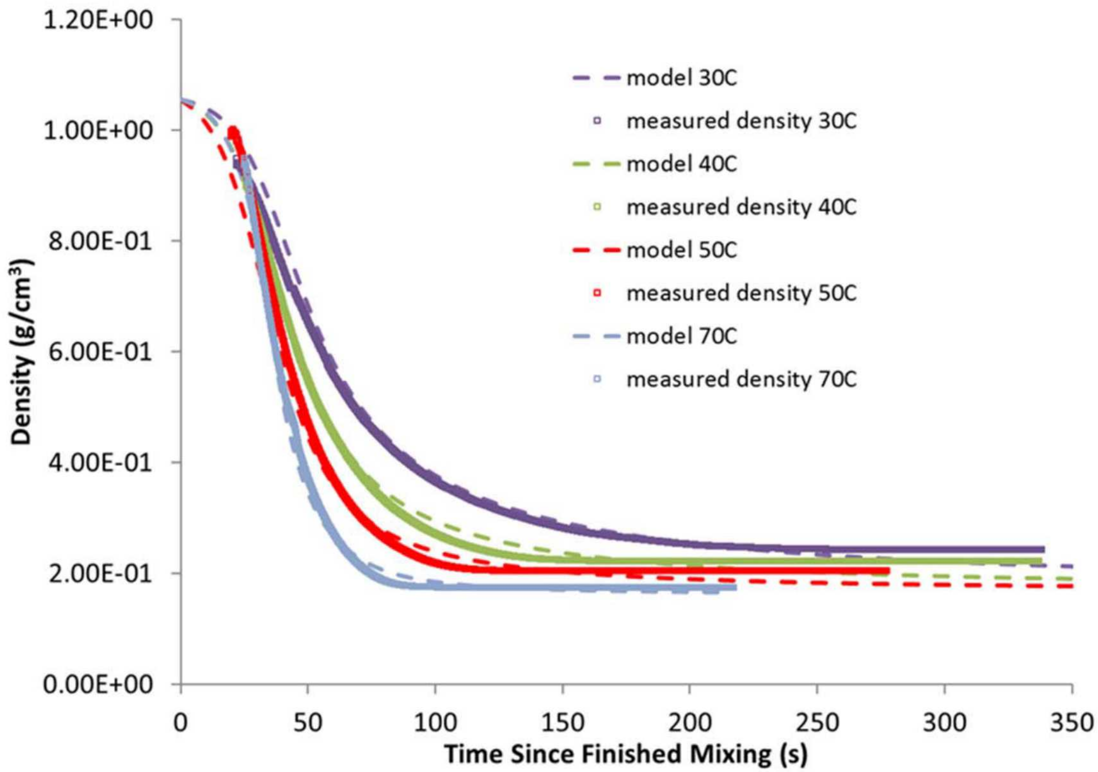
$$\frac{dC_{CO_2}}{dt} = +Nk_{H_2O}C_{H_2O}{}^{n}$$

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

- 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.



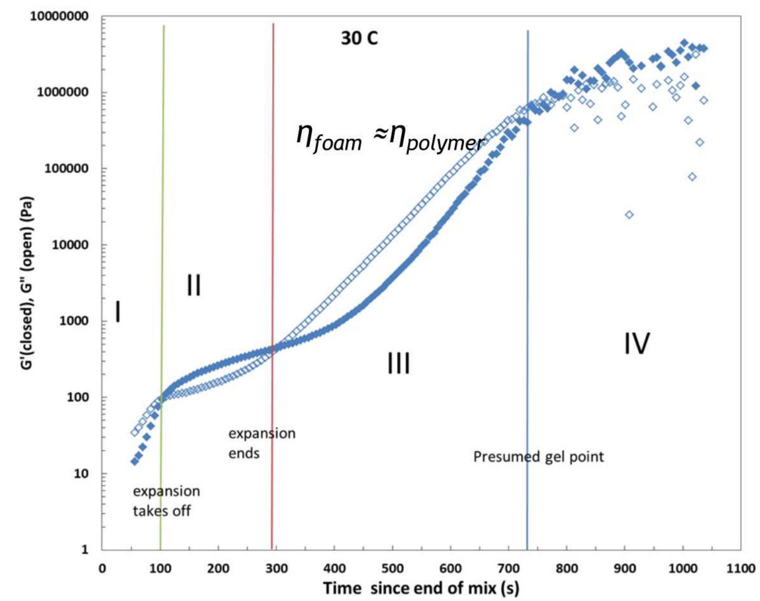
$$\frac{dC_{H_2O}}{dt} = -Nk_{H_2O}C_{H_2O}{}^{n}$$

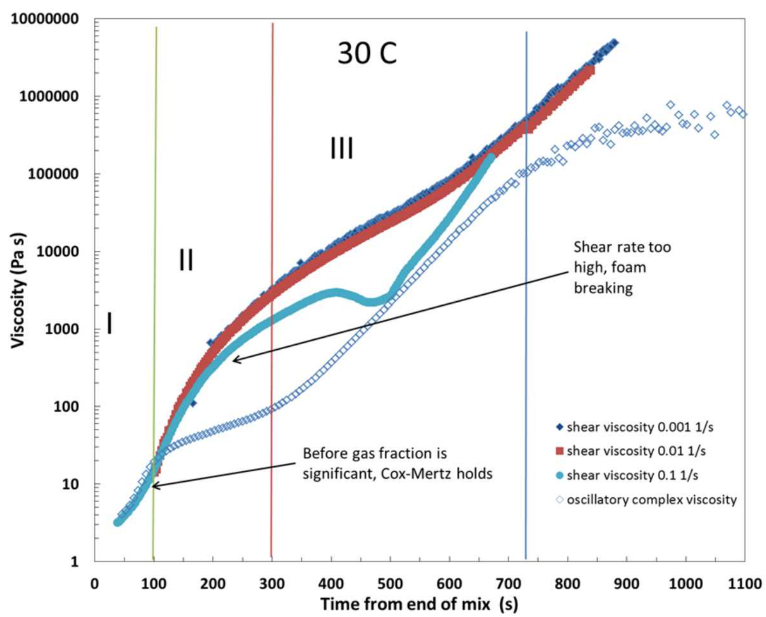
$$\frac{dC_{CO_2}}{dt} = +Nk_{H_2O}C_{H_2O}{}^{n}$$

- 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," *AICHE Journal*, 2017

Viscosity of Foam is Complex

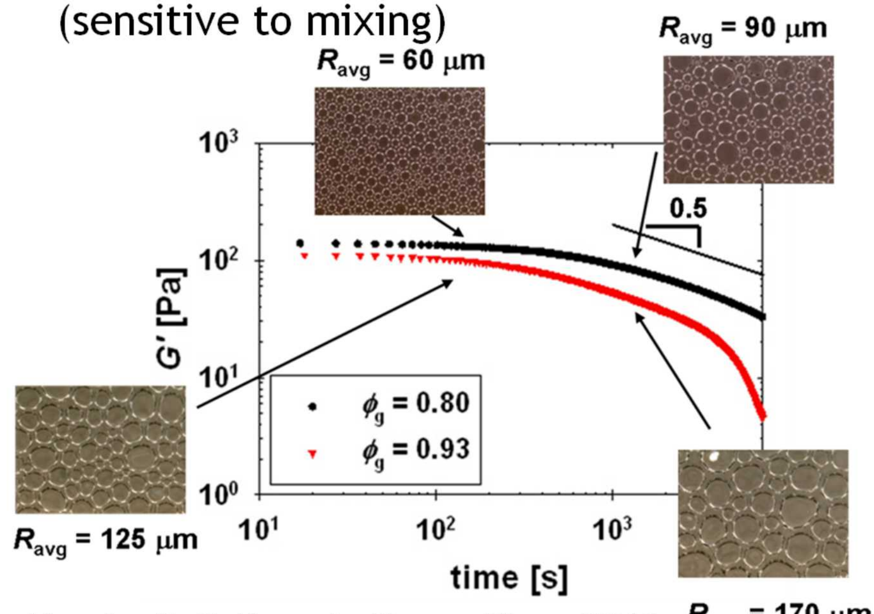




- Foam rheology evolves as gas fraction and polymerization increase

$$\eta_{foam} = \eta_{polymer}\,\eta_{\phi}$$

- After Bouayad et al. Int J. Mater Form (2009), plot foam rheology as function of distinct phenomenological characteristic times
- Test foam viscosity with steady shear at low shear rates
- Be aware of slip
- Effect of bubble size & coarsening (sensitive to mixing)



Kropka & Celina, J. Chem. Phys. 2010

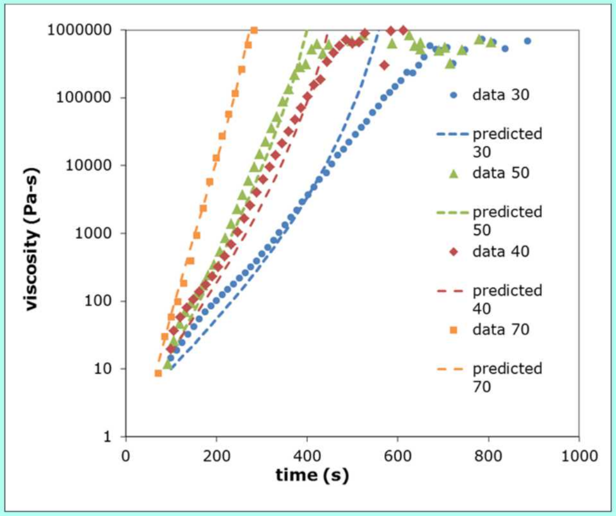
Model Foam Viscosity as f(ξ,φ)

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.

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

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

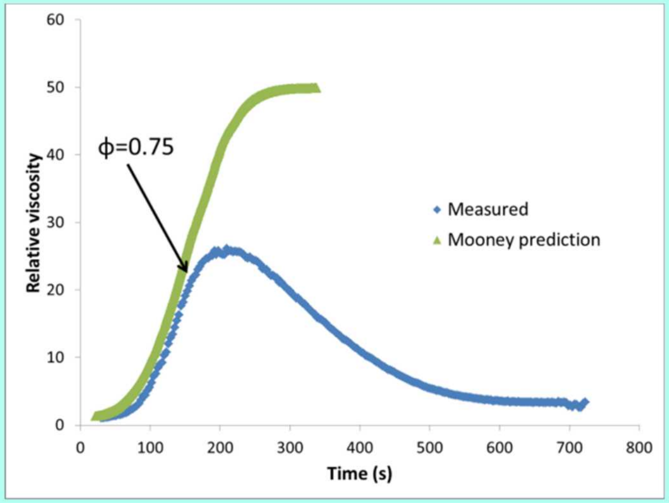


Relate foam viscosity to continuous phase viscosity

- 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 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.

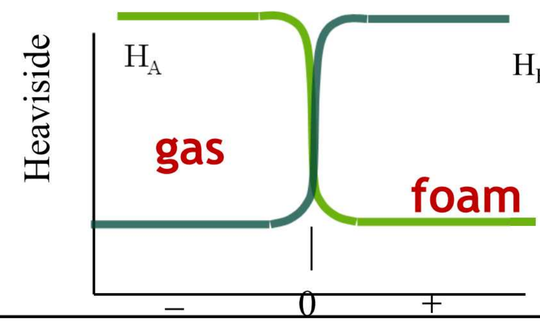
- Equations of motion, kinetics and energy balance averaged based on level set, ϕ

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

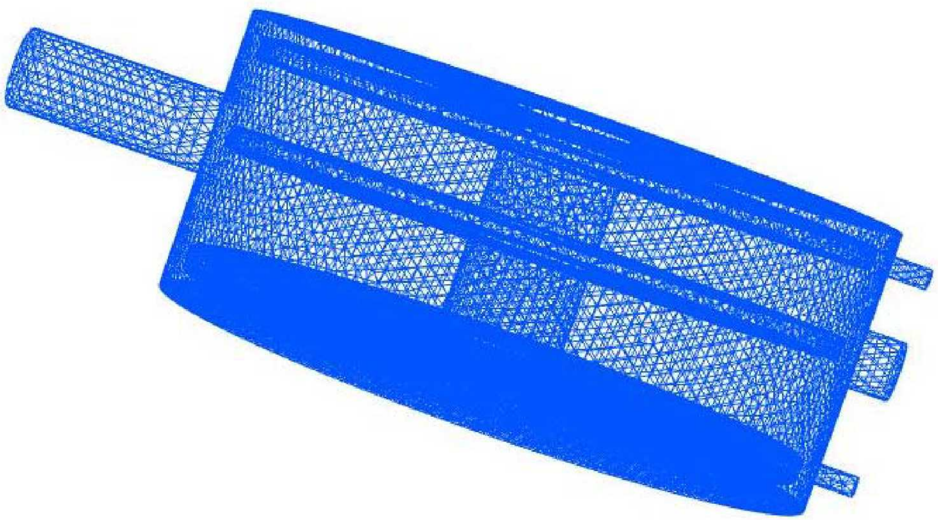
$$H_A\frac{D\rho_A}{Dt}+H_B\frac{D\rho_B}{Dt}+(H_A\rho_A+H_B\rho_B)\nabla\cdot u=0$$

$$H_A+H_B=1$$

Rao et al, IJNMF, 2012



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



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

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

Mold is preheated to ten degrees hotter than the foam

Inflow is asymmetric and fills thinner area first

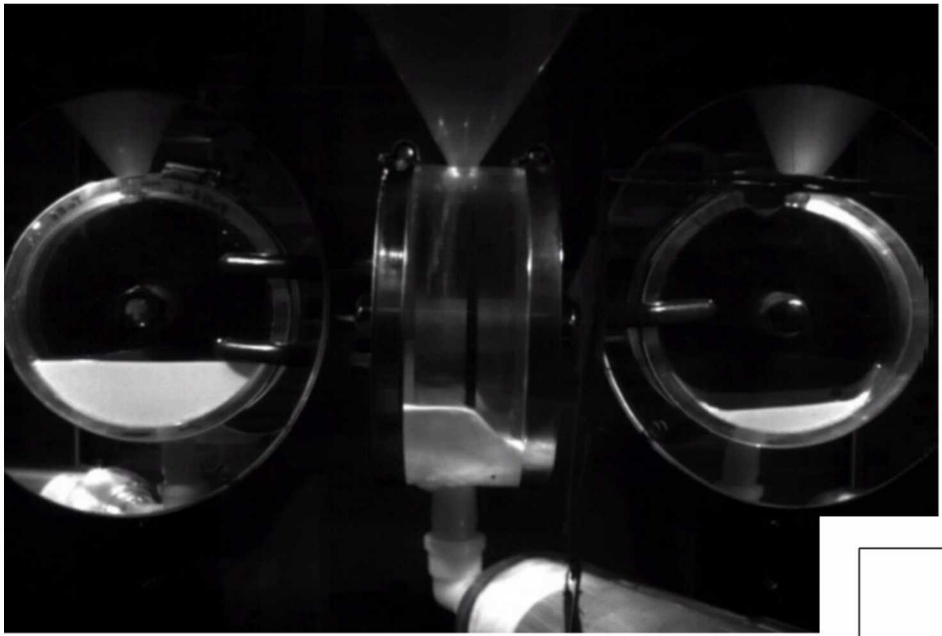
Boards have different thicknesses of foam

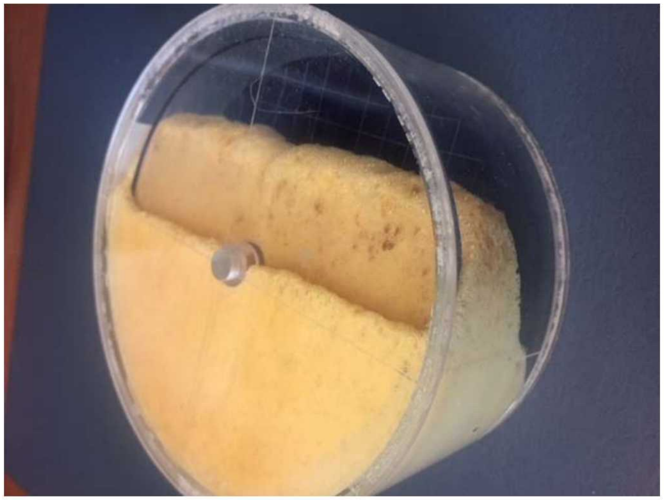
Three vents are used to improve filling

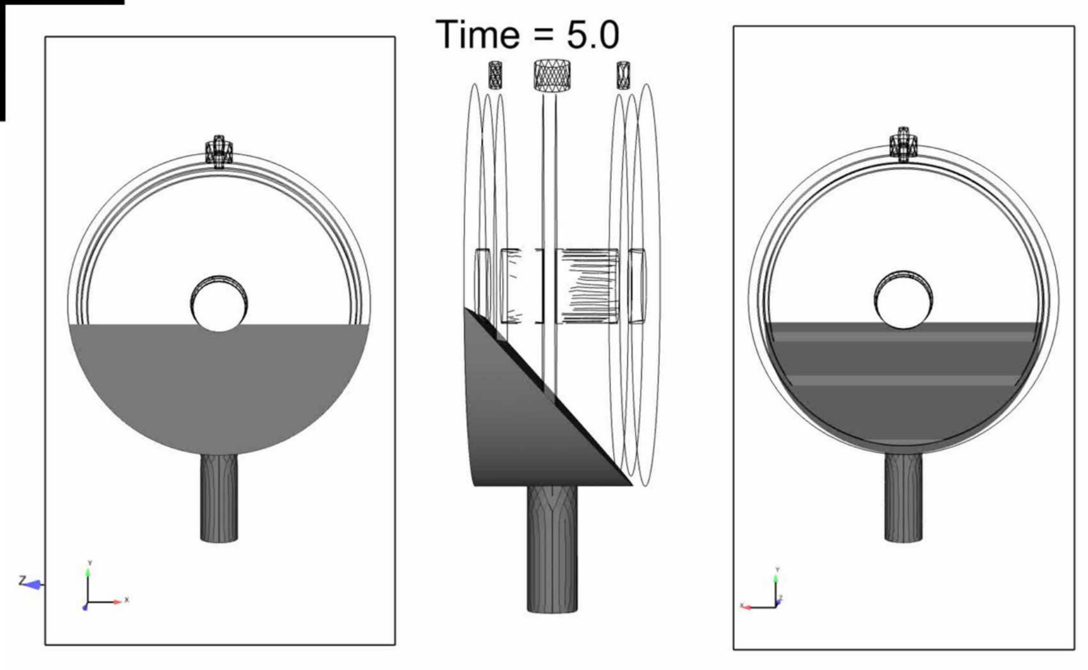
Foam slips at the wall using a Navier slip condition with Beta = .001

Gas slips ten times more than the foam

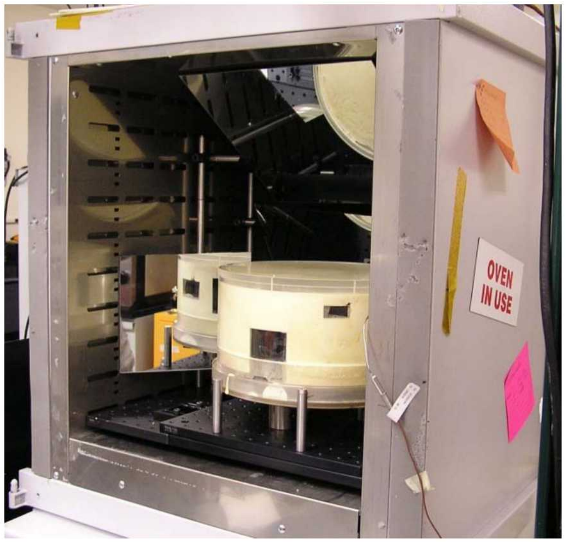
Foam Filling Simulation of Complex Part with Plates

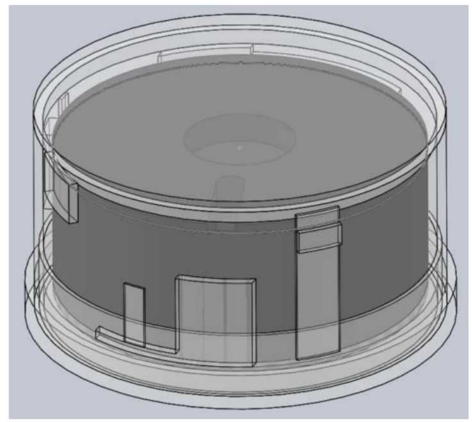


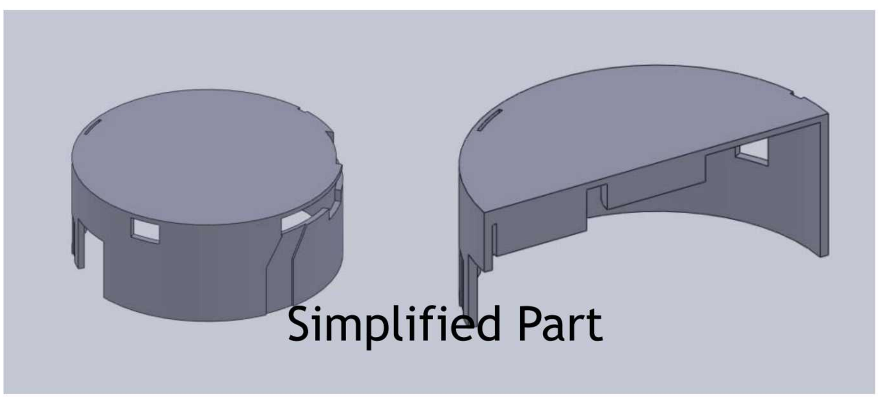


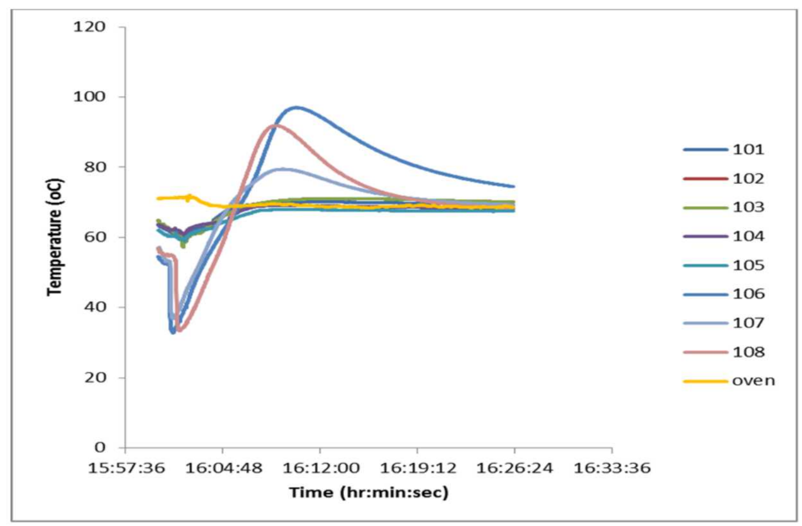


Simplified Structural Support Mold Tests

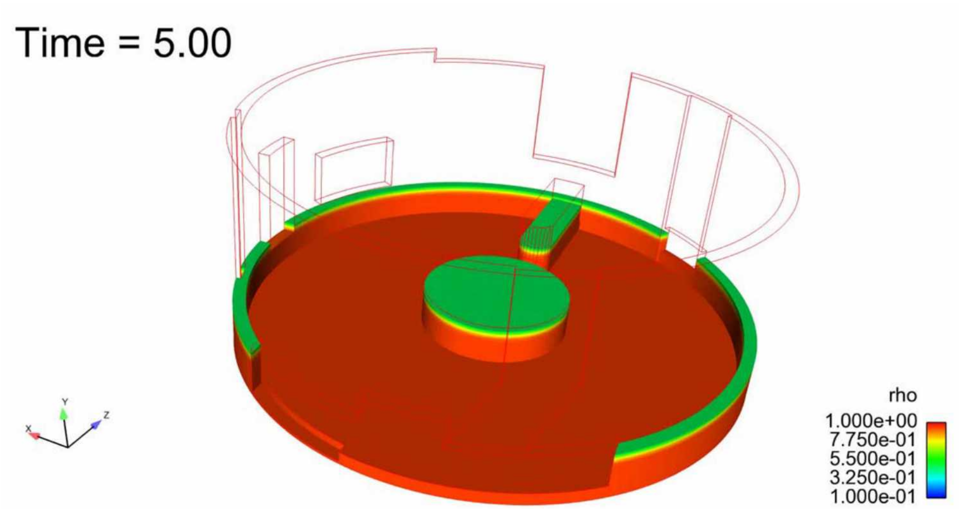


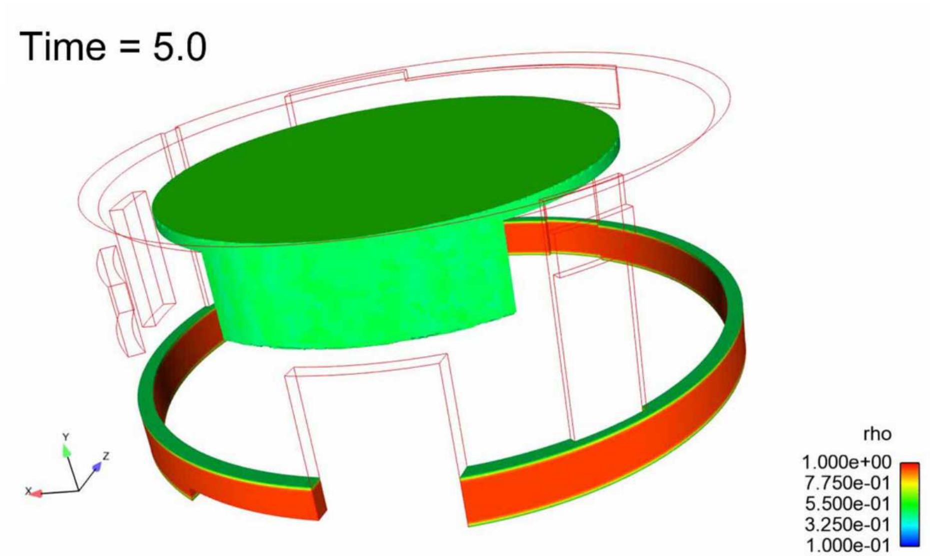




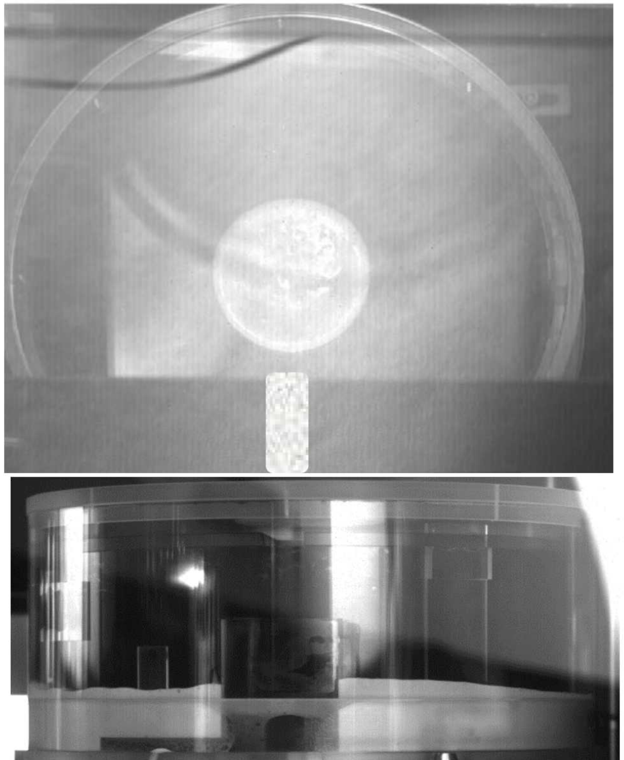


Expansion Can Help Design a Mold Filling Process

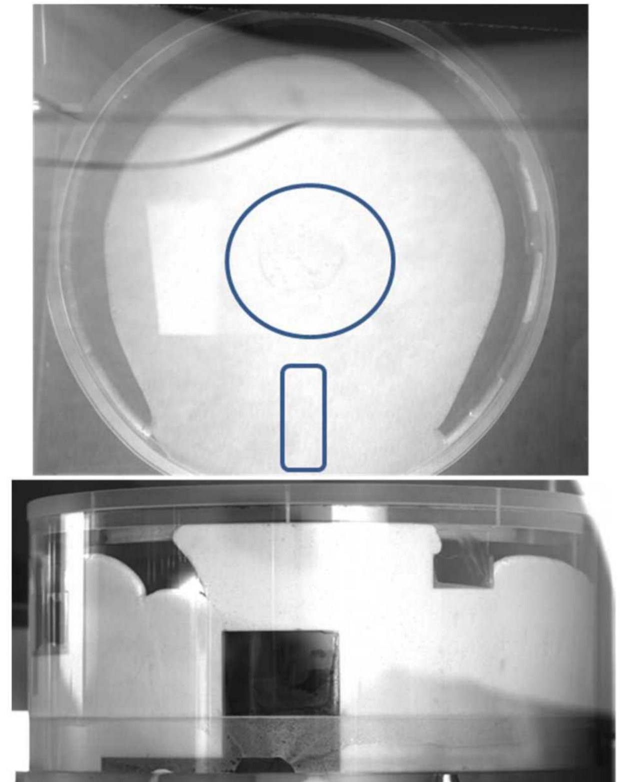


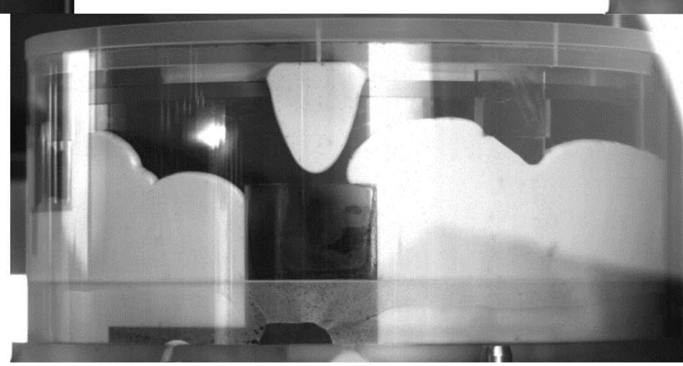


Filling Method Creates Knit Lines

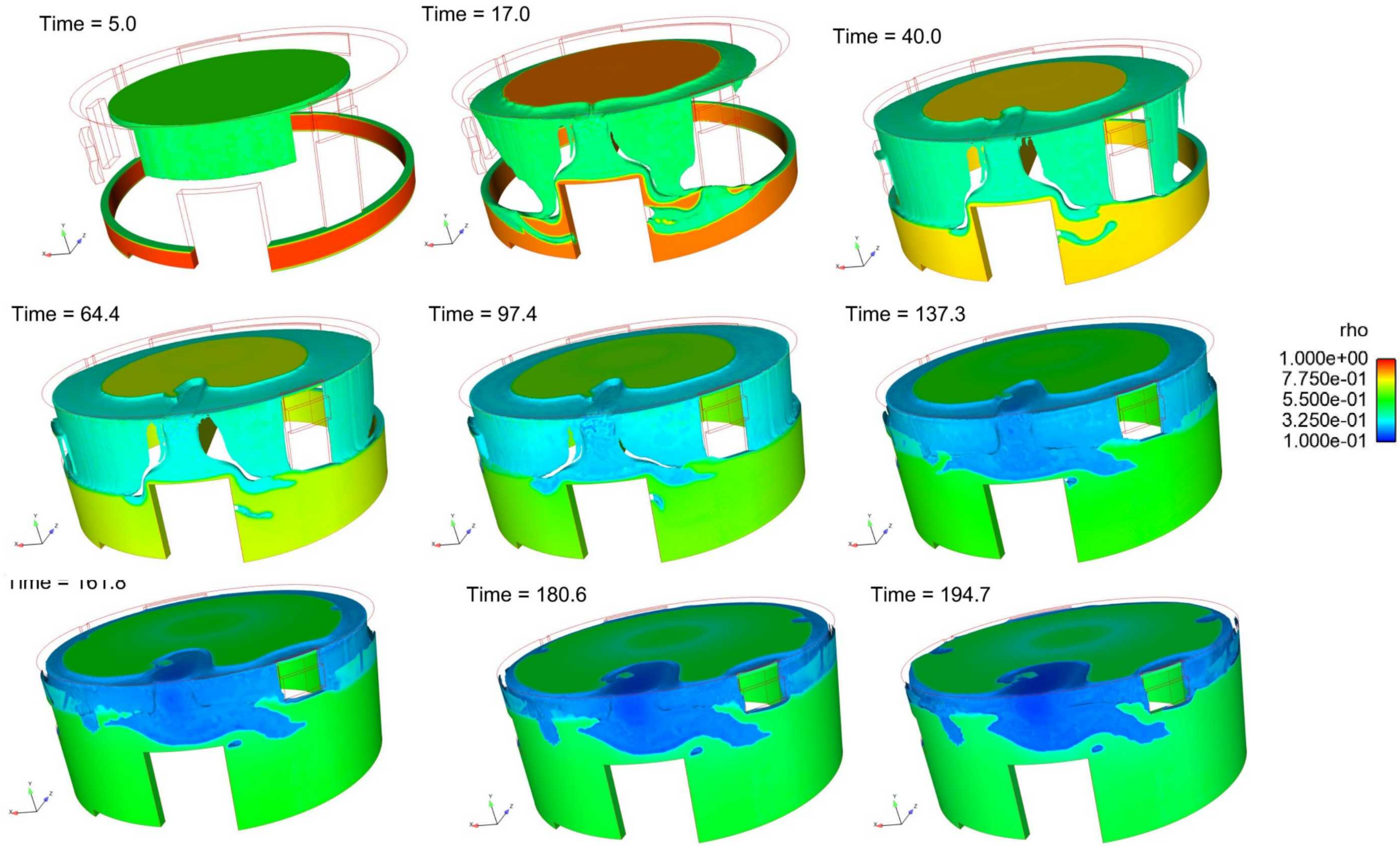


Foaming material is originally placed in top rectangular and cylindrical reservoirs and in bottom rim reservoir, to simulate legacy KC filling method

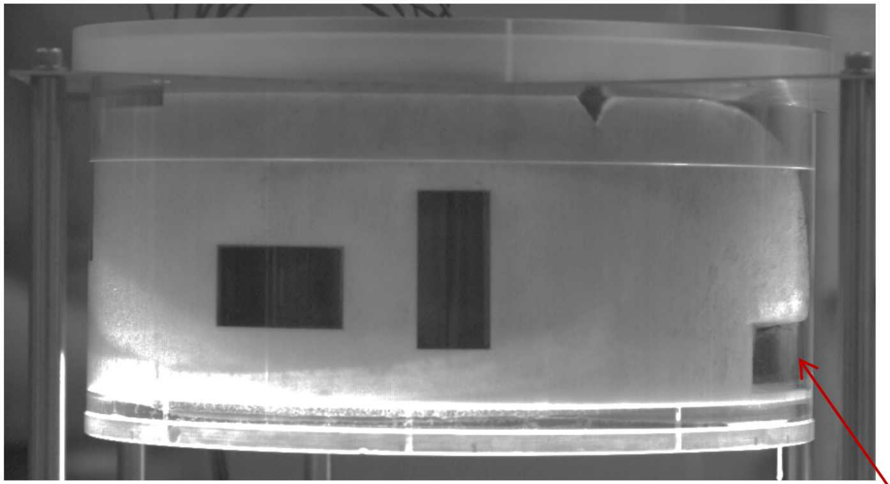


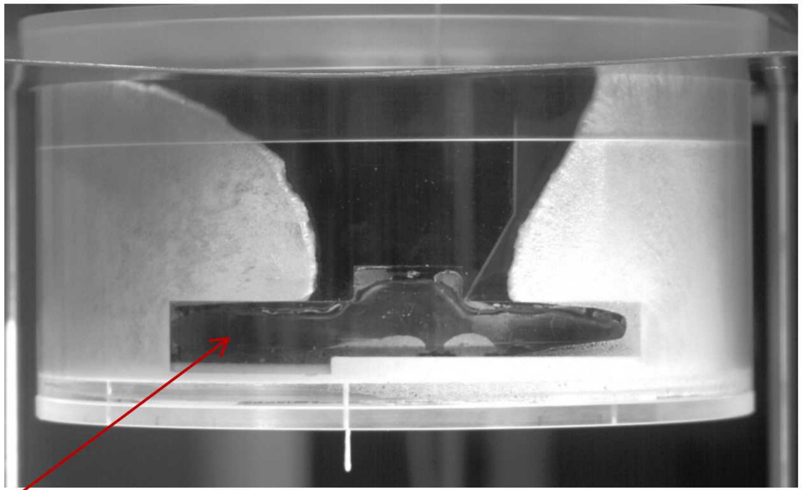


Computational Modeling of Foam Expansion Can Help Design a Mold Filling Process



Last Place to Fill Now on Other Side of Largest Feature

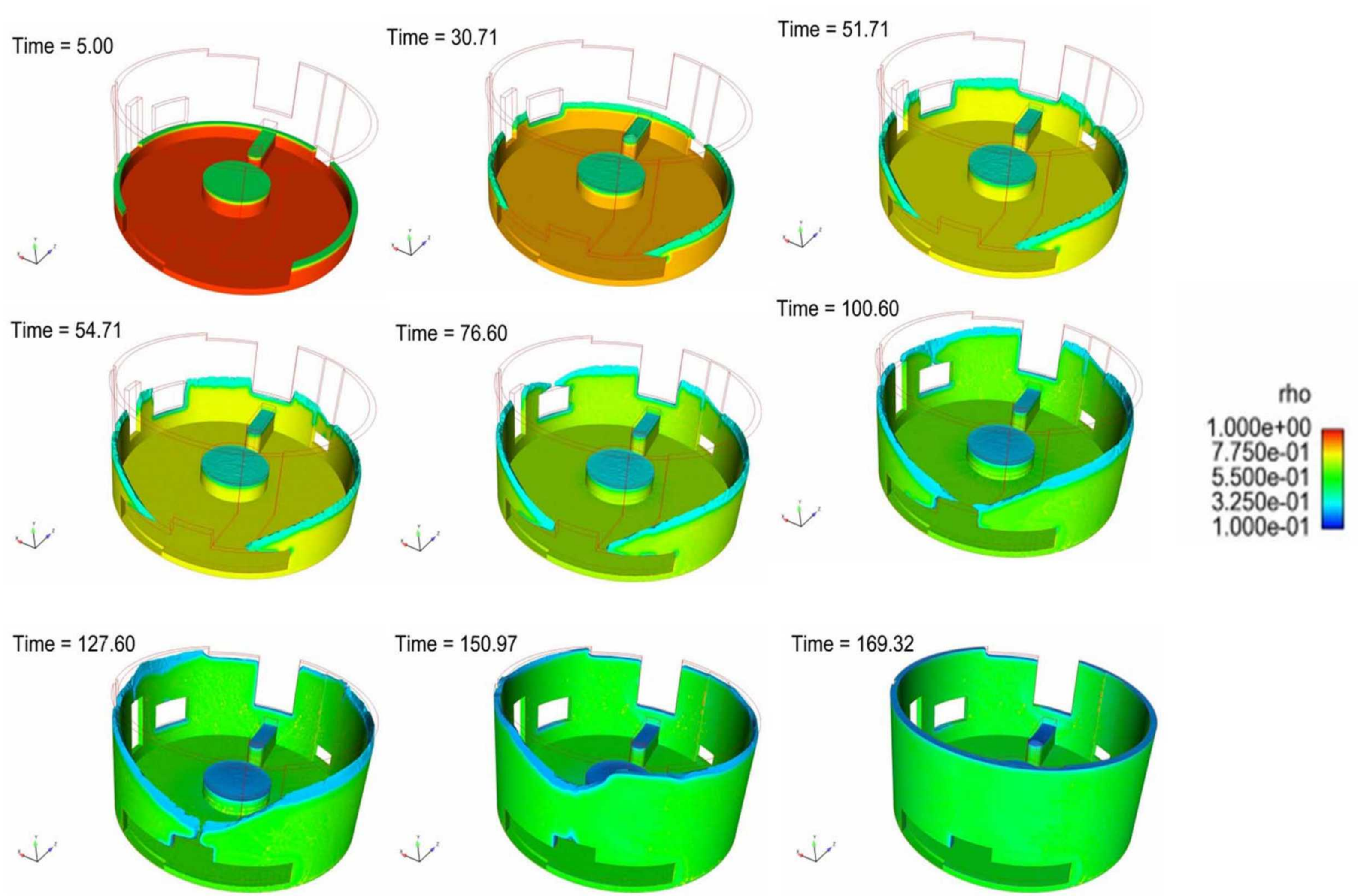




Largest feature

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.

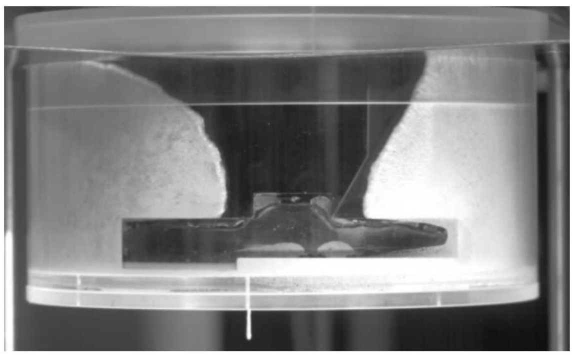
Computational Modeling of Foam Expansion Can Help Design a Mold Filling Process

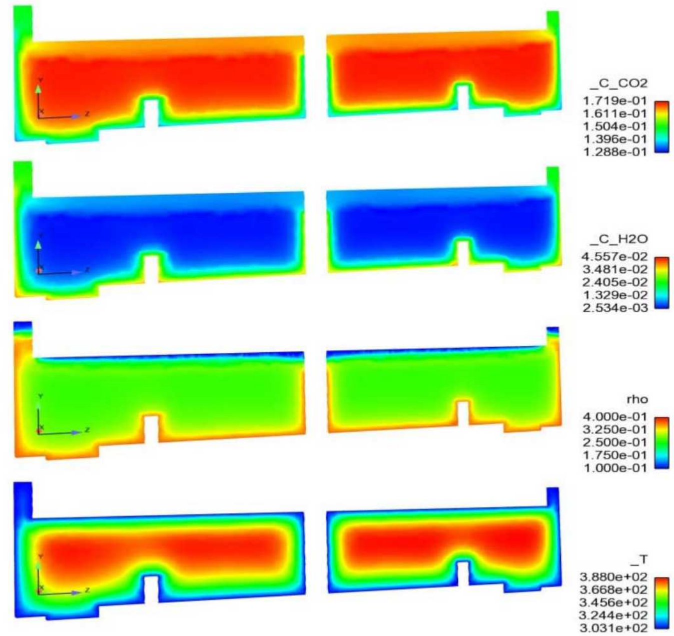


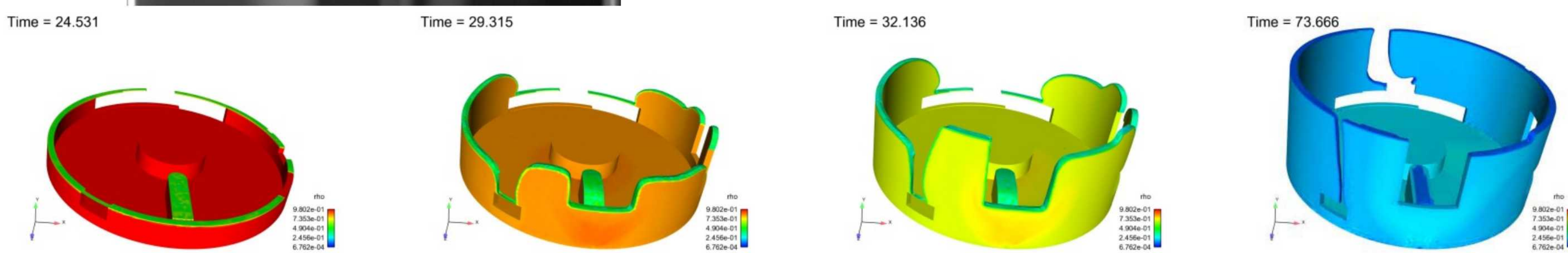
Models Give More Physics than Just the Filling Locations

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

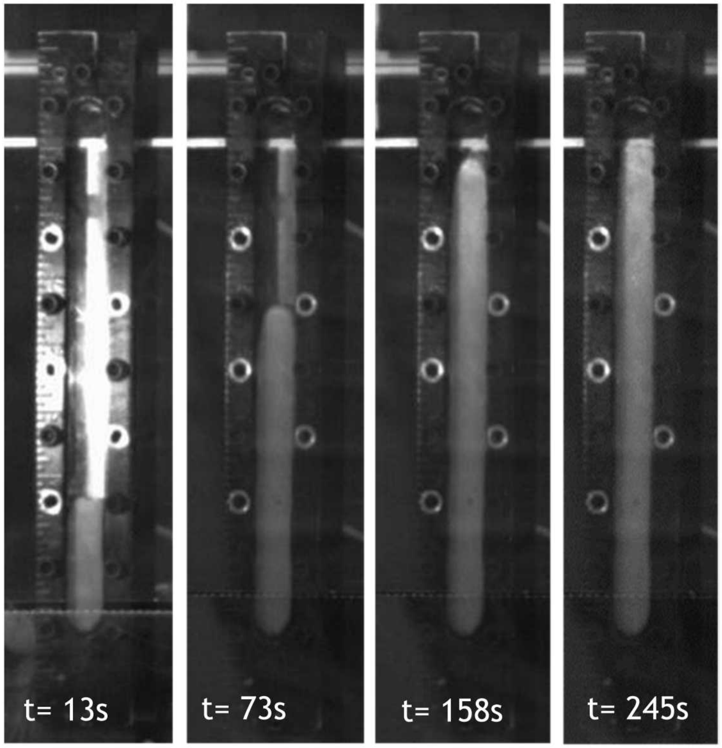




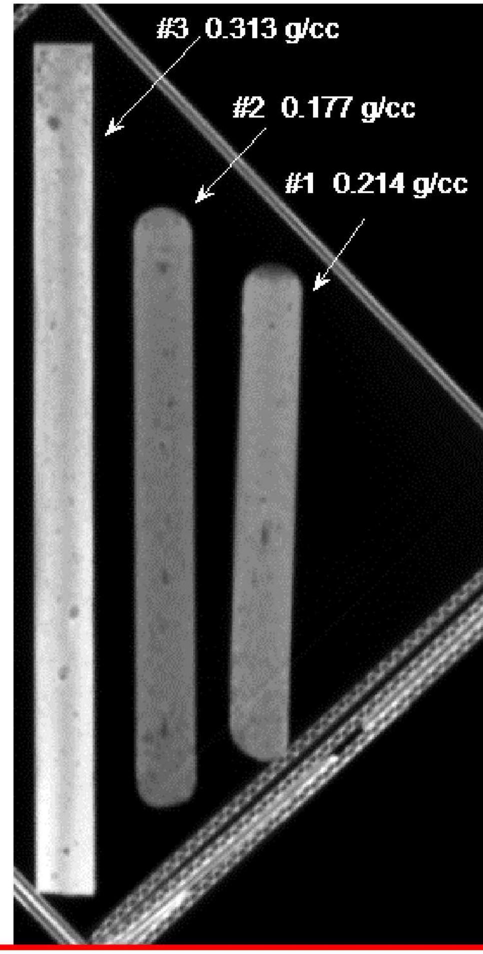


Rao et al., “Density Predictions for polyurethane foam using a finite element/level set method,” submitted

Density Study for Structural Foam PMDI-10



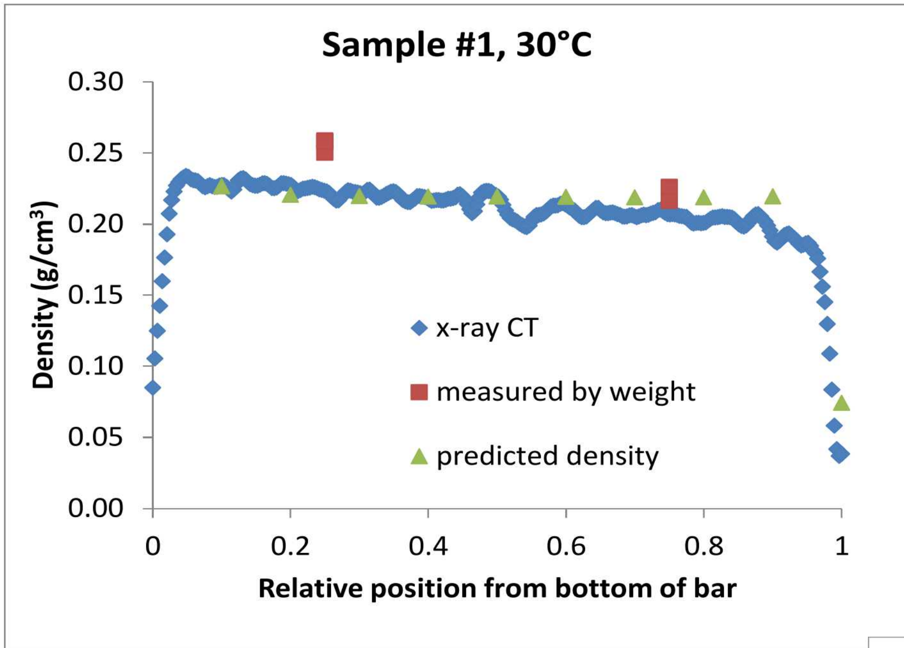
Foam expanding in a mold at 30°C. Time shown on frames is after the end of mixing the resin and the curative together for 45 seconds.

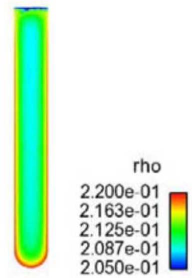


X-ray image of PMDI-10 foam bars: 1) free rise at 30°C, 2) free rise at 50°C, 3) over packed (1.5) at 30°C

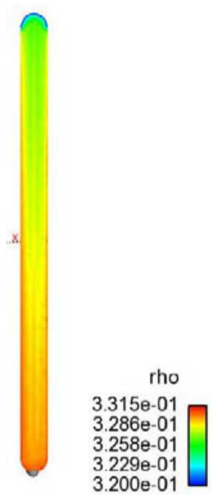
- Can the model predict the effects of over packing seen experimentally?
- Over-packed sample shows higher density and greater density variation
- 17% for free rise and 31% for over-packed foam bars

Density Study for Structural Foam PMDI-10

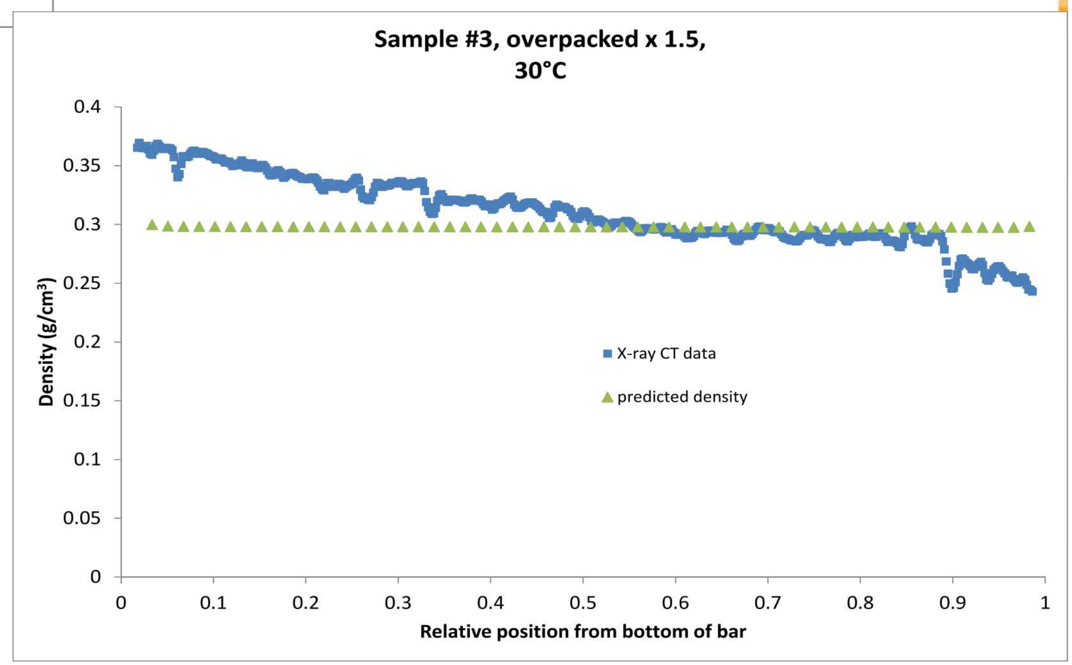




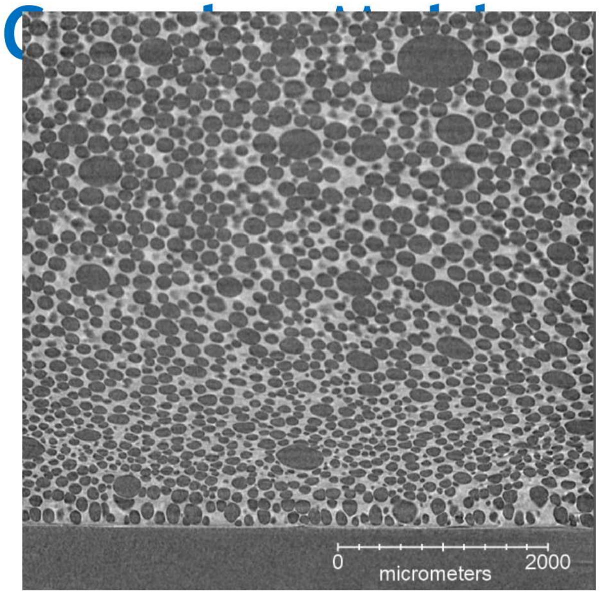
- Free rise foam density gradients. Plots are shown at the centerline of the foam cylinder
- Cylinder is under filled to give the free rise density

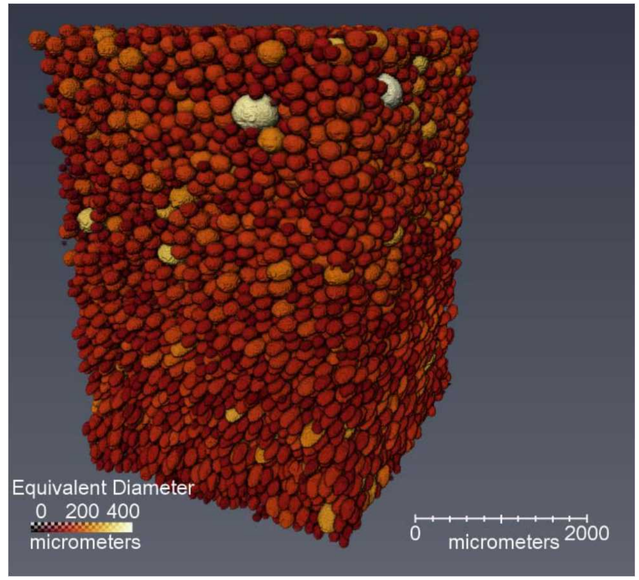


- Over packed (1.5) foam density gradients. Plots are shown at the centerline of the foam cylinder
- Self-closing vent lets air out, but keeps foam in for pressurization



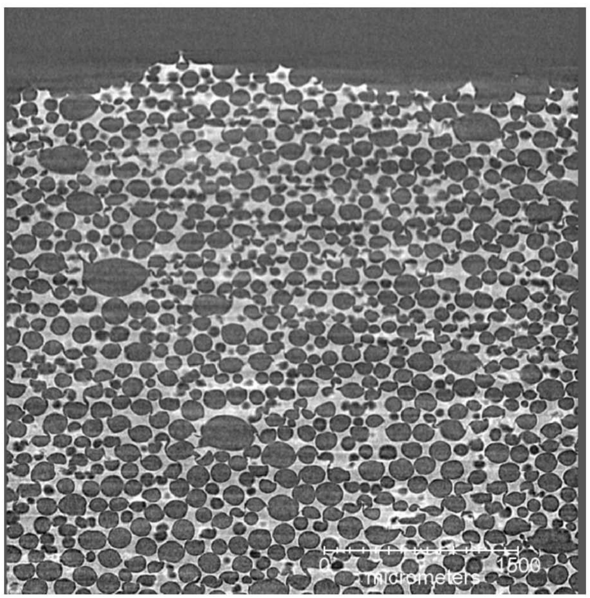
CT Microstructure of Bubbles from Large

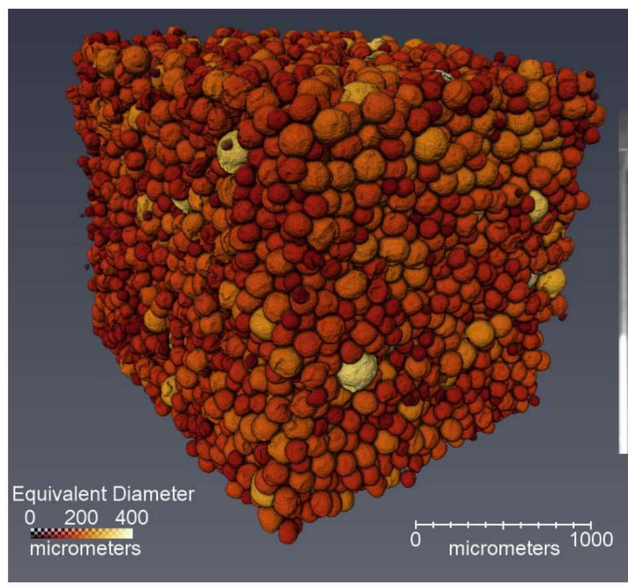


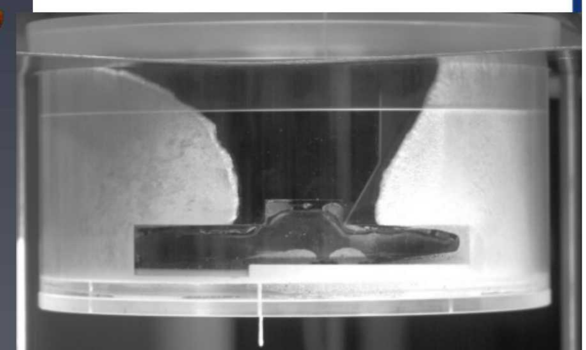


Sample 1 top

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



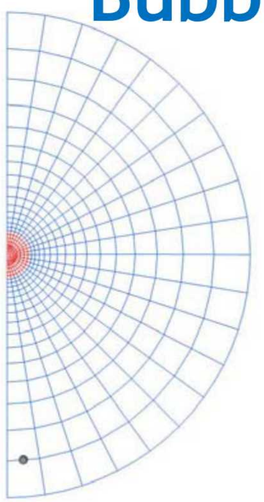




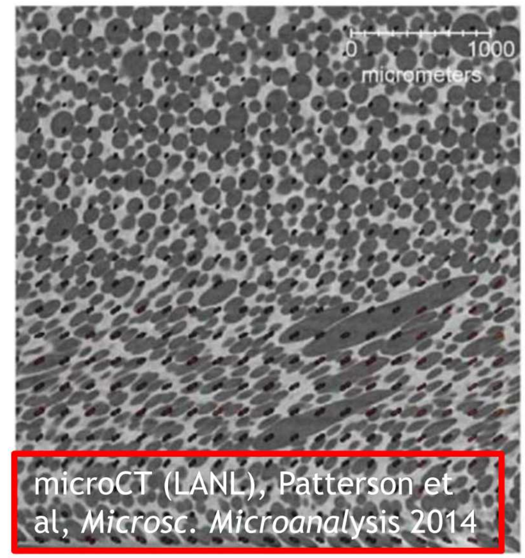
Sample 1 bottom

Brian M. Patterson, LANL, July 2016

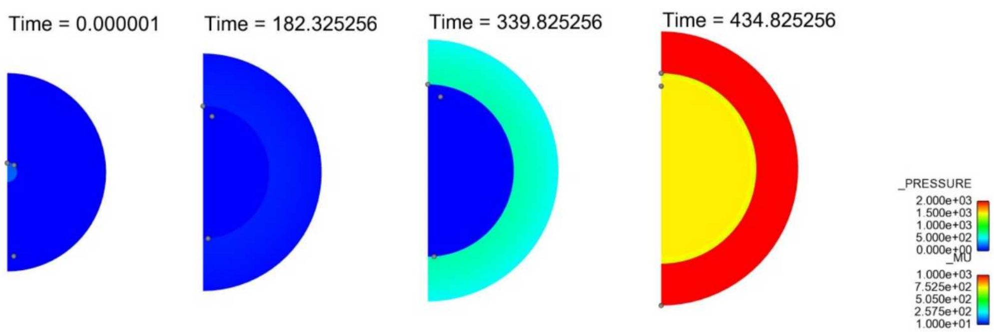
Bubble Expansion in a Polymerizing Fluid

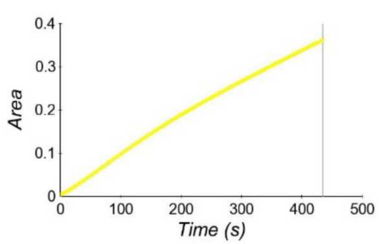


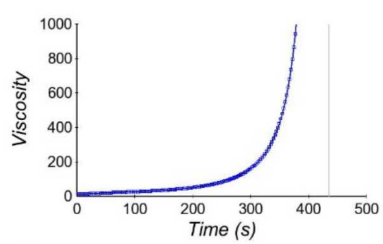
- Bubble grows as CO_2 enters the bubble (VLE model)
- Growth is halted abruptly once the polymer reaches the gel point and the viscosity diverges
- Post-gelation, bubble pressurization is observed
- ALE mesh is robust over shape change
- Data shows the correct trends when compared to experiment

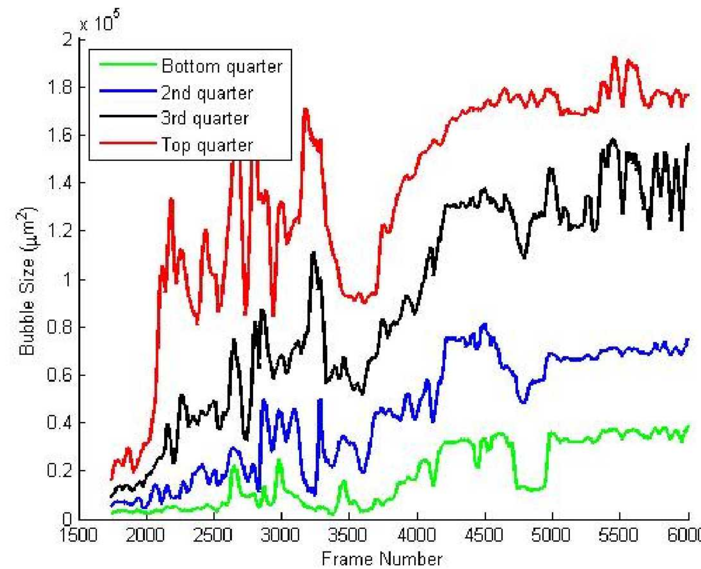


microCT (LANL), Patterson et al, *Microsc. Microanalysis* 2014



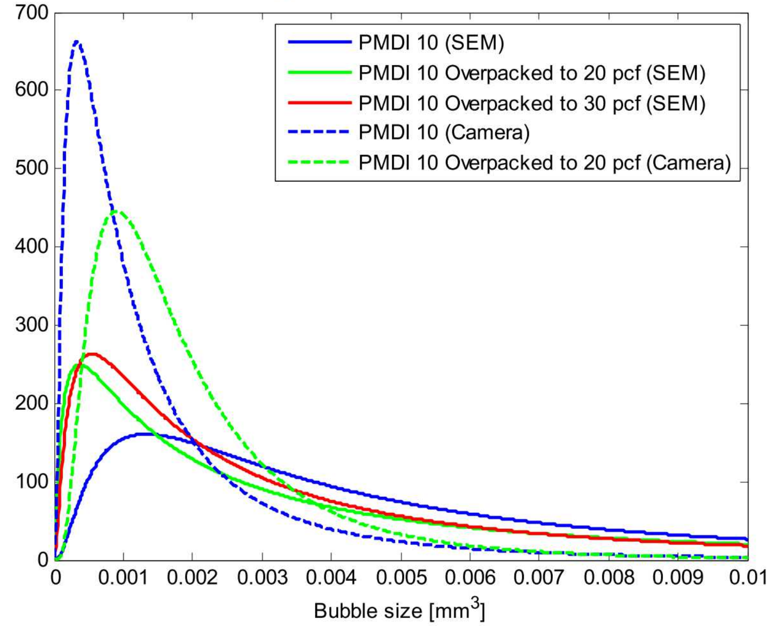


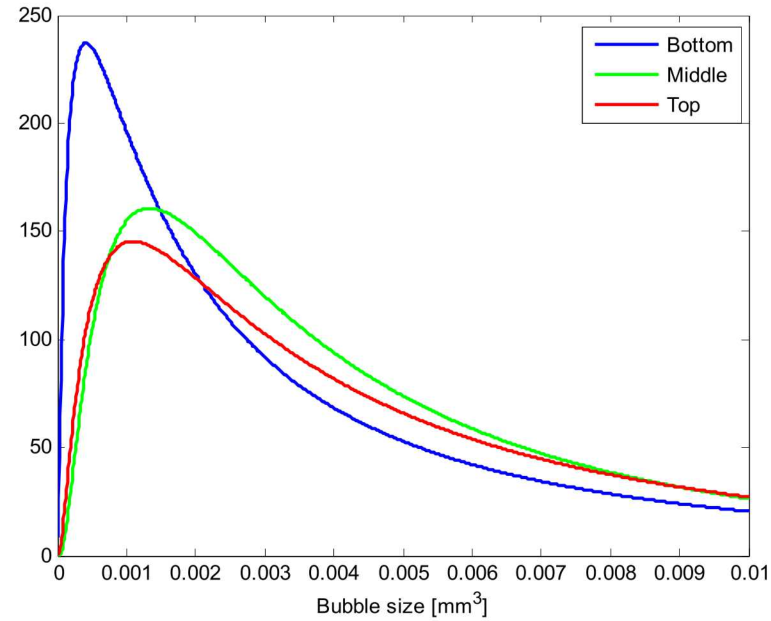


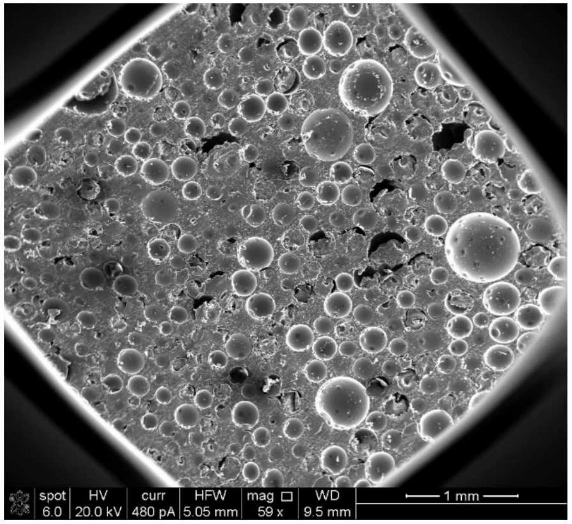


$$\rho\left(\frac{3}{2}\dot{R}^2 + R\ddot{R}\right) = p_{gas} - p_{liq} - 2\frac{\sigma}{R} - 4\eta_{polymer}\frac{\dot{R}}{R}$$

Bubble Size Data for PMDI-10 and Various Processing Conditions





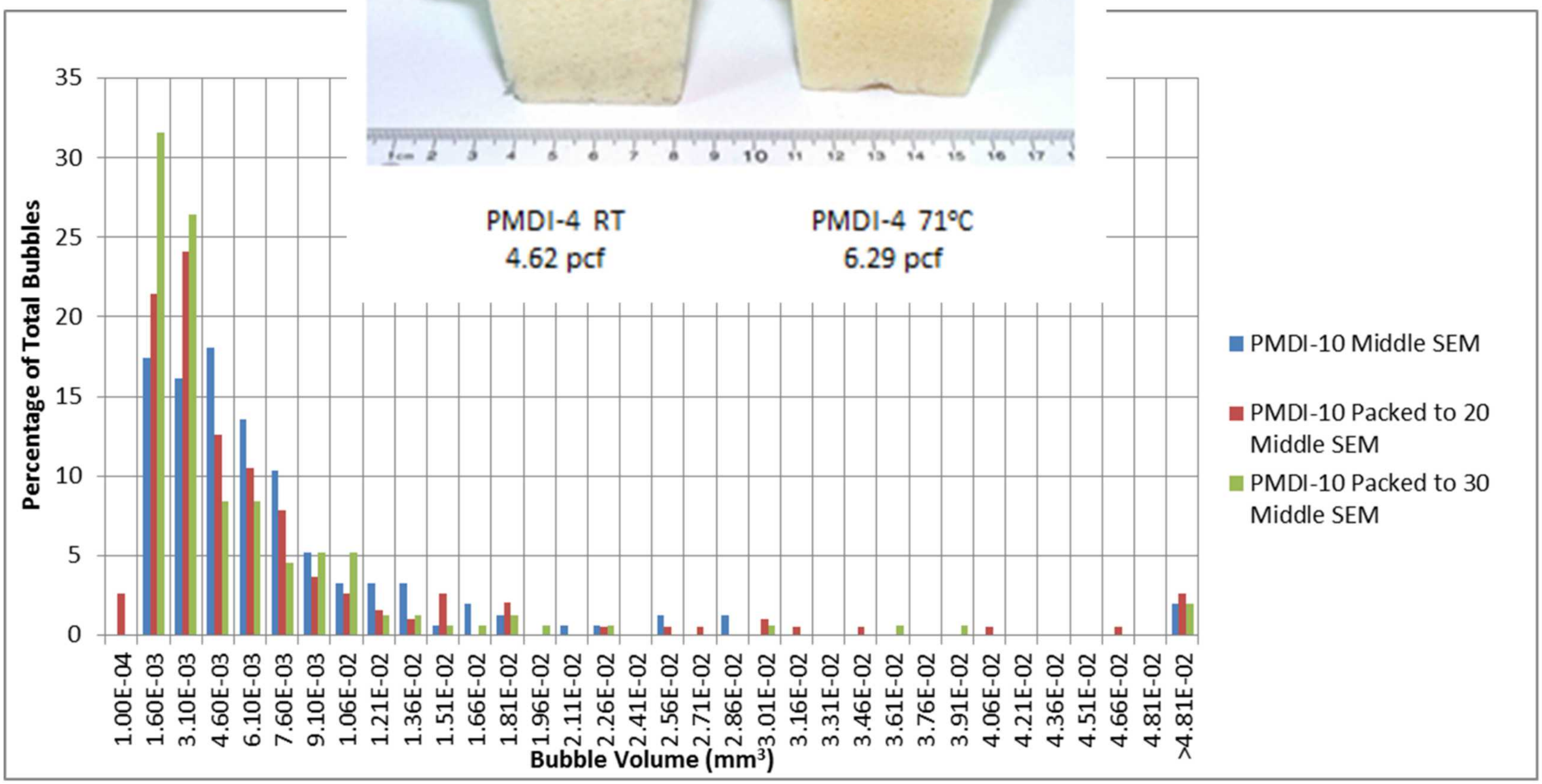


Log-normal fits to bubble size measurements for (left) overpacked PMDI 10 foam and (right) PMDI 10 free rise foam of various channel height

Processing Conditions Change Bubble-Size and Final Density

PMDI-4 RT
4.62 pcf

PMDI-4 71ºC
6.29 pcf

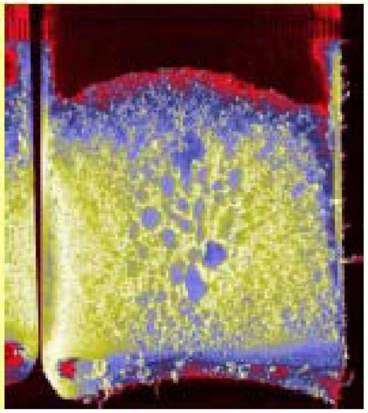


Equations of Motion Include Evolving Material Models

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

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

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



NMR imaging shows coarse microstructure (Altobelli, 2006)

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

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

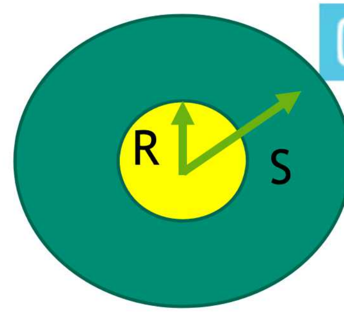
Extent of reaction equation for polymerization: condensation chemistry with T_g evolution

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

New molar concentration equations for water and carbon dioxide on the next page: kinetics stay the same

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

Influence Volume Approach (IVA)



Interchange between bubbles and liquid phase occurs at interface

$$S_{pg} = 3\frac{\varphi}{R} D_g \frac{\partial C}{\partial R}\Big|_{r=R} \qquad R_{av} = [\frac{3}{4\pi}\frac{\varphi}{n}]^{1/3}, \quad S_{av} = [\frac{3}{4\pi}\frac{1}{n}]^{1/3}$$

IVA approach assumes a linear profile of CO_2 in the fluid (blue):

$$\frac{\partial C}{\partial R}\Big|_{r=R} = \frac{C_{CO_2} - C(R)}{\Delta r}, \quad C(R) = K_H p_{gas} \qquad p_{gas} = \rho_{gas}\Re T / M_{CO_2}$$

$$S_{pg} = 3\frac{\varphi}{R_{av}} D_g \frac{C_{CO_2} - K_H p_{gas}}{\Delta r} \qquad \Delta r = \frac{(S_{av}^4 - R_{av}^4) - R_{av}(S_{av}^3 - R_{av}^3)}{S_{av}^3 - R_{av}^3}$$

Advection of Number Density Equation:

- We can either solve an advection equation (more accurate and expensive) or

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

Nomenclature

- n = nucleation sites/total volume (the number, *N*, is constant but the density changes over time (#/cc)
- m_{in} = initial mass injected (g)
- K_H = Henry's law coefficient

Newer Foam Expansion: Two-phase Carbon Dioxide Models

Water balance in the liquid phase (mol H_2O/volume total):

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

Carbon dioxide balance in the liquid phase(mol CO_2/volume total):

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

Bubble conservation equation: it adve

Carbon dioxide balance in the gas phase (mol CO_2/volume total):

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

$$S_v = \frac{3}{R} \dot{R} \approx \frac{1}{4\eta_{polymer}} ((p_{gas} - p_{liq}) - \frac{2\sigma}{R_{av}})$$

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

Carbon dioxide balance in the gas phase (mass CO_2/volume bubbles):

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

This term couples to the subscale. It is the added volume from the bubble size increase during a time step. S_v has unit of continuity. S_{pg} is the added mass from reactions.

Newer Foam Expansion: Two-phase Carbon Dioxide models

Continuity equation is foam density balance (g total/volume foam):

$$\frac{\partial \rho_f}{\partial t} + \vec{\boldsymbol{v}} \cdot \nabla \rho_f + \rho_f \nabla \cdot \vec{\boldsymbol{v}} = 0$$

Gas Volume Fraction (volume foam/volume total):

$$\phi(t) = \frac{\rho_{foam} Y_g}{\rho_{gas}} = \frac{M_{CO_2} C_{CO_2}^{g}}{\rho_{gas}}$$

Foam Density relationship is the same as before:

$$\rho_f = (\rho_{gas} - \rho_{liq})\phi(t) + \rho_{liq}$$

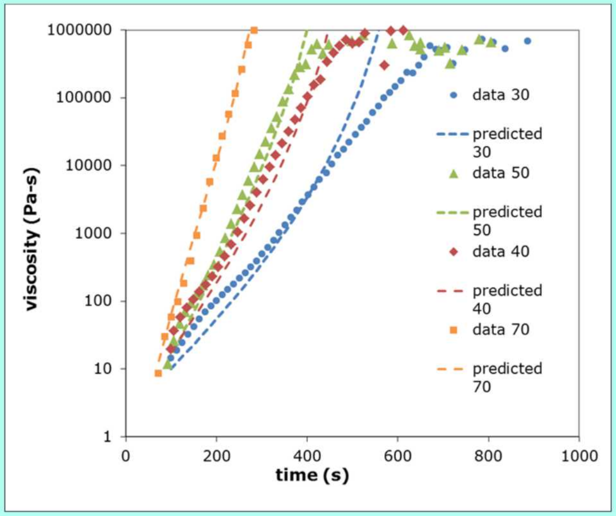
Model Foam Viscosity as f(ξ,φ)

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.

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

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

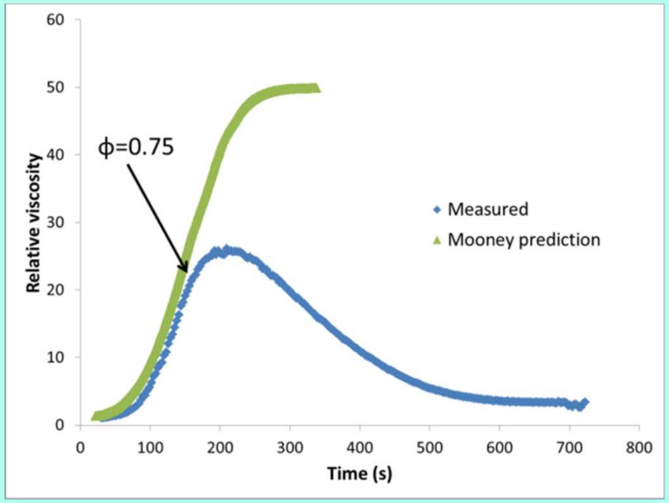


Relate foam viscosity to continuous phase viscosity

- 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 $\mu_{foam} = \mu_{cure} * f(\xi)$



Including Bubble-Scale Effects

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

Existing equation with minor mods

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

Existing equation with mods including source

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

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

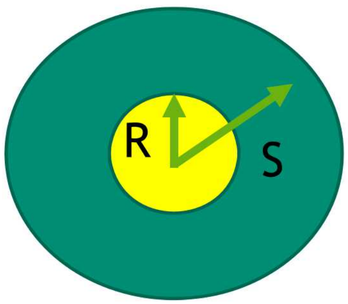
$$\varphi(t) = \frac{\rho_{foam} Y_g}{\rho_{gas}} = \frac{M_{CO_2} C_{CO_2}^g}{\rho_{gas}} \qquad \rho_f = (\rho_{gas} - \rho_{liq}) \varphi(t) + \rho_{liq}$$

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

Source terms from bubble scale:

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

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

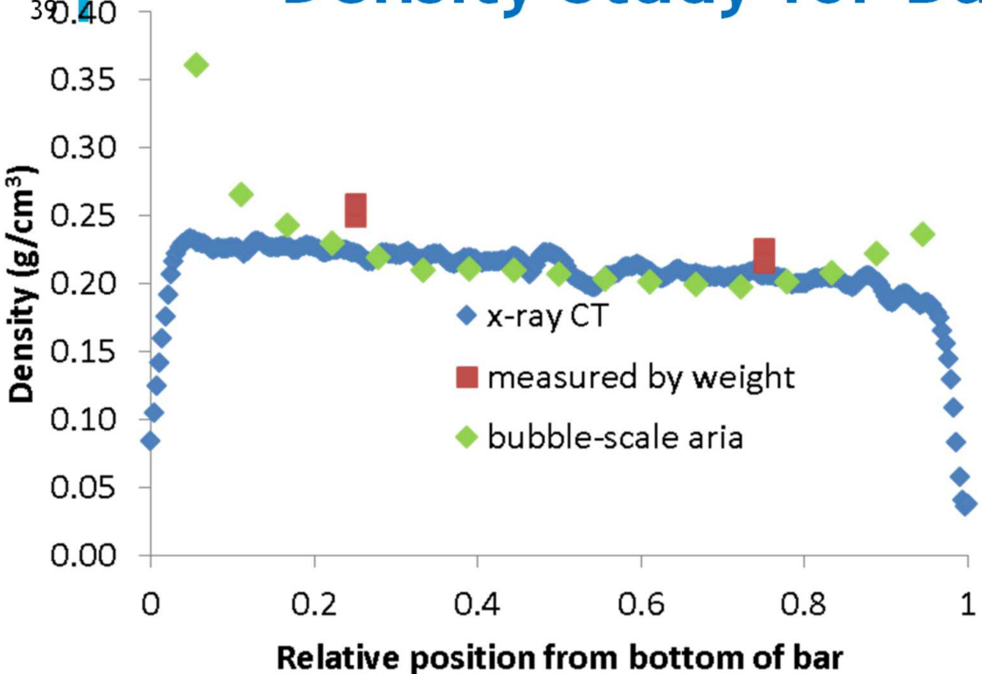


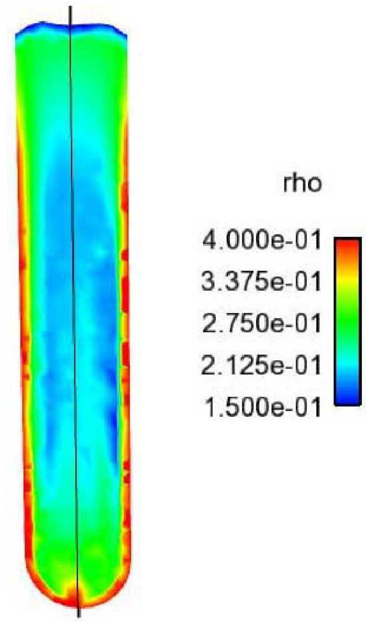
Influence volume approach

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

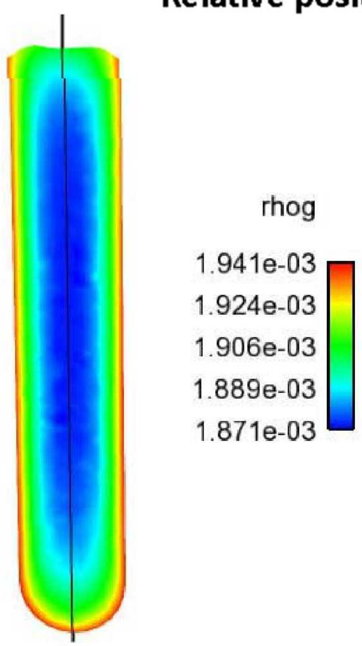
$$\eta_{polymer} = \eta_0^0 \exp(\frac{E_\mu}{RT}) (\frac{\xi_c^p - \xi^p}{\xi_c^p})^{-q}$$

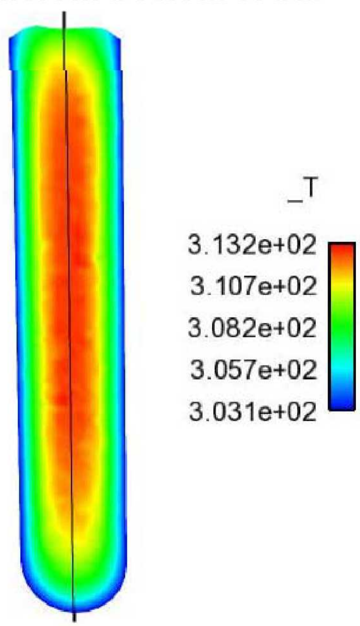
Density Study for Bubble-Scale Model

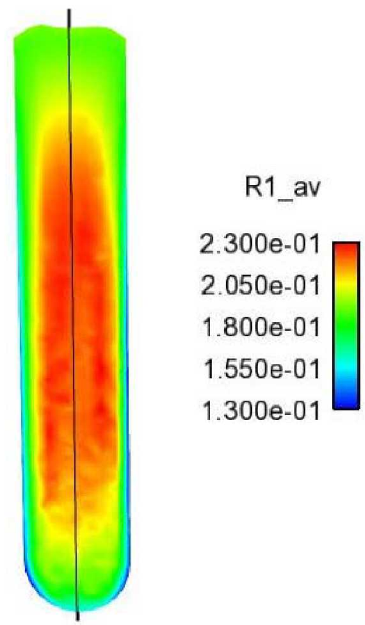




- Free rise foam density gradients. Plots are shown at the centerline of the foam cylinder

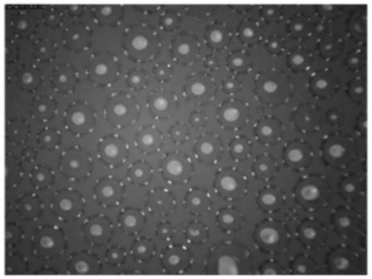




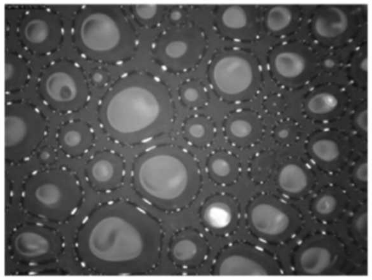


Density Study for Bubble-Scale Model

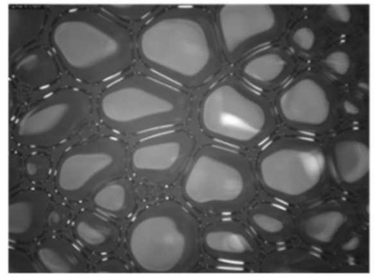
PMDI-4 free rise (bottom camera)



Time =79.5s

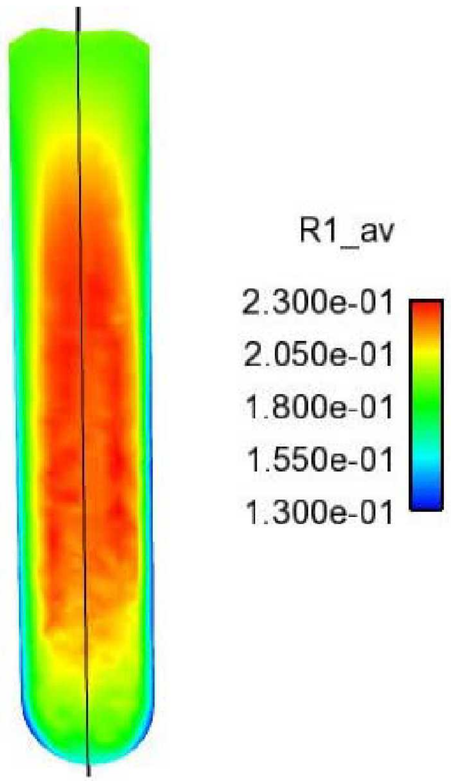


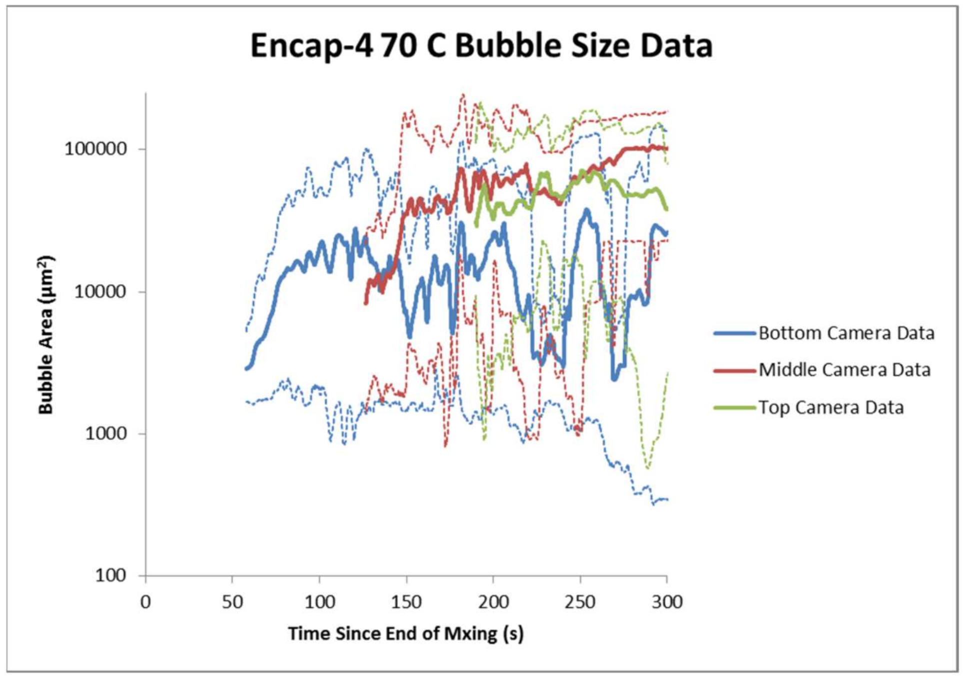
Time =152s



Time =266s

- Free rise foam density gradients. Plots are shown at the centerline of the foam cylinder





Population Balance Equation (PBE)

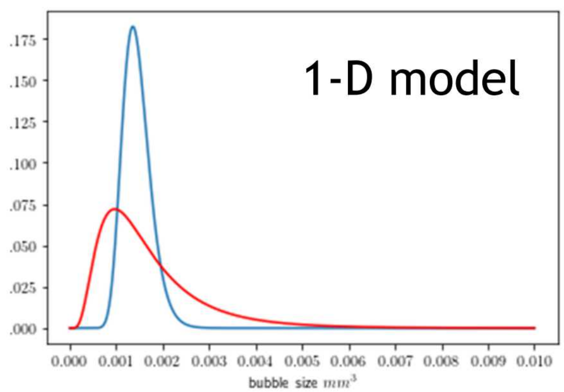
Bubble size distribution (BSD) is described by a number density function, $n(v)$, representing the number of bubbles per unit volume of liquid in volume between the range v and $v + dv$ (*Karimi et al. 2017*)

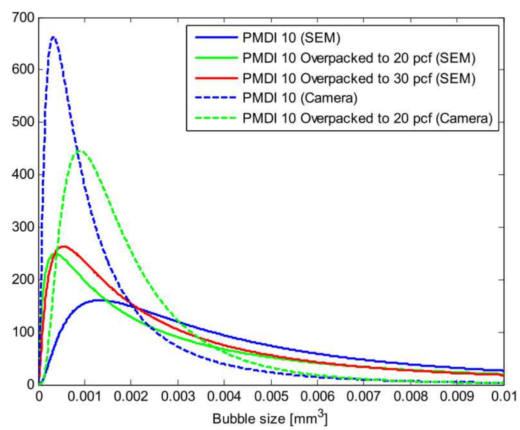
Evolution of the BSD is governed by the following Population Balance Equation (*Karimi et al. 2016, 2017*):

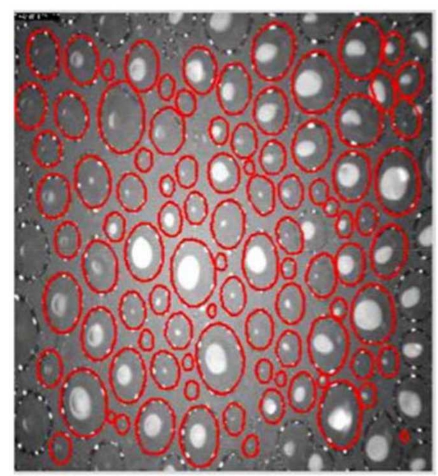
$$\frac{\partial n(v)}{\partial t} + \nabla \cdot (n(v)\mathbf{u}) + \frac{\partial}{\partial v}[n(v)G(v)] = \frac{1}{2}\int_0^v \beta(v', v - v')n(v')n(v - v')dv' - \int_0^\infty \beta(v, v')n(v)n(v')dv'$$

Where $\beta(\mathrm{v}', \mathrm{v})$ represents the coalescence kernel, and $G(v)$ represents the growth rate of bubbles.

References: Marchisio, Fox 2005, Karimi et al 2016, 2017







Bottom camera example free rise PMDI-10

Extending Kinetics Formulation to Include PBE

Equation for concentration H_2O remains unchanged

$$\frac{\partial C_{H_2O}}{\partial t} + \nabla \cdot (C_{H_2O}\mathbf{u}) - D_{H_2O}\nabla^2 C_{H_2O} = -Nk_{H_2O}C_{H_2O}^n$$

But now to account for growth rates of bubbles we have equations for both concentrations of liquid CO_2 and gaseous CO_2 and relate these based on growth rate determined by the QMOM

$$\frac{\partial C_{CO_2}^{liq}}{\partial t} + \nabla \cdot (C_{CO_2}^{liq}\mathbf{u}) - D_{CO_2}^{liq}\nabla^2 C_{CO_2}^{liq} = Nk_{H_2O}C_{H_2O}^n - \bar{G}_1 \frac{P}{RT}$$

$$\frac{\partial C_{CO_2}^{gas}}{\partial t} + \nabla \cdot (C_{CO_2}^{gas}\mathbf{u}) - D_{CO_2}^{gas}\nabla^2 C_{CO_2}^{gas} = \bar{G}_1 \frac{P}{RT}$$

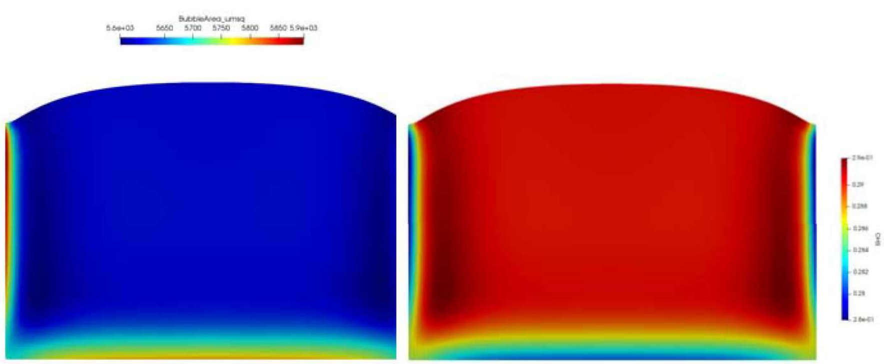
Following Karimi et al. 2017 our growth rate currently is a simple constant growth rate based on the mass fraction of liquid CO_2

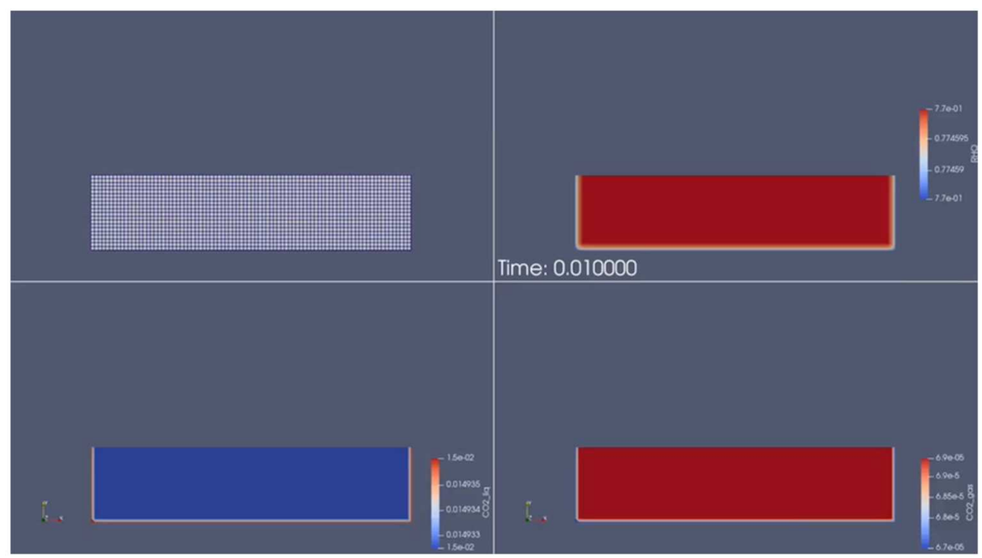
$$\bar{G}_k \cong \sum_{i=1}^{N} w_i G(v_i) v_i^{k-1}$$

$$G(v_i) = G_0(w_{CO_2} - w_{max}) / w_{max}$$

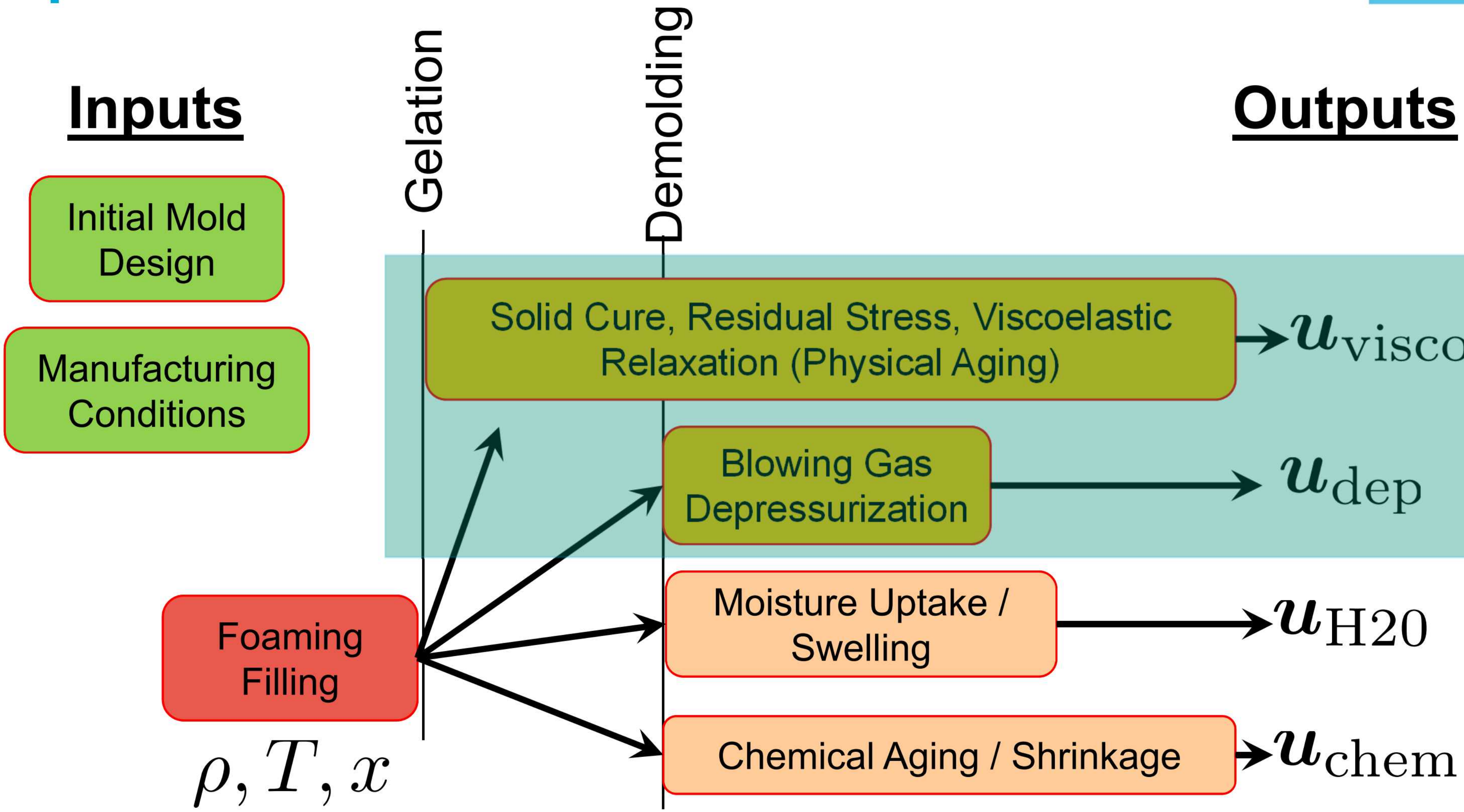
Where w_{CO_2} and w_{max} are mass fraction of liquid CO_2 and mass fraction related to the maximum solubility of liquid CO_2

$$G_0 = \frac{\partial V}{\partial t} \approx 5x10^{-8}\,\frac{cm^3}{s}$$





Cradle-to-Grave Simulation Process



$$\boldsymbol{u} = \boldsymbol{u}_{\mathrm{visco}} + \boldsymbol{u}_{\mathrm{dep}} + \boldsymbol{u}_{\mathrm{H20}} + \boldsymbol{u}_{\mathrm{chem}}$$

Inverse Mold Design Process

Inputs

Manufacturing Conditions

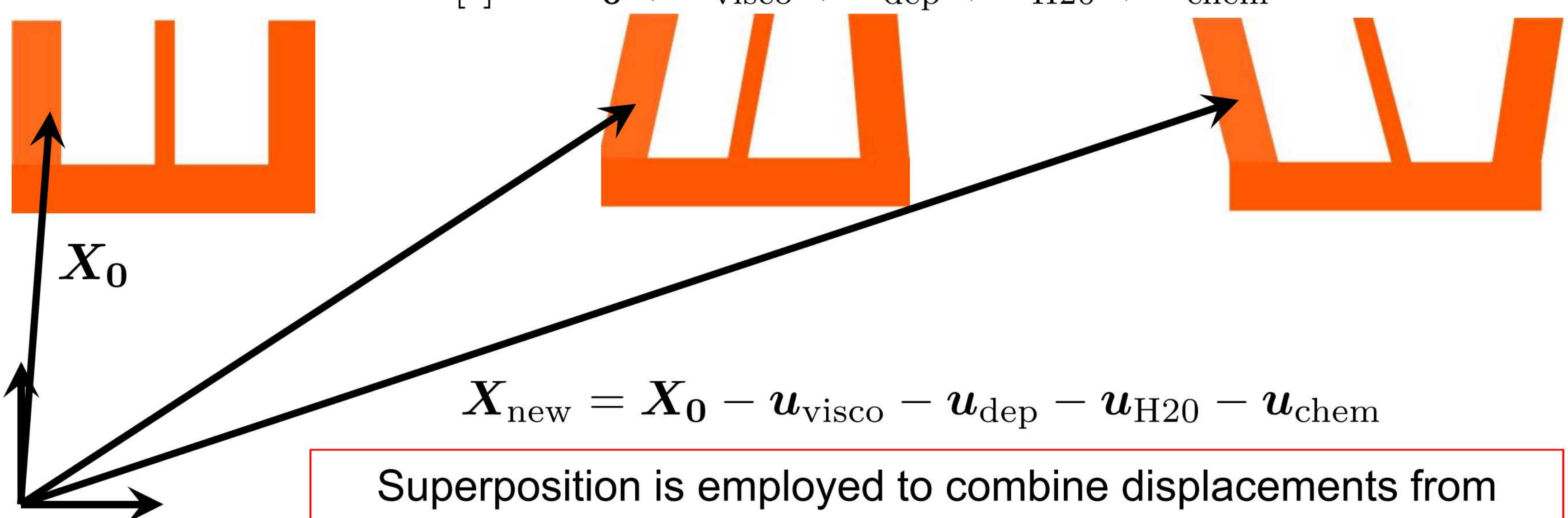
Initial Mold Design

→ Cradle-to-Grave Simulation →

Output

Final Mold Shape

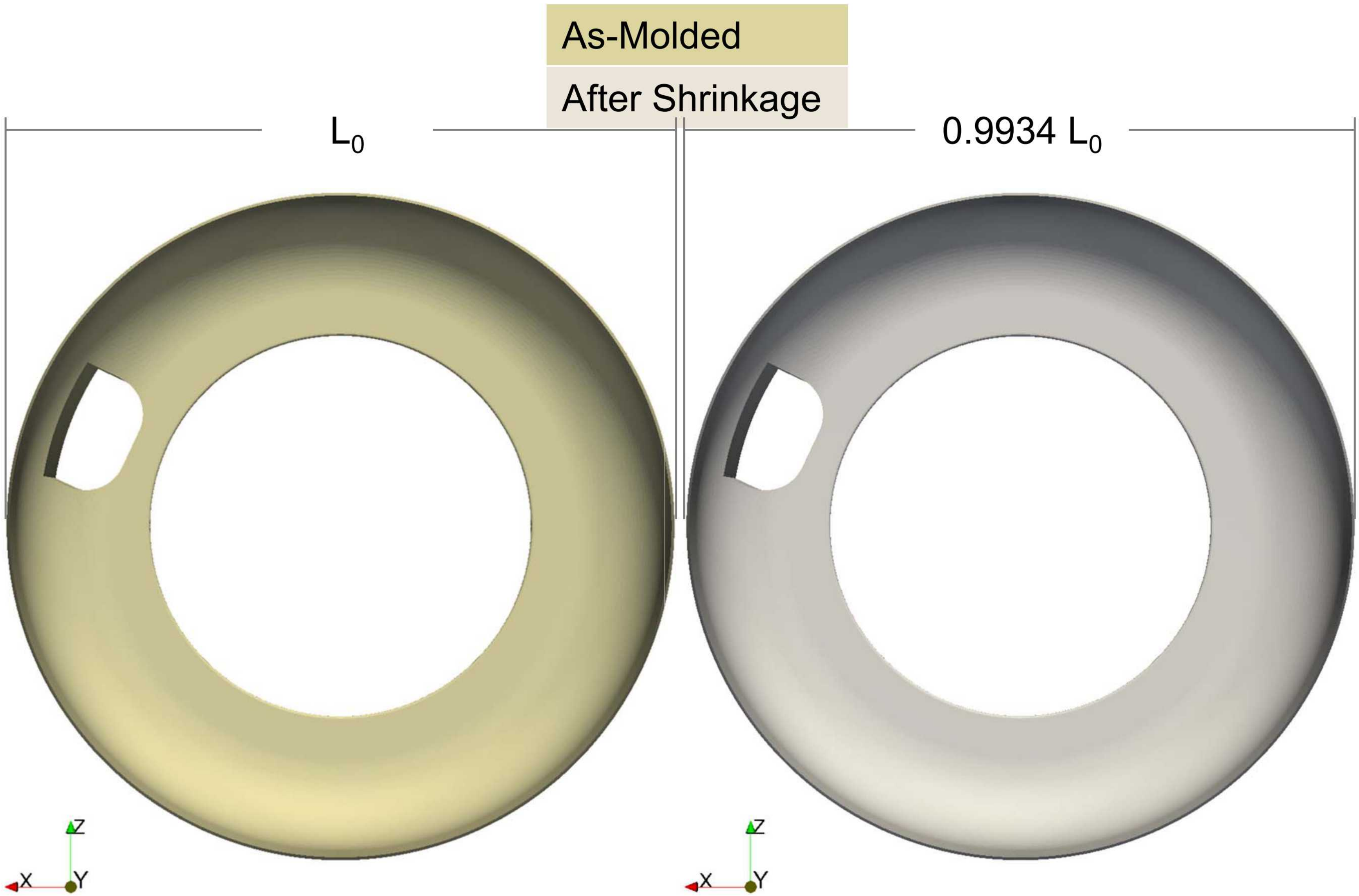
$$\boldsymbol{X}[t] = \boldsymbol{X_0} + \boldsymbol{u}_{\text{visco}} + \boldsymbol{u}_{\text{dep}} + \boldsymbol{u}_{\text{H20}} + \boldsymbol{u}_{\text{chem}}$$



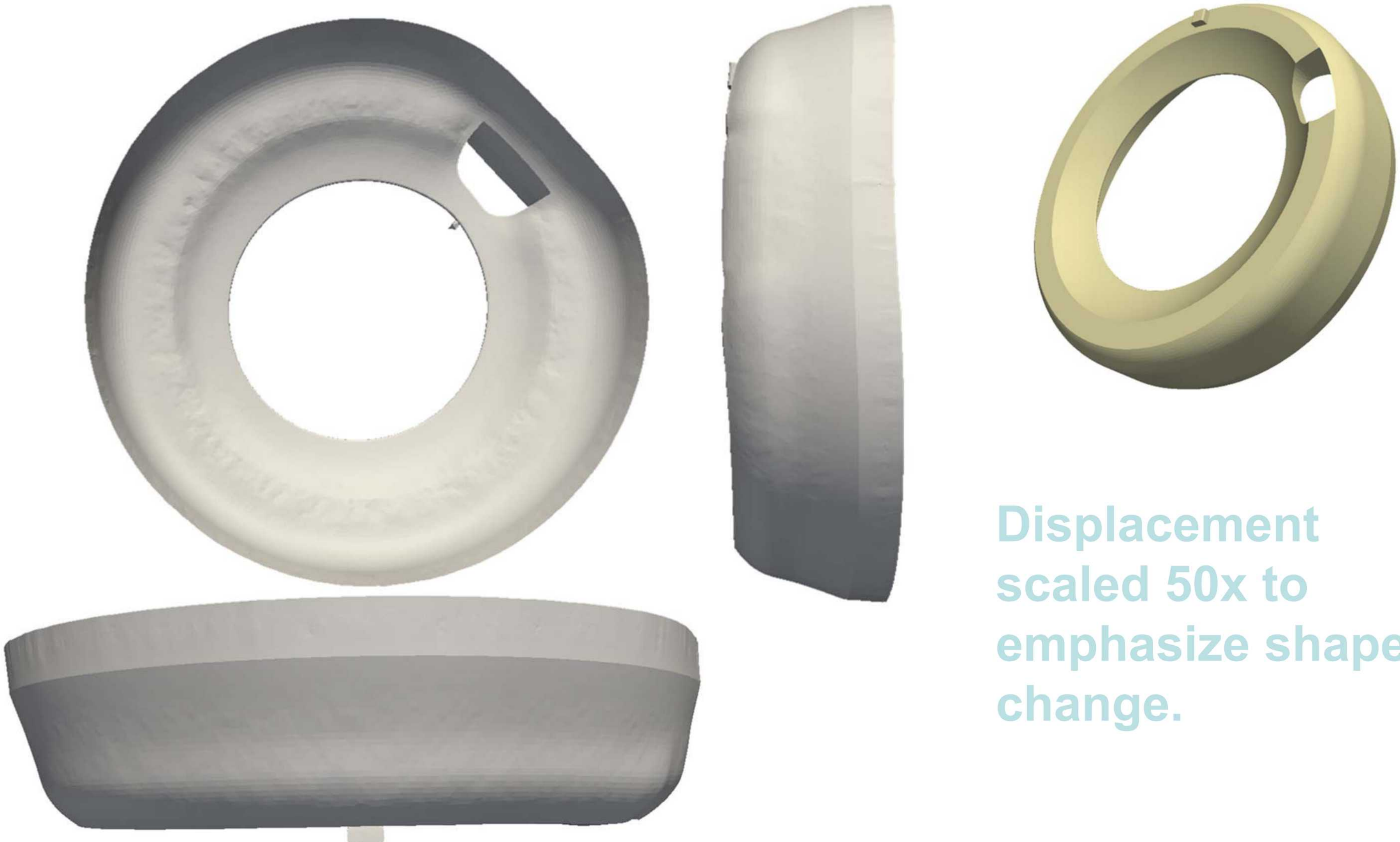
$$\boldsymbol{X}_{\text{new}} = \boldsymbol{X_0} - \boldsymbol{u}_{\text{visco}} - \boldsymbol{u}_{\text{dep}} - \boldsymbol{u}_{\text{H20}} - \boldsymbol{u}_{\text{chem}}$$

Superposition is employed to combine displacements from different mechanisms and then to “inverse warp” the initial mold design

Exemplar Part With Featured Regions



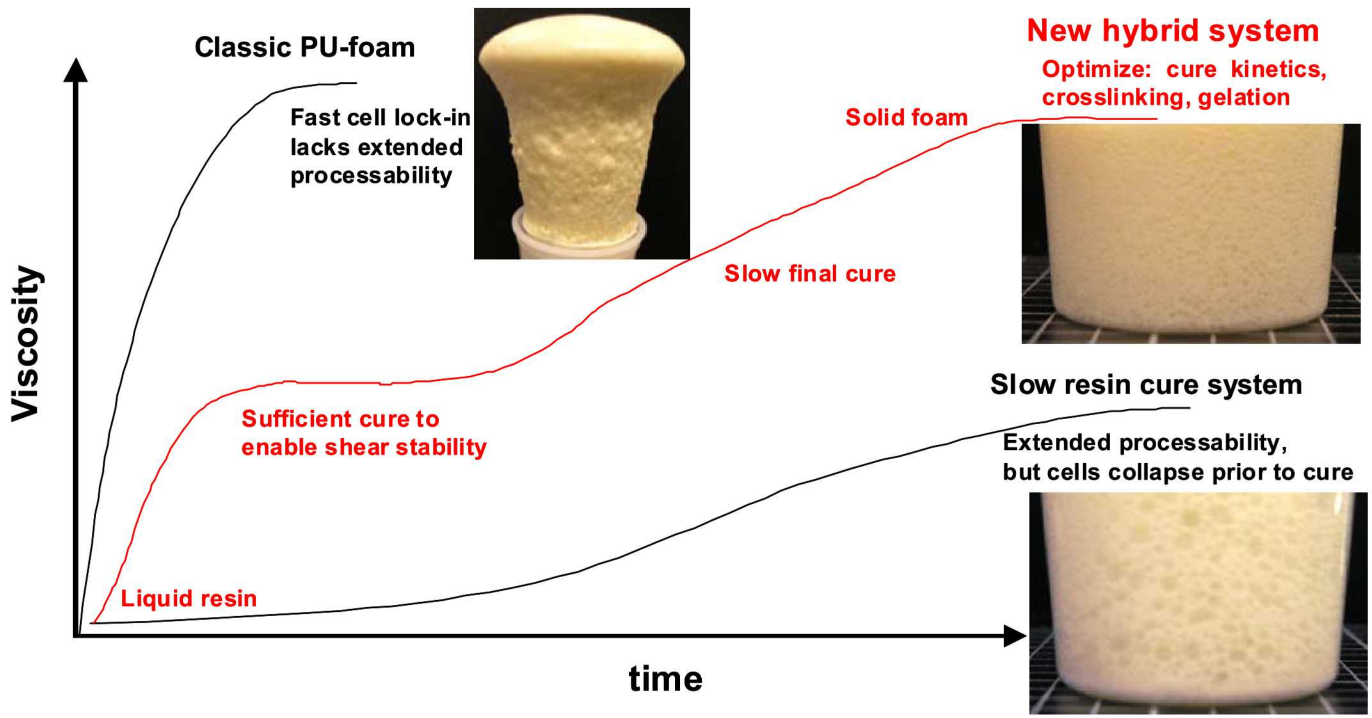
Warpage accentuated near holes and slender regions



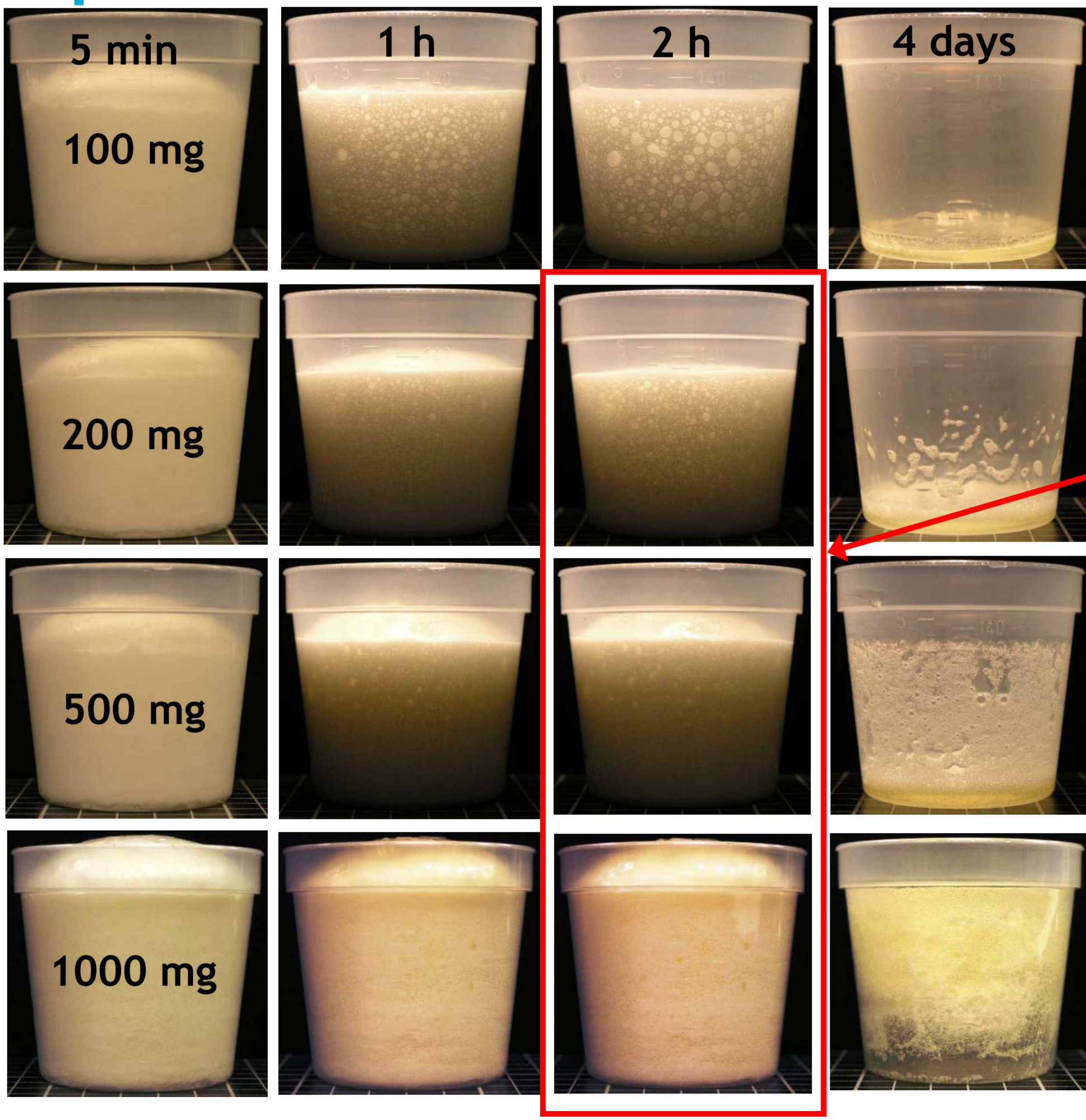
Displacement scaled 50x to emphasize shape change.

Efforts to Develop Chemically Blown Curing Epoxy Foam to Eliminate Problems in Physically Blown Foams

- Chemically blown foam less sensitive to mixing, so easier to control
- Strategy: Develop shear-stable foam system that has sufficient polymer network support, but is still amenable to flow and processing (slow penetration of gaps) AND minimize exotherm



Example: Enhanced persistence with additional crosslinking

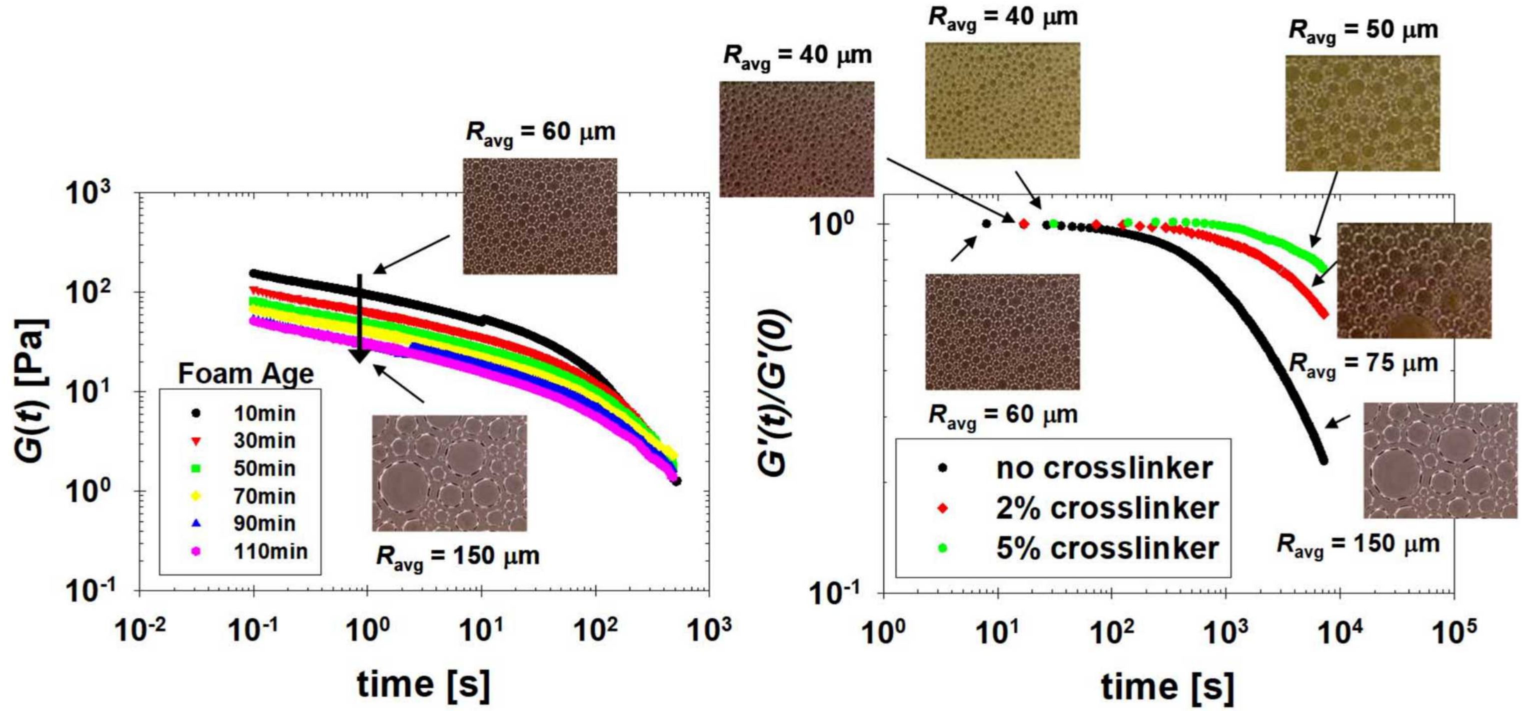


- Addition of low conc. fast reacting p-MDI
- Assists forming an early weak support network, beginning gelation and higher Mw
- Can support long-term fine cell structure

- <u>Network chemistry</u>
- Crosslinking
- Gelation
- Enhanced viscosity, elasticity

Stability Studies Using Rheology and Observation

- Small amounts of PMDI yields additional stabilization to prevent coarsening
- Rheological tests correlated with bubble size measurements



Early Gelation Through Light Cross-linking Stabilizes Foam Cells While Foam Remains Processable

Approach towards more stable foams

Foam with improved processing stability: Goals are controllable cure, broad processing window and stable foam features, good flow stability under strain

Basic approach for a chemically blown, epoxy foam:

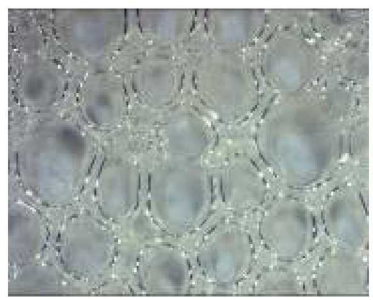
Base epoxy resin: Epon 154, 100 parts
Anhydride curative ECA100, 75 phr
Reactive polyol AD310, 8.7 phr
Isocyanate 9561, 12.2 phr
BOC foaming aid, 1 phr
Surfactant DC5986, 0.5% in total resin
Catalyst, imidazole, 1% in total resin

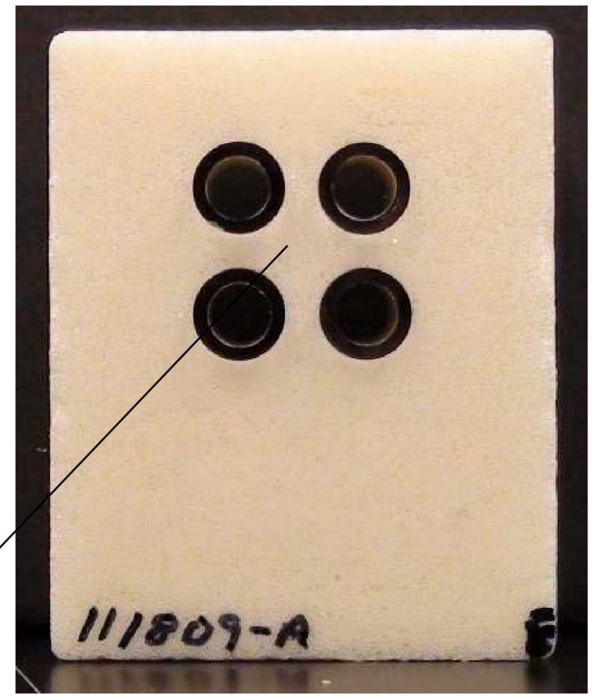
→ Main epoxy resin cure (Base epoxy resin; Anhydride curative)

→ Initial cell stabilizing urethane condensation (Reactive polyol)

→ Contribute to foaming (Isocyanate; BOC foaming aid)

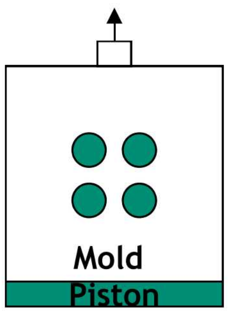
Note: Traces of water in resins will react with isocyanate to produce some CO_2



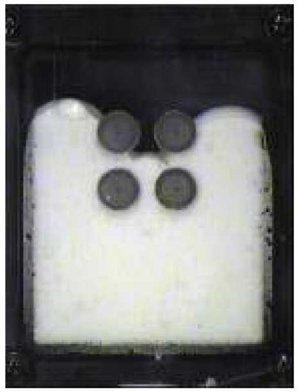


Pushed foam into mold (density~0.18g/cc)

Candidate Foams Tested in "Push" Process

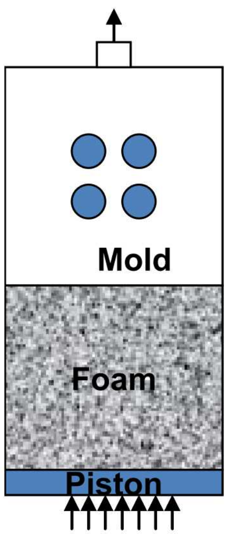


Low viscosity



High viscosity

- In general, lower viscosity resins fill narrow spaces better when self-rising (pictured here) or when pushed.



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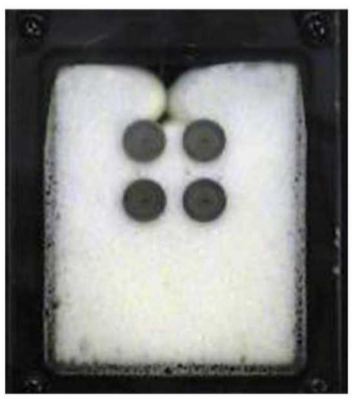
Free-rise



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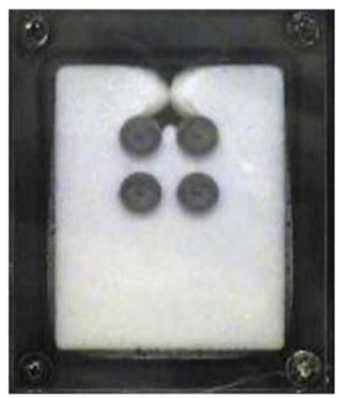
Push



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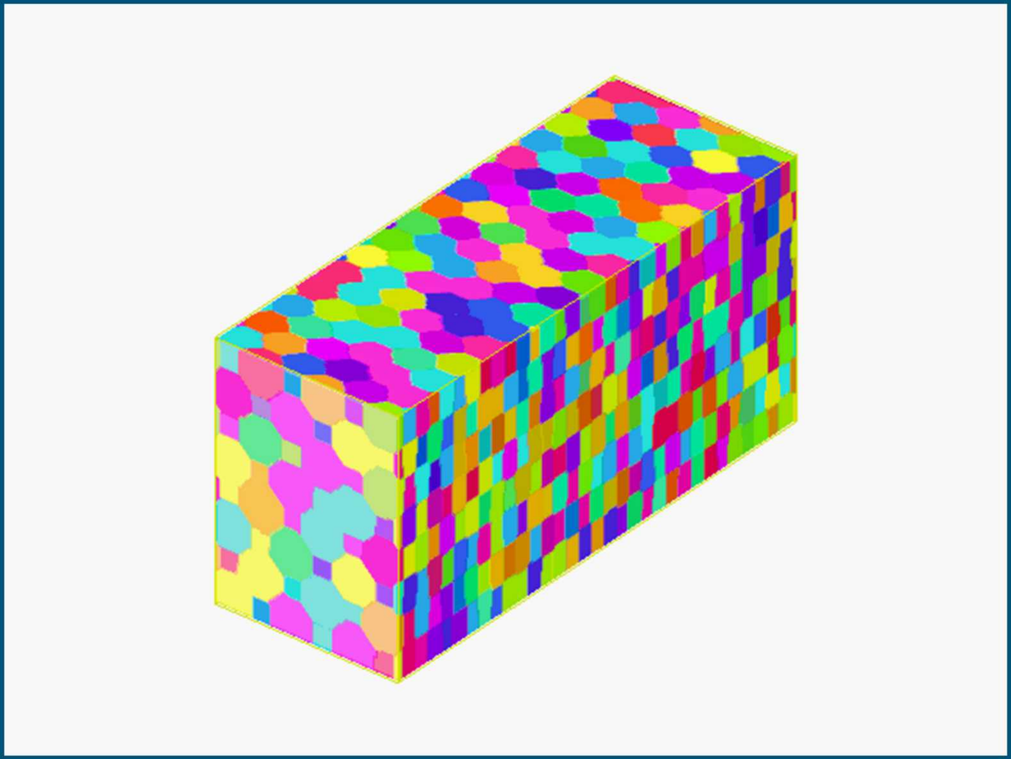
- Optimized candidate shows good filling in either process, self-rising or pushed after foamed.
- Pushing compresses material to become slightly more dense.
- Pushed here for 1 minute
- Free rise took about 5 minutes

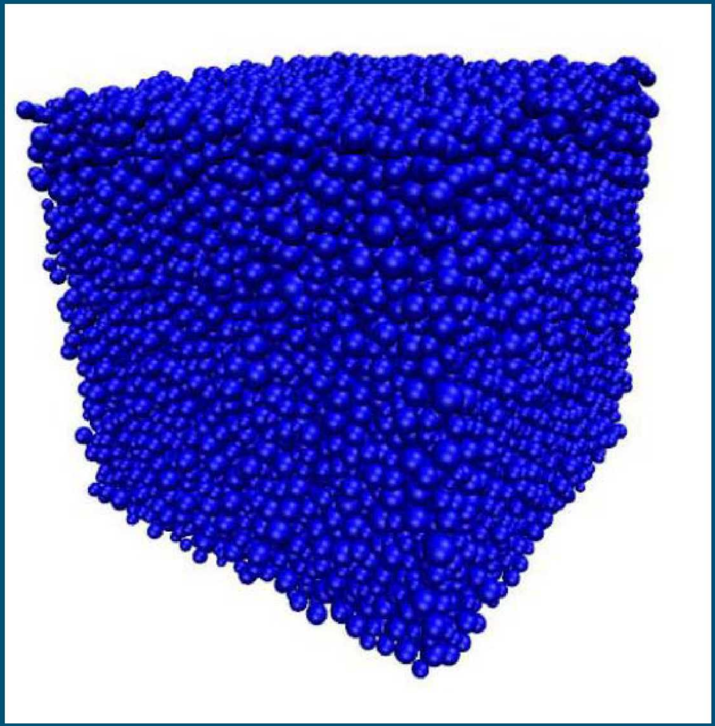
Conclusions and Future Work

- **Current model is adequate for production calculation**
  - Determining metering, initial placement, voids, gate, and vent location, manufacturing stresses and initial foam shape
  - Current model is "first order." We are working to make the model more predictive
- **Next generation model needs 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
  - Foam depressurization and its linkage to shape change
- **Include local bubble size and bubble-scale interactions**
  - Predict bubble size with Rayleigh-Plesset equation using an influence volume approach
  - 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 for both foaming and aging

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)