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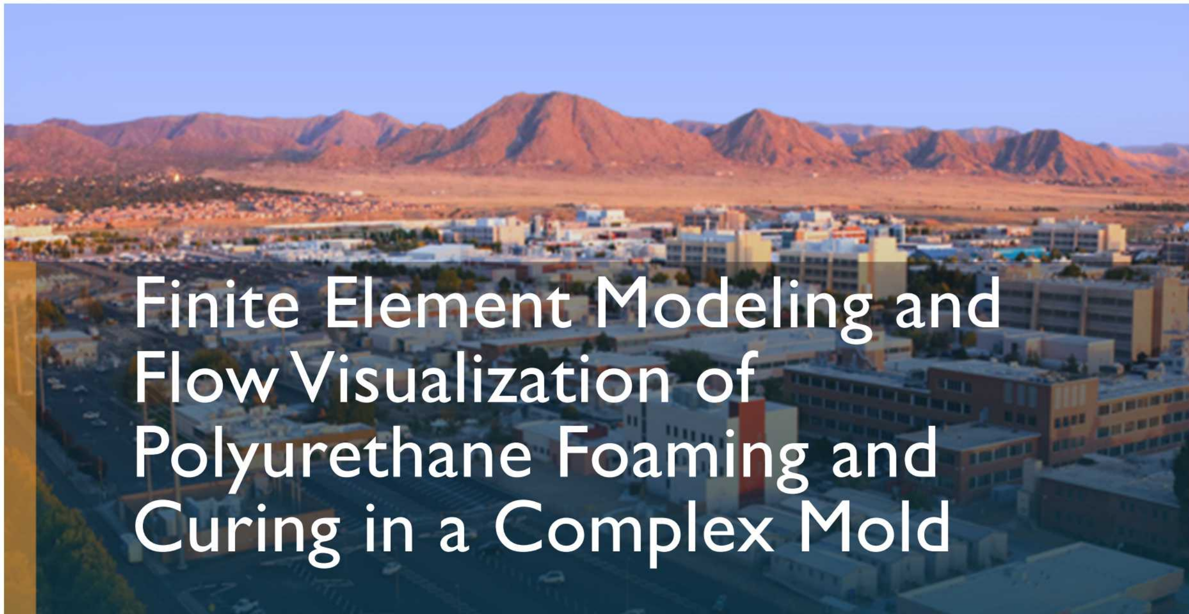
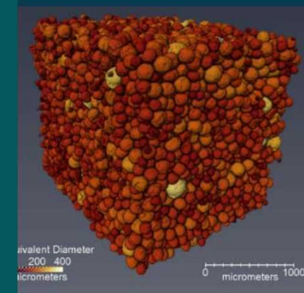
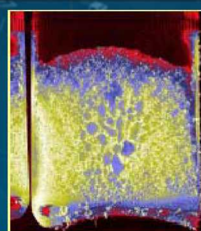


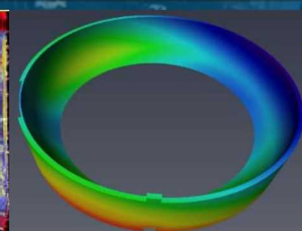
Sandia National Laboratories

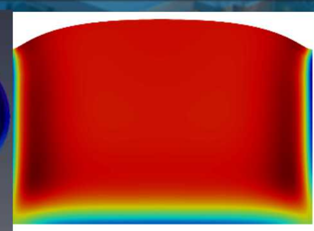
Finite Element Modeling and Flow Visualization of Polyurethane Foaming and Curing in a Complex Mold

ENGINEERING SCIENCES CENTER









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PRESENTED BY

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Albuquerque, NM

For: Christine Roberts, Melissa Soehnel, Kevin Long, David Noble (SNL), James Tinsley(KCNSC)

U.S. DEPARTMENT OF ENERGY NNSA

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Cradle-to-Grave Model of PMDI Foam

Overarching Goal: **A computational model for foaming, vitrification, cure, aging to help us design molds and determine how inhomogeneities effect the structural response of the final part, including long term shape stability**

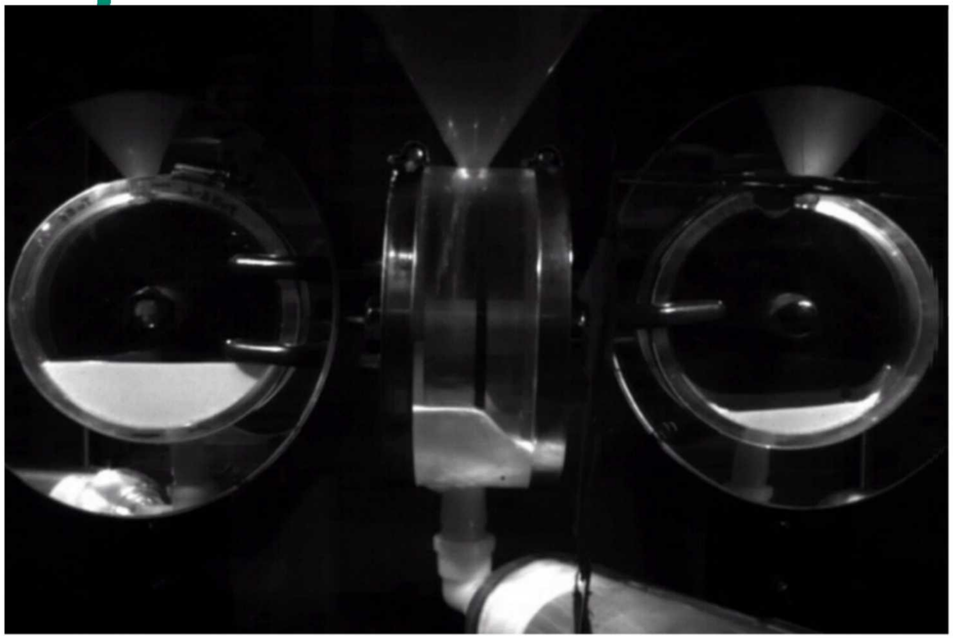
Injection, foaming and initial curing at lower T

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

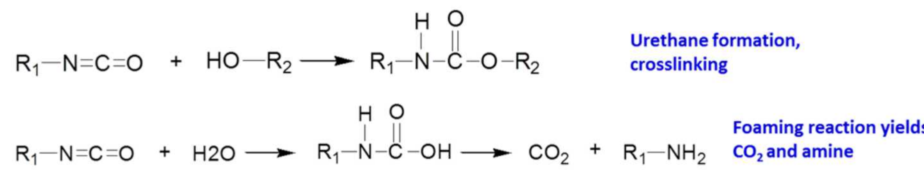
Remove from mold – predict cure and thermal stresses

Predict shape and size over years

PMDI Foam Filling Simulation of Complex Part



Two key reactions: Isocyanate reaction with polyols and water

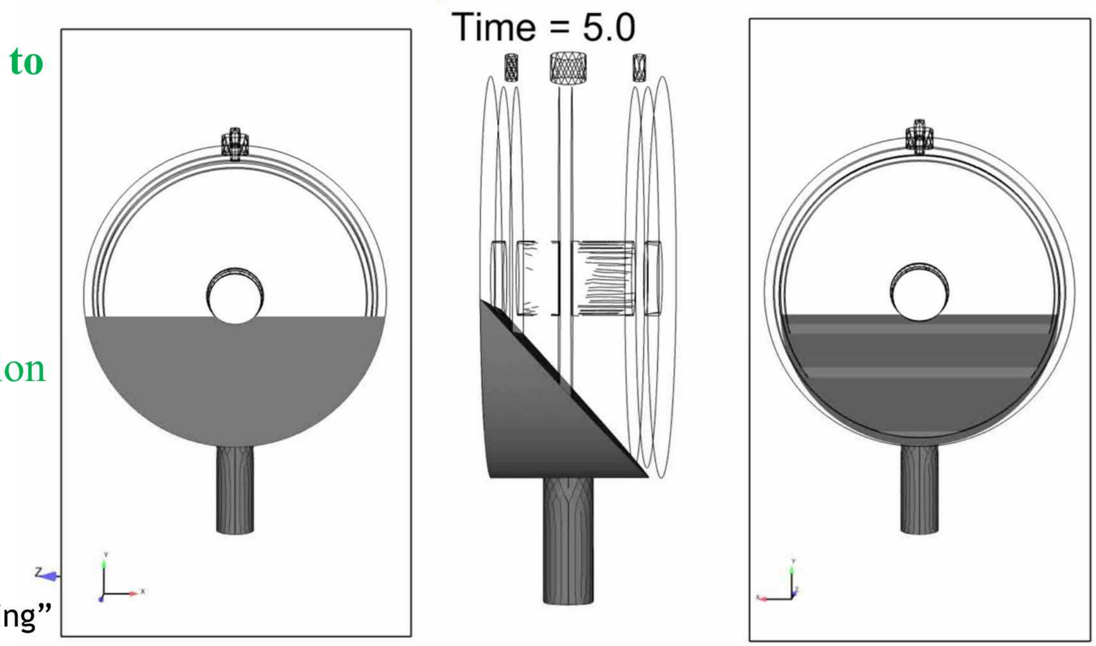


Various follow up reactions: Isocyanate reaction with amine, urea and urethane

- Isocyanate reacts with water to create gas and foam expansion, changing the material from a viscous liquid to a multiphase material.
- Isocyanate reacts with polyol to polymerize and vitrify to a solid.

Coupled Finite Element Method/Level Set to Solve Foam Dynamics

- Gas and liquid are homogenized to a continuum
- Density evolves based on kinetics of gas expansion
- Viscosity evolves with cure and gas fraction



Rao et al., “Polyurethane kinetics for foaming and polymerization” , *AICHE Journal*, February 2017

Rao et al, “A Level Set Method to Study Foam Processing” *IJNMF*, 2012

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

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

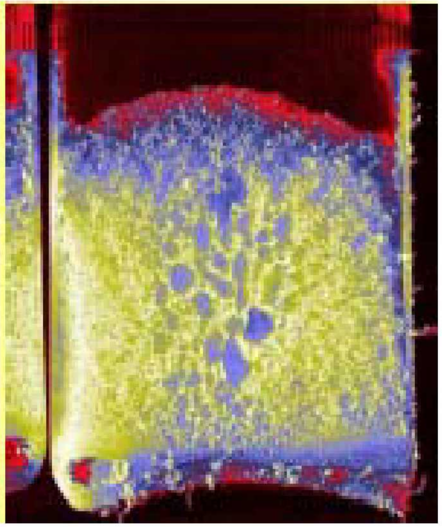
Extent of reaction equation for polymerization: condensation chemistry

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

Molar concentration equations for water and carbon dioxide

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

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



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

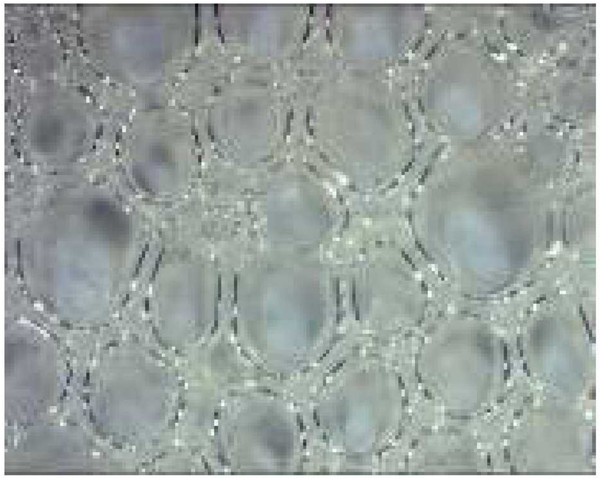
Foaming reaction predicts moles of gas from which we can calculate density

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

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

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

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



Foam is a collection of bubbles in curing polymer

Thermal properties depend on gas volume fraction and polymer properties

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

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

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

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

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

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

- 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)

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

Coupled Finite Element Method/Level Set to Solve Foam Dynamics

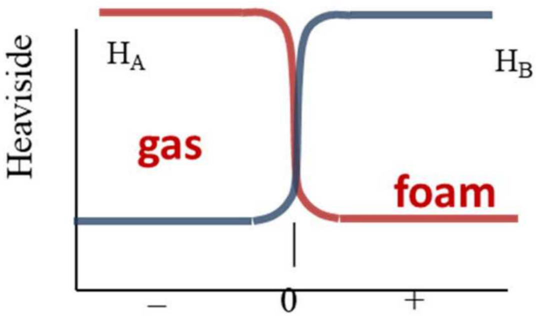
- Level set advects with the fluid velocity:
- Properties vary with the level set based on the level set and modulated using the Heaviside

$$\frac{\partial \phi}{\partial t} + v \cdot \nabla \phi = 0$$

$$\eta(\phi) = (\eta_{gas} - \eta_{foam})H(\phi) + \eta_{foam}$$

$$\kappa(\phi) = (\kappa_{gas} - \kappa_{foam})H(\phi) + \kappa_{foam}$$

$$\rho(\phi) = (\rho_{gas} - \rho_{foam})H(\phi) + \rho_{foam}$$



$$H(\phi) = \frac{1}{2}\left(1 + \frac{\phi}{2} + \frac{\sin(\frac{\pi\phi}{\alpha})}{\pi}\right), \; -\alpha < \phi < \alpha$$

- Equations of motion, kinetics and energy balance use averaged properties based on level set, ϕ
- Momentum and Continuity shown for an example. Energy is similar

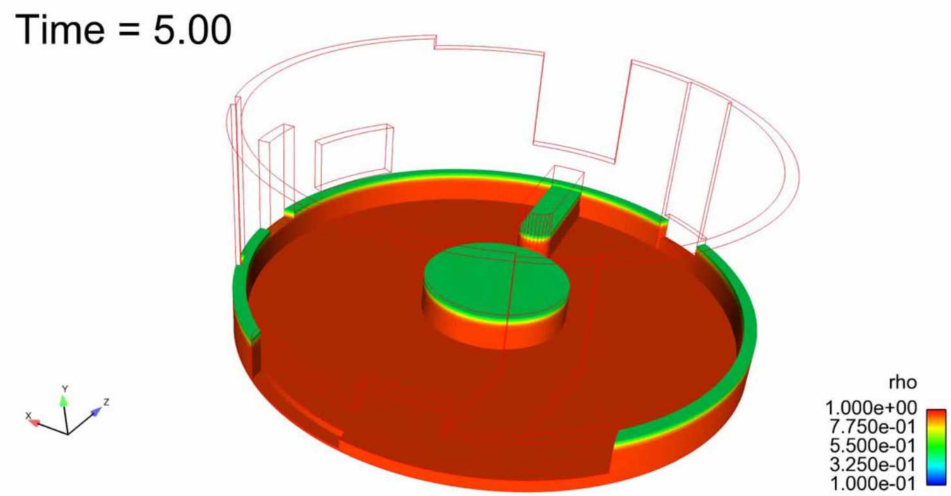
$$\rho(\phi)\left(\frac{\partial \boldsymbol{v}}{\partial t} + \boldsymbol{v} \bullet \nabla \boldsymbol{v}\right) = -\nabla P + \nabla \cdot \left(\eta(\phi)(\nabla \boldsymbol{v} + \nabla \boldsymbol{v}^t) - \left(\frac{2}{3}\eta(\phi) - \kappa(\phi)\right)(\nabla \cdot \boldsymbol{v})\underline{\underline{\boldsymbol{I}}}\right) + \rho(\phi) g$$

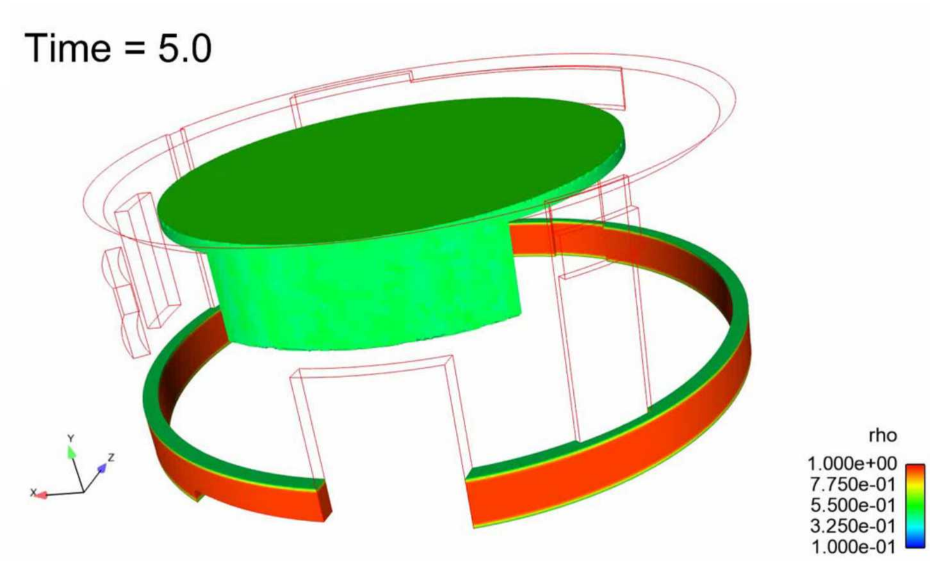
$$\frac{\partial \rho(\phi)}{\partial t} + \nabla \cdot \rho(\phi)\boldsymbol{v} = 0$$

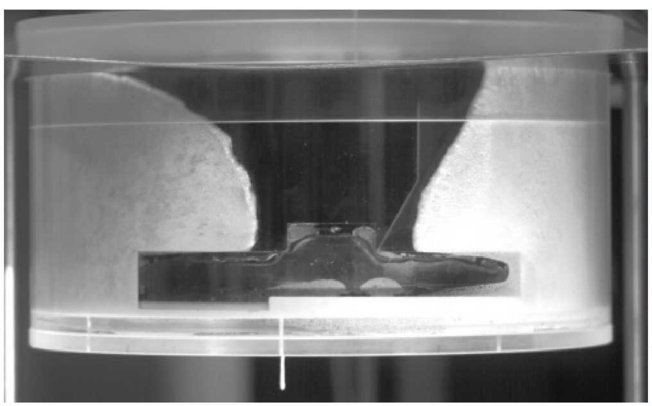
- Reactions equations use equation averaging and a Heaviside directly on the equations

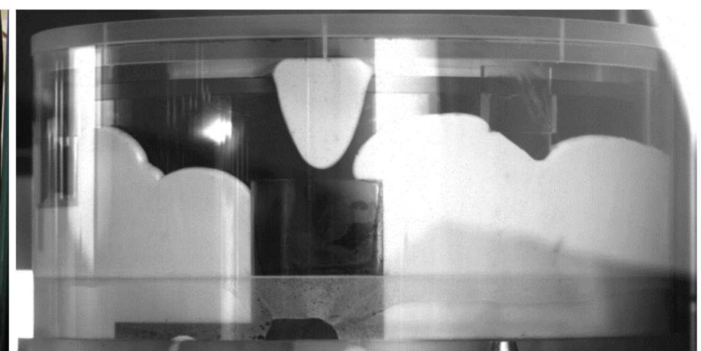
Rao et al, C&F, 2018

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





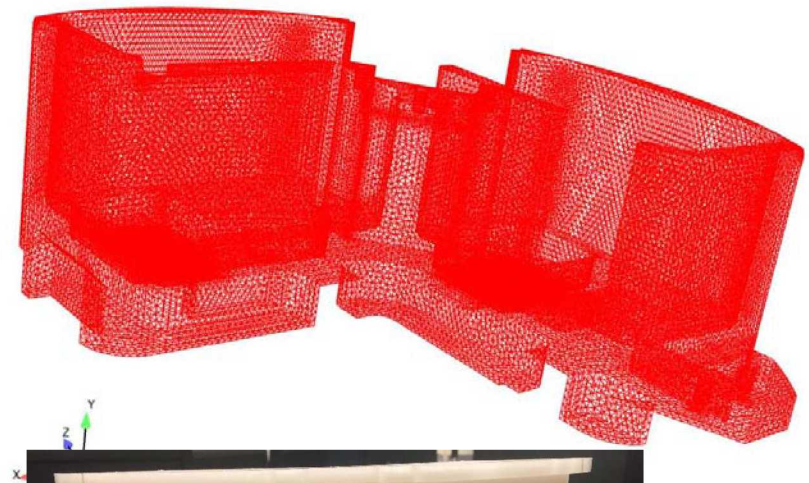


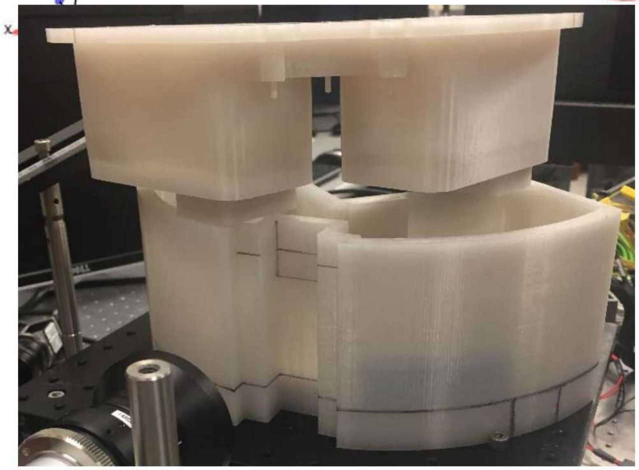


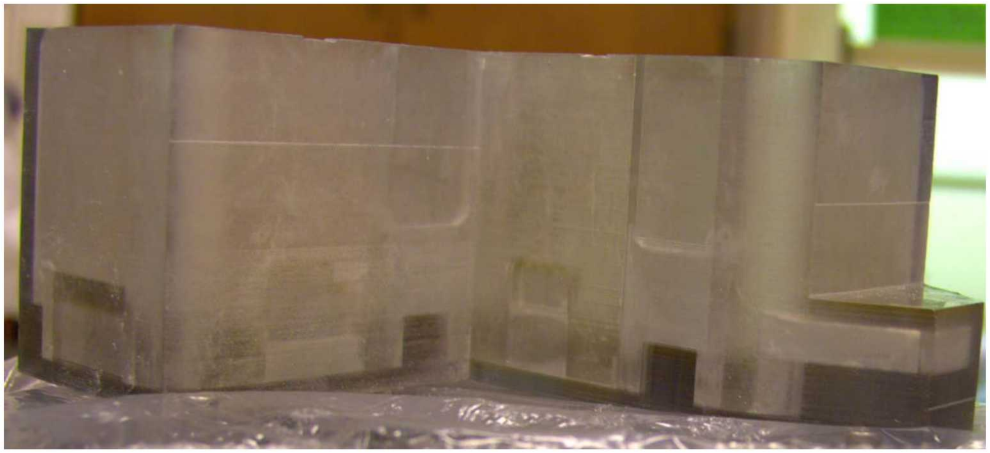
Simulations & Experiments

Simulations
- Flat configuration
- 5^{o} tilt
- 20^{o} tilt
- 20^{o} tilt toward the shelf feature
- Study of vent locations

Experiments
- Flow visualization experiments
- Additive manufacture mold

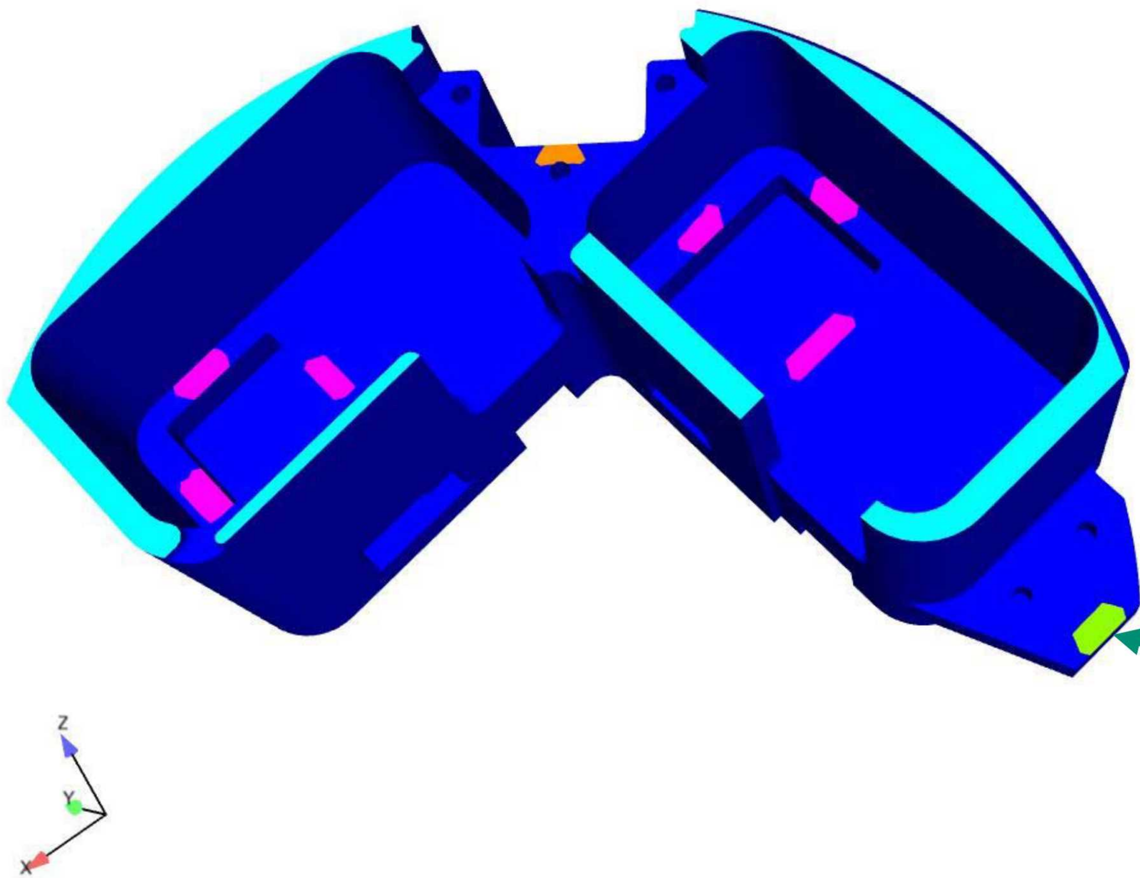






Goal: Use foaming and filling modeling and flow visualization experiments to develop confidence in foam model

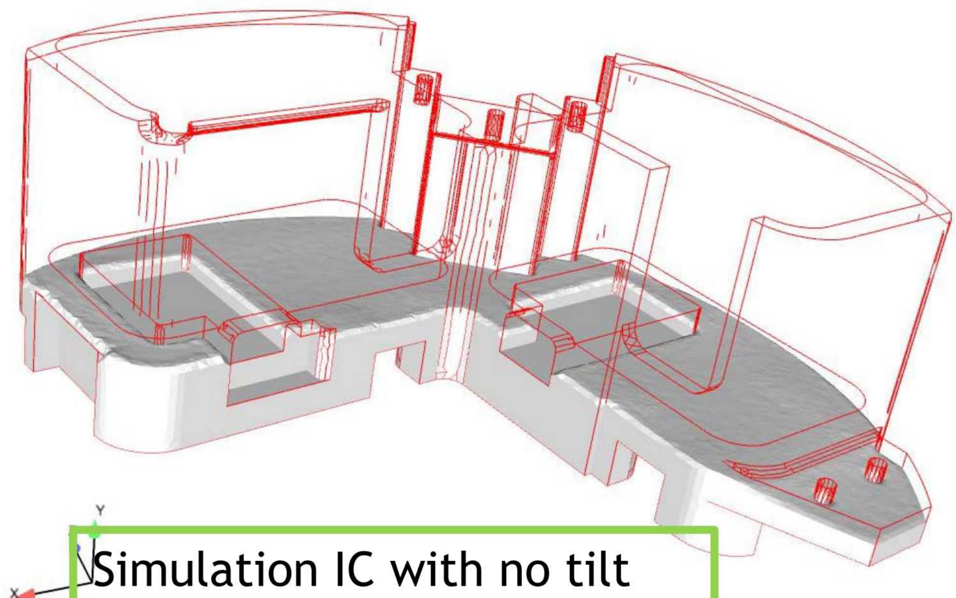
These Vent Locations Seem Representative of a Foaming Process



Simulation tests the idea of adding a vent on the shelf feature

Initial Conditions for Model: Experiments Show Shelf Starts Well-Filled

Flow visualization study using opaque mold to determine filling of shelf supports use of flat initial condition



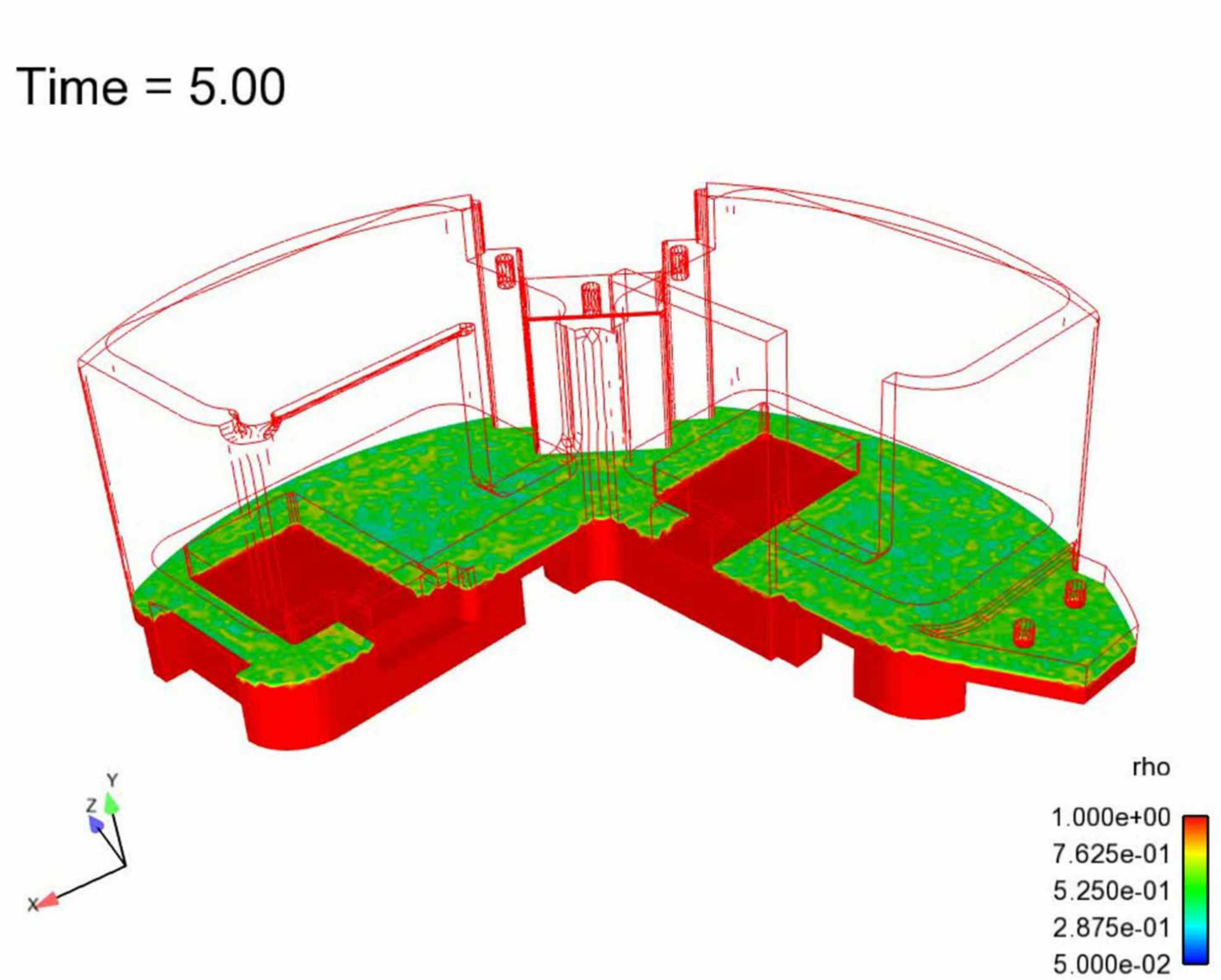
Flow visualization verifies initial condition:

- *Foam levels well and flows to fill she area*
- *Simulation initial condition of a flat interface seems fairly accurate*

Simulation IC with no tilt

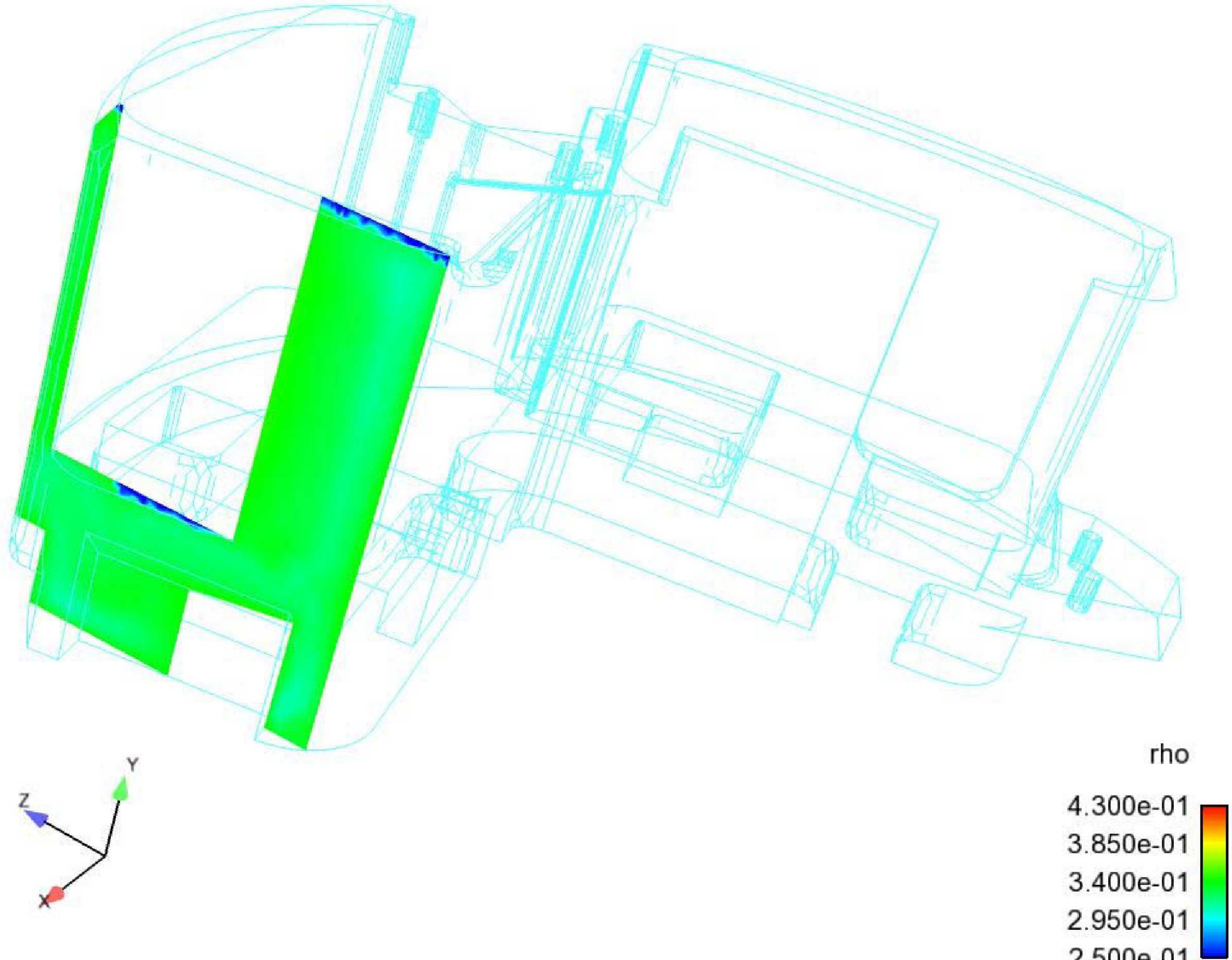
- Shelf is half-filled at start of the simulation

Foam Filling and Curing for Flat Configuration



Base Case:

- Look at issues for filling the mold when it is flat on the table
- Model shows density evolution and filling profile over time



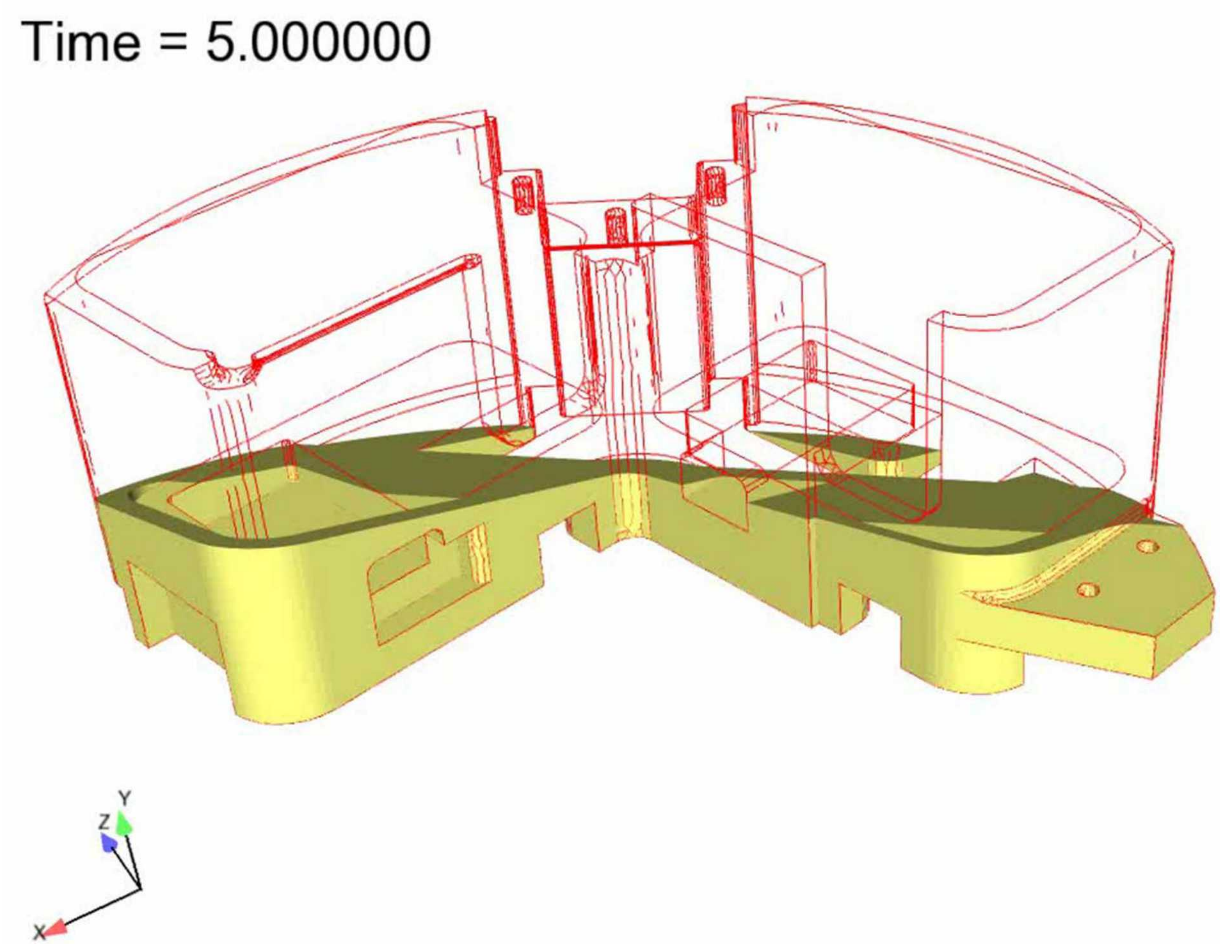
time=82.7s
voids = 3.6%

Density Variations at Different Locations: Flat Mold with Shelf Vent

Dynamics of Filling with 20o Tilt Angle

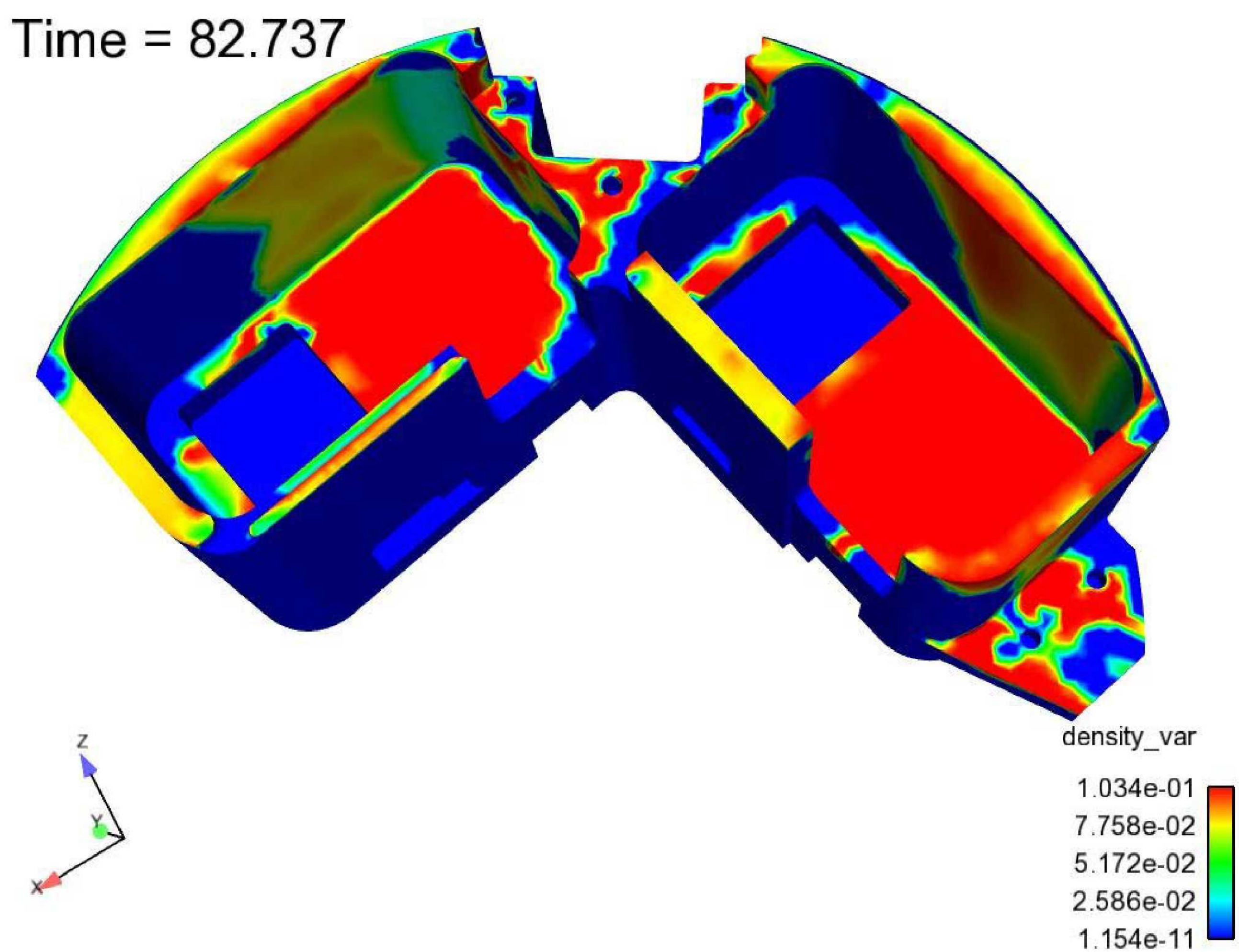
Foam Using a 20º Tilt Angle forward similar to legacy process

- Initial condition has a tilt forward for foam position and a flat interface
- Gravity vector is also tilted



Plot of Density Variation From Nominal

FLAT FILL



Density Variation:
$(\rho_{local} - \rho_{nominal})^2$

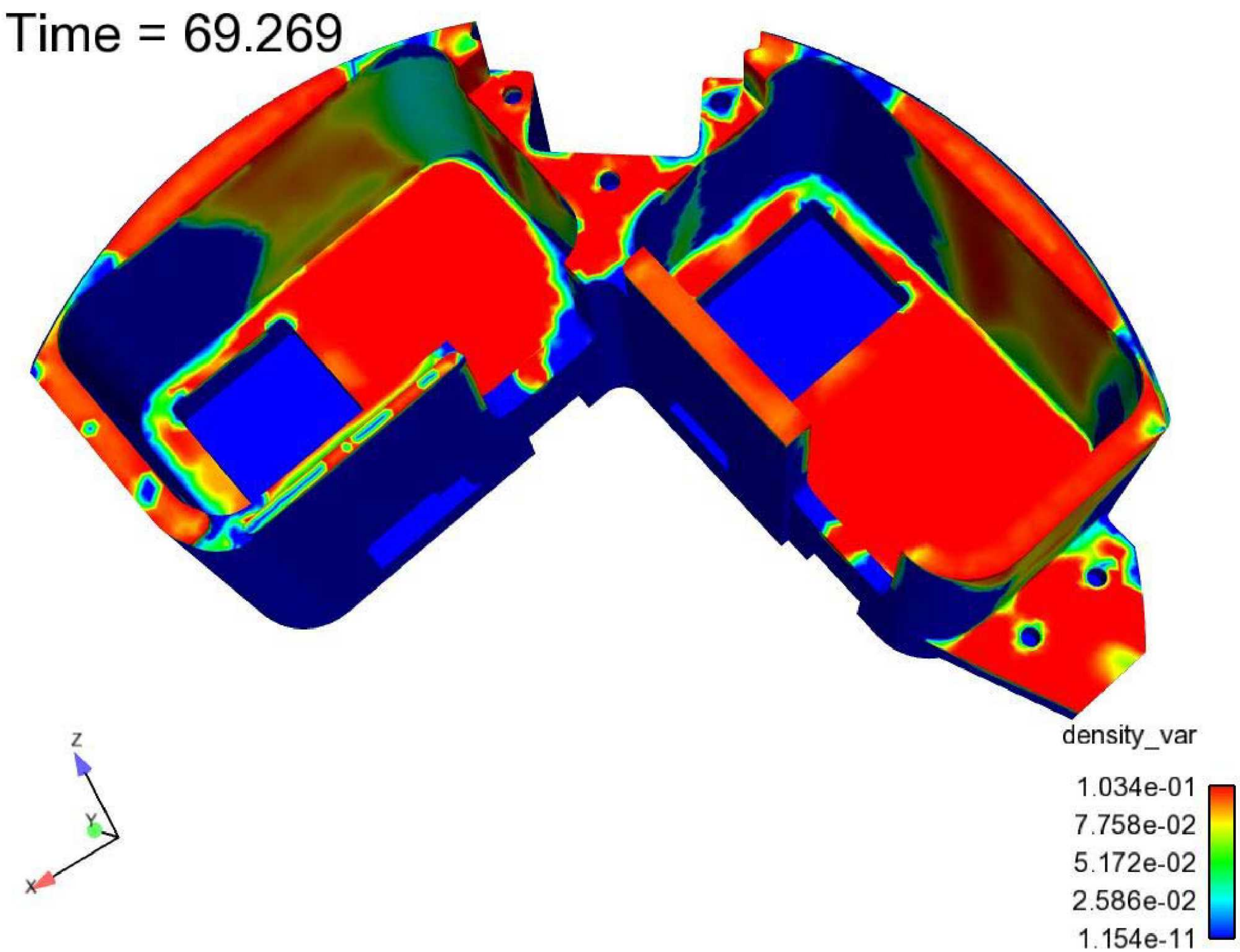
$$\int (\rho - \rho_{nom})^2 \, dV$$

$\rho_{nominal}$ = 240g/745ml
= 0.322g/ml

time=82.7s
voids = 3.6%
Int. var. = 2.81

Plot of Density Variation From Nominal

FLAT FILL HOT



Density Variation:
$(\rho_{local} - \rho_{nominal})^2$

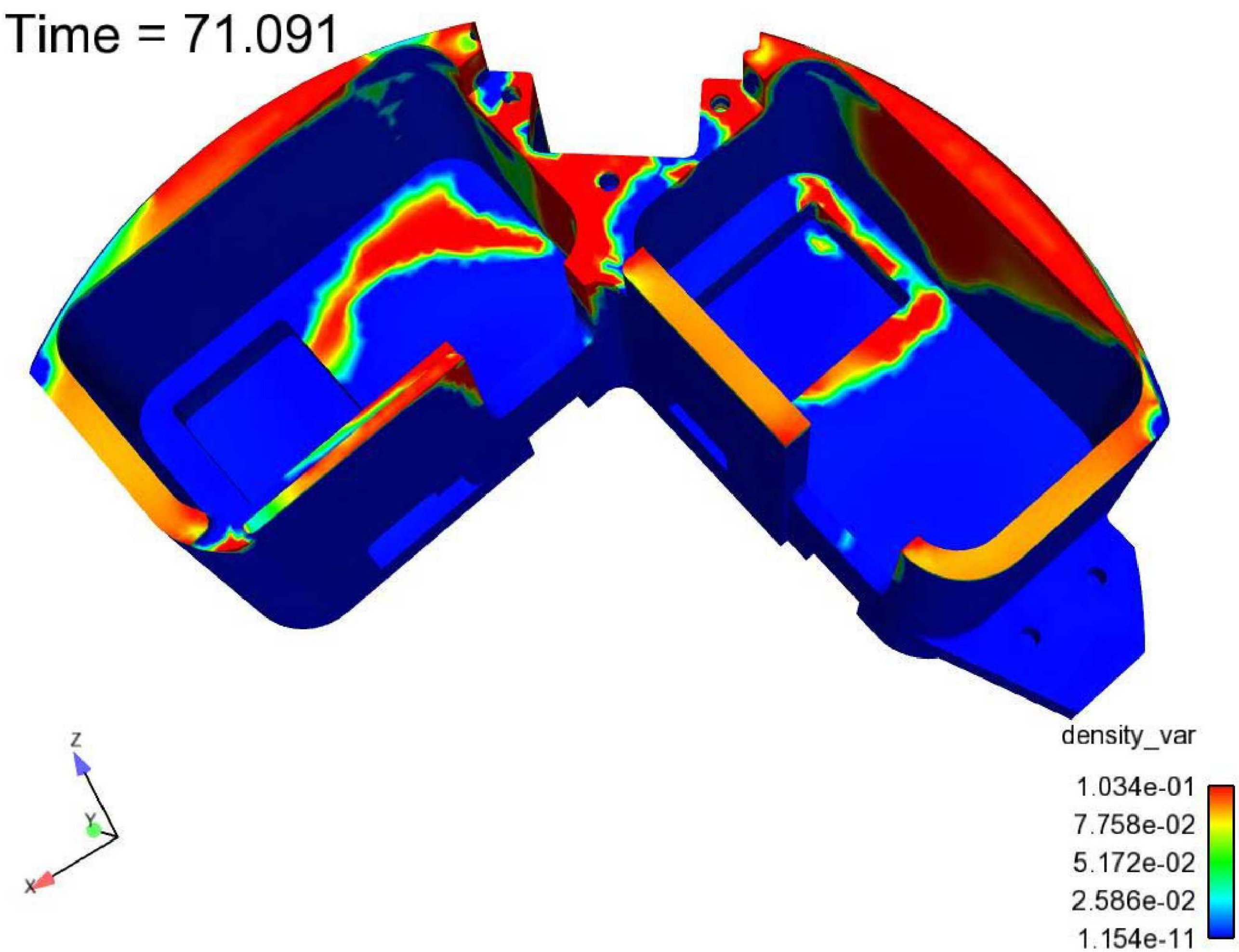
$$\int (\rho - \rho_{nom})^2 \, dV$$

$\rho_{nominal}$ = 240g/745ml
= 0.322g/ml

time=69.3s
voids = 4.5%
Int. var. =
3.56

Plot of Density Variation From Nominal

TILT 20 DEGREES FILL



Density Variation:
$(\rho_{local} - \rho_{nominal})^2$

$$\int (\rho - \rho_{nom})^2 \, dV$$

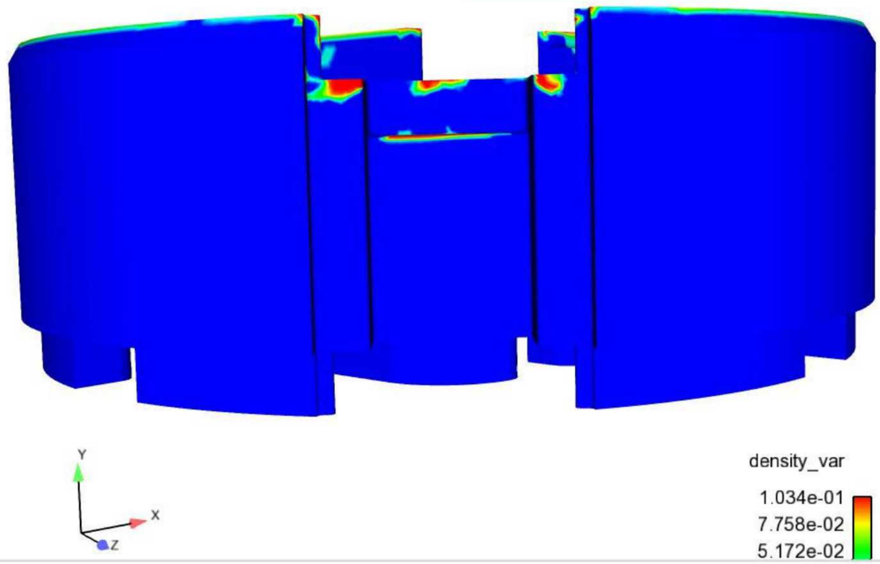
$\rho_{nominal}$ = 240g/745ml
= 0.322g/ml

time=71.1s
voids = 2.9%
int. var. = 2.87

Density Variations: Back View

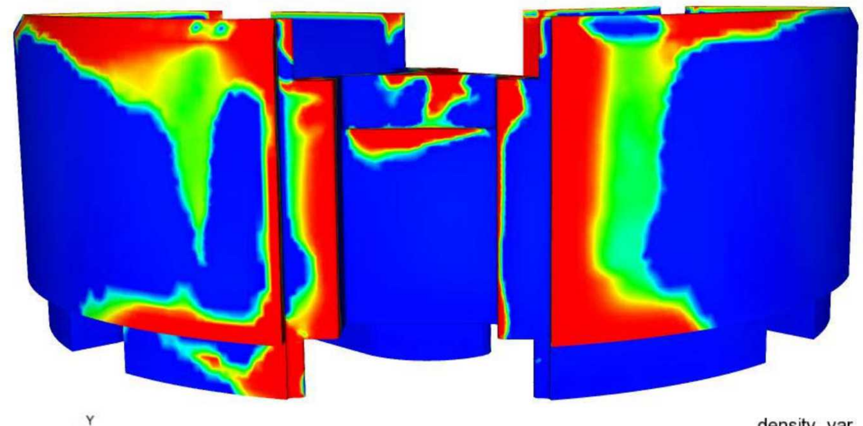
Time = 82.737

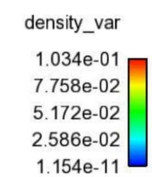
FLAT FILL



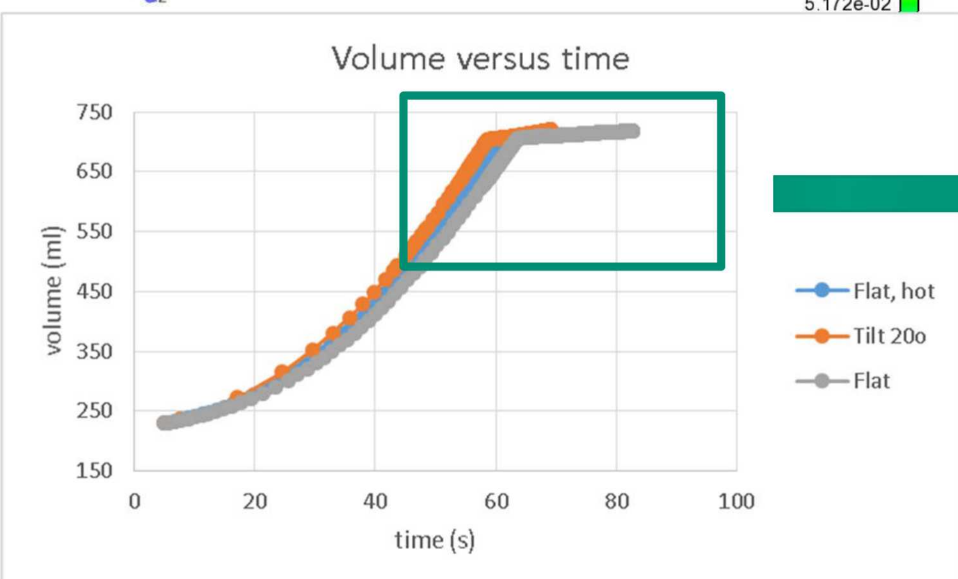
Time = 71.091

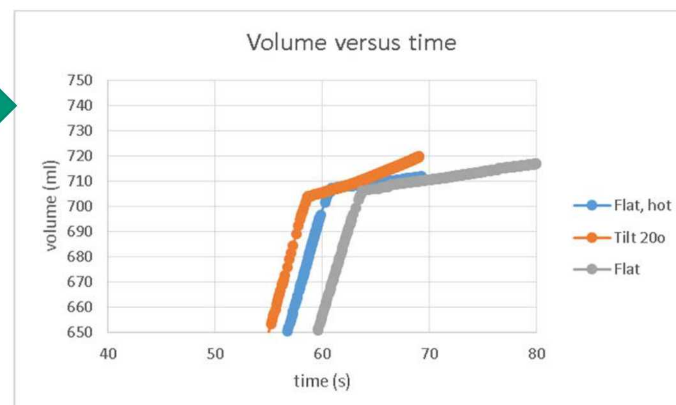
TILT 20 DEGREES FILL



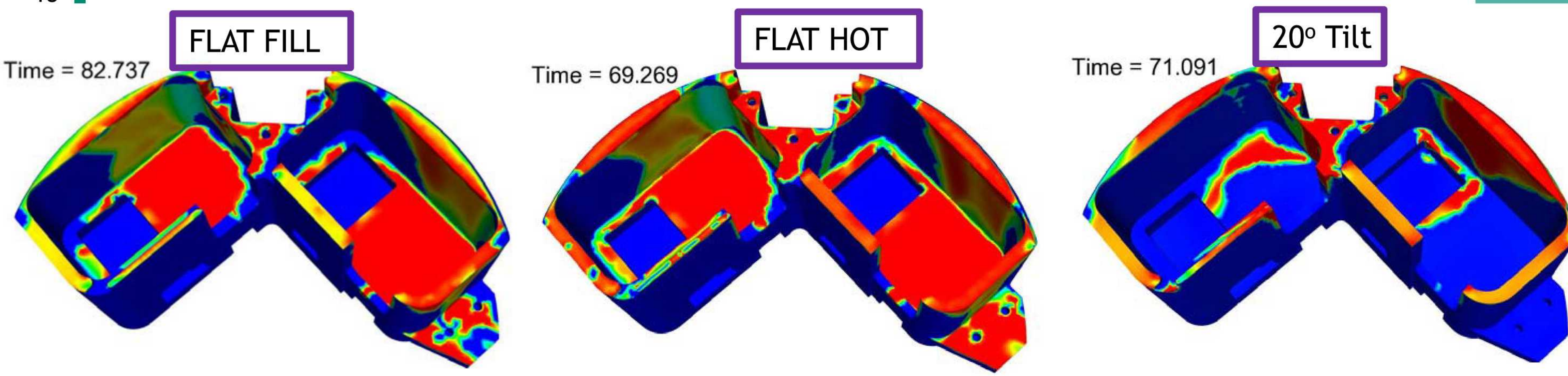


- Forward tilt moves defects to the back part of the mold
- Tilt fills faster than flat

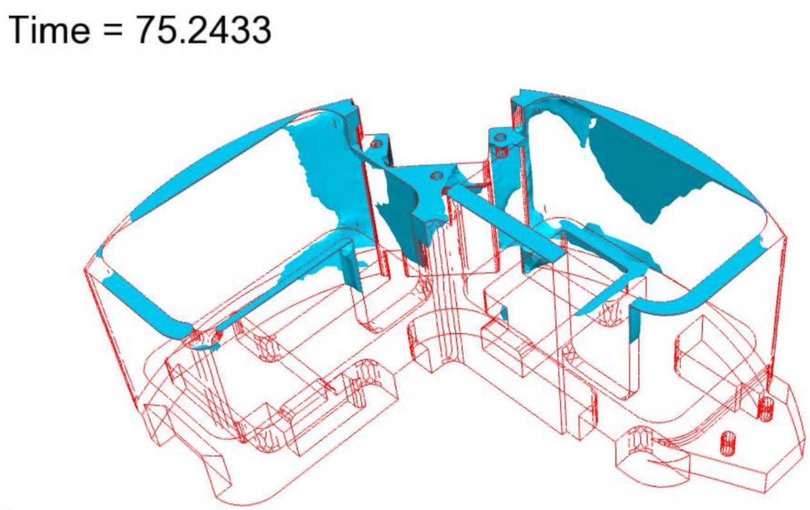




Computational Models of Foam



Density variations for three cases of interest



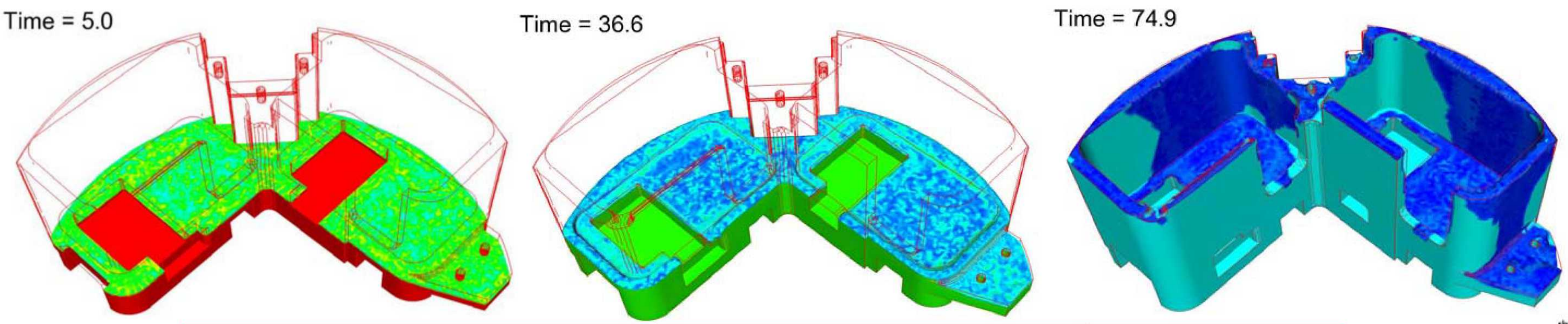
Foam filling for 20^{o} tilt: the angled fill reduces voids on the new shelf

Case	Flat	Flat Hot	20^{o} Tilt
Max. Time (s)	83s	70s	71s
Voids	3.6%	4.4%	2.9%
Density variation	2.8	2.9	3.6

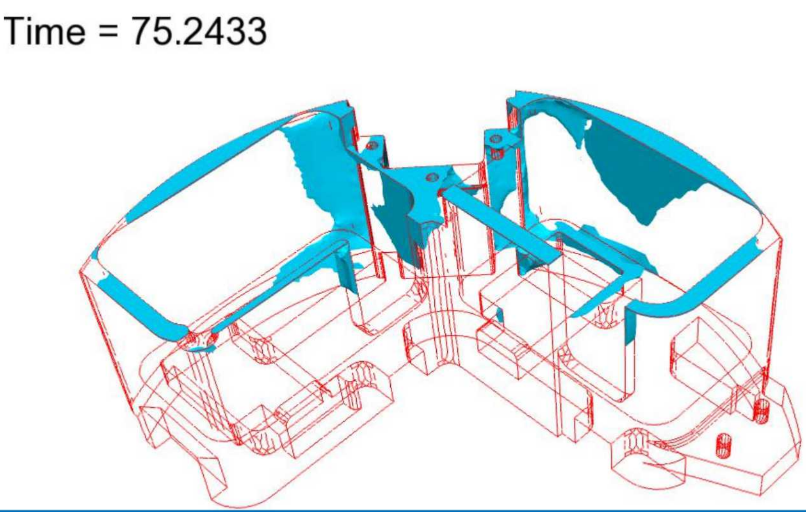
All cases fill well!

- Model over-predicts voids, but predictions are small
- Density variation greater with tilt

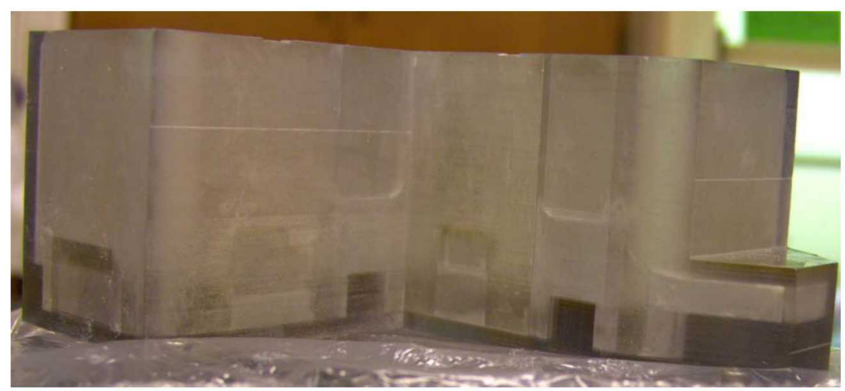
Computational Models of Foam



Evolution of density for flat mold with vent on the shelf feature

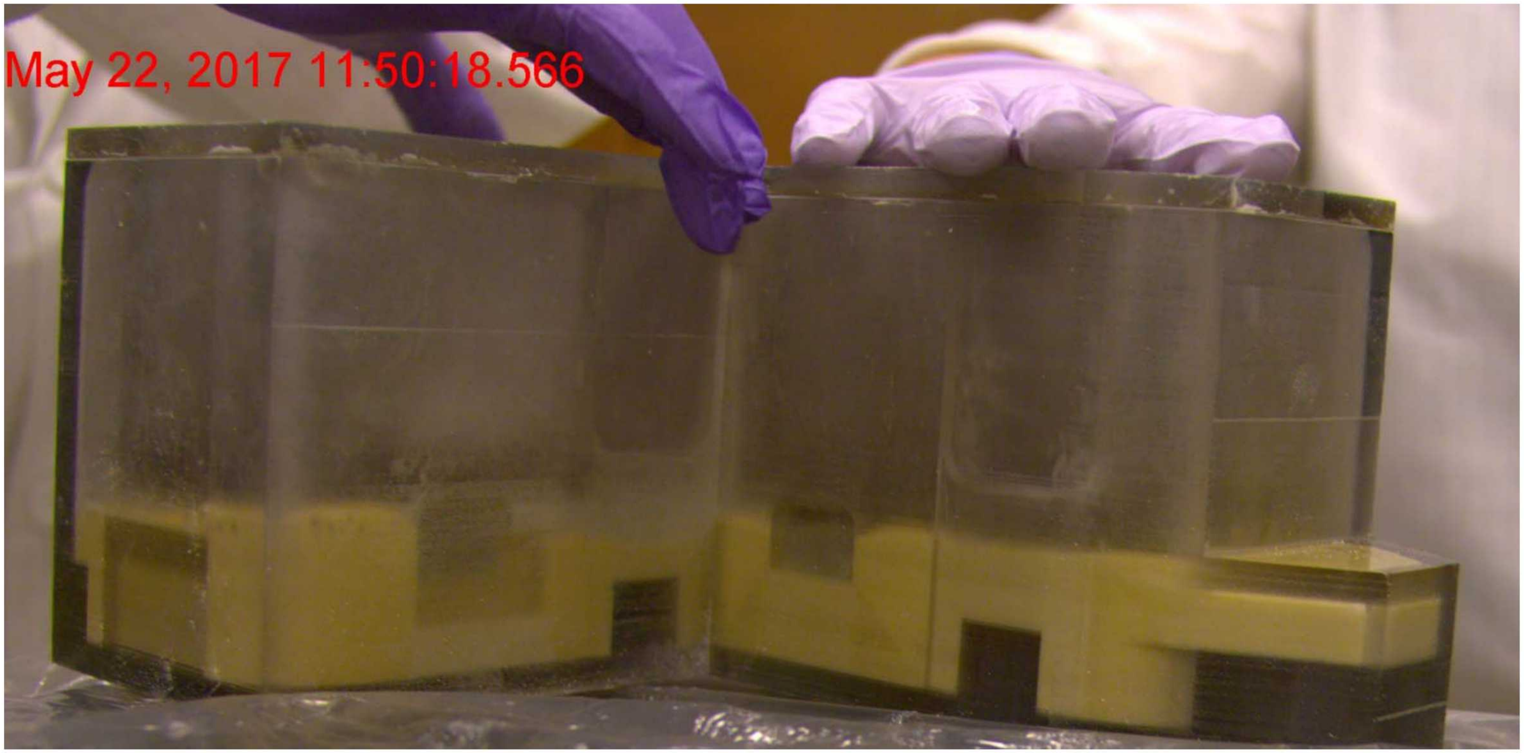


Flow visualization study supports computational conclusions



Foam filling for 20º tilt: the angled fill reduces voids on the new shelf

Validation Experiment: 5 Degree Tilt: Foam Fills Shelf and Levels Quickly

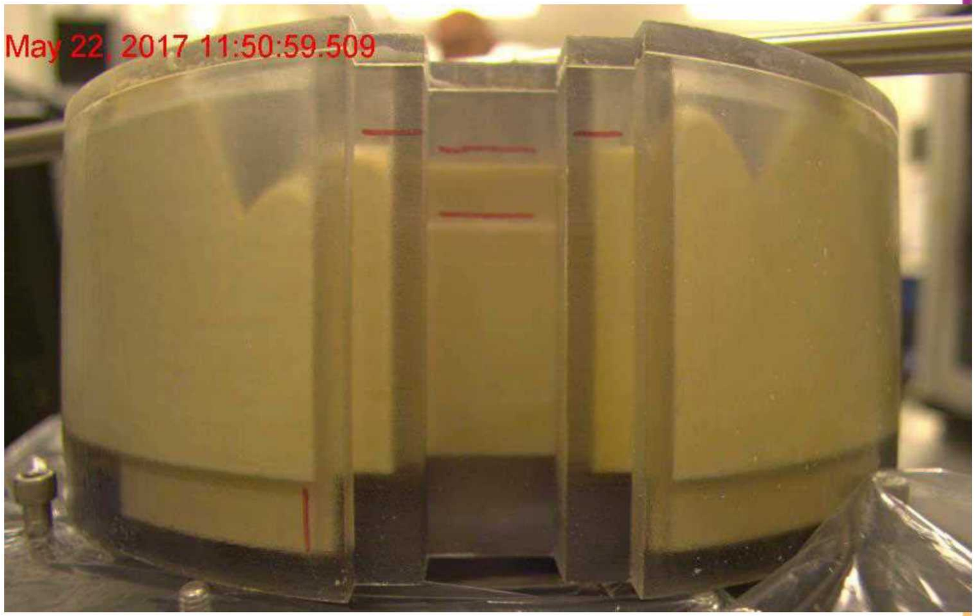


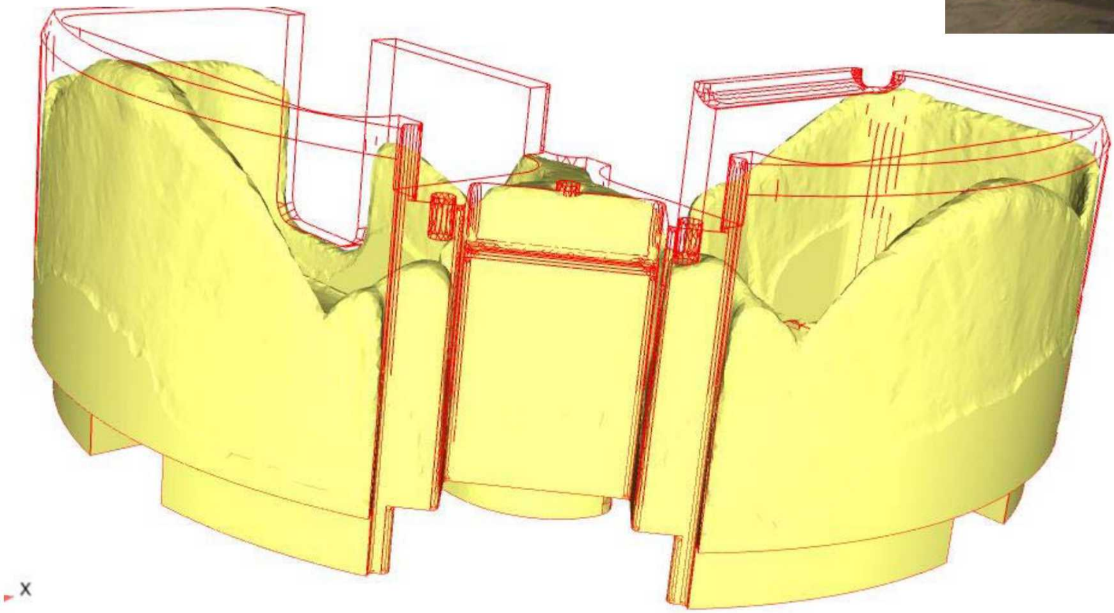
- New experiment using clear mold
- Room temperature mix of foam, which heats up to 24°C
- Mold stays roughly 22°C
- 5 degree tilt towards the front of the mold

Experimental Conditions: Back of Mold

Run model with similar initial conditions:

- 240g material
- 4 degree tilt
- Room temperature mold and foam

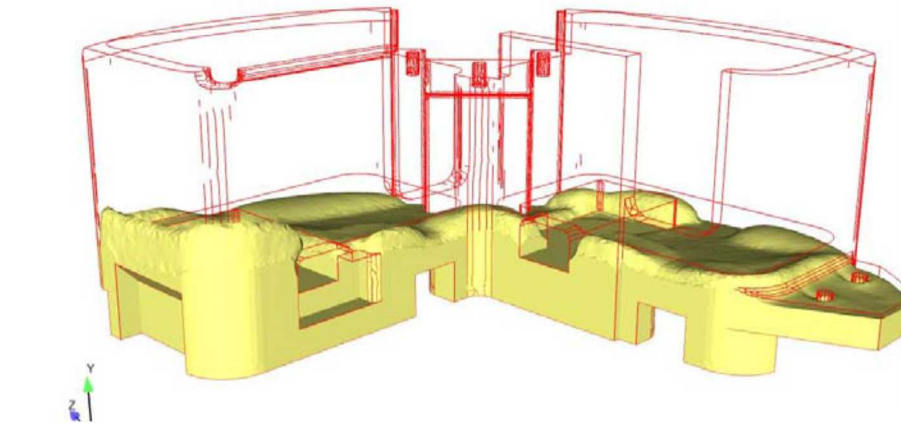


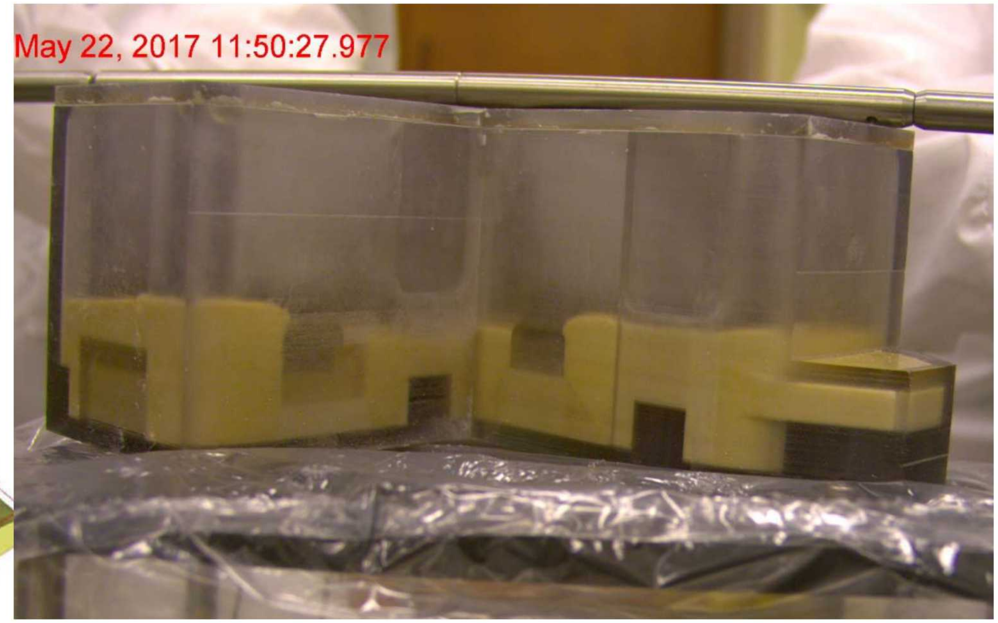


Shape of the model interface matches well with shape of experiment thought model fills back feature faster

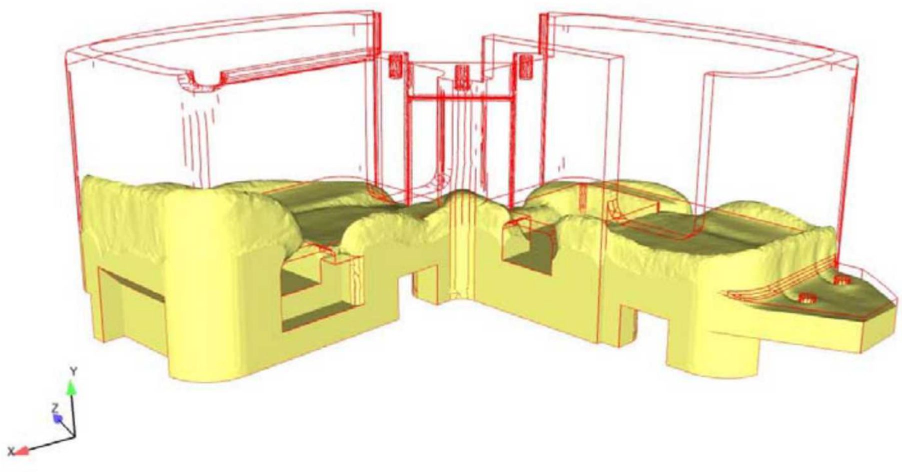
Compare Mold Front: Early Times

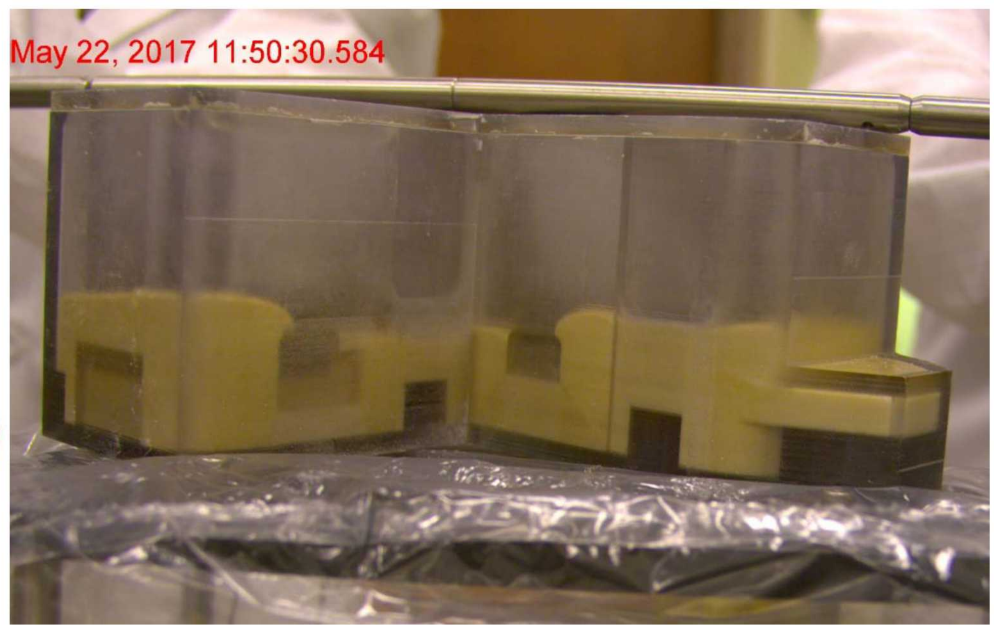
Time = 34.184





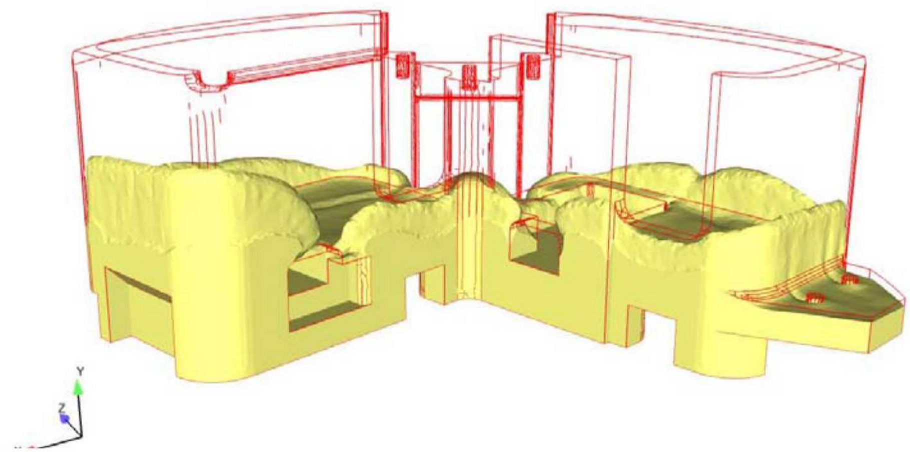
Time = 44.617

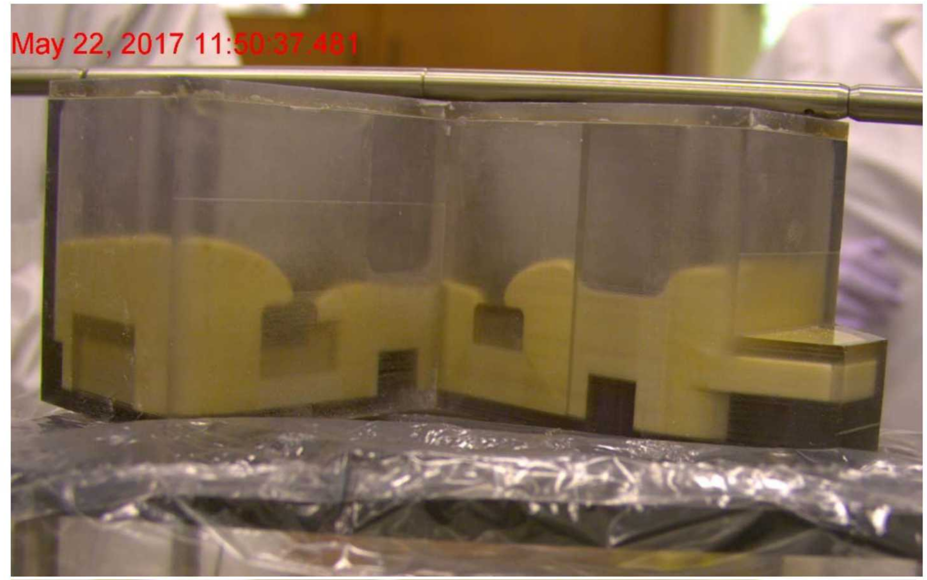




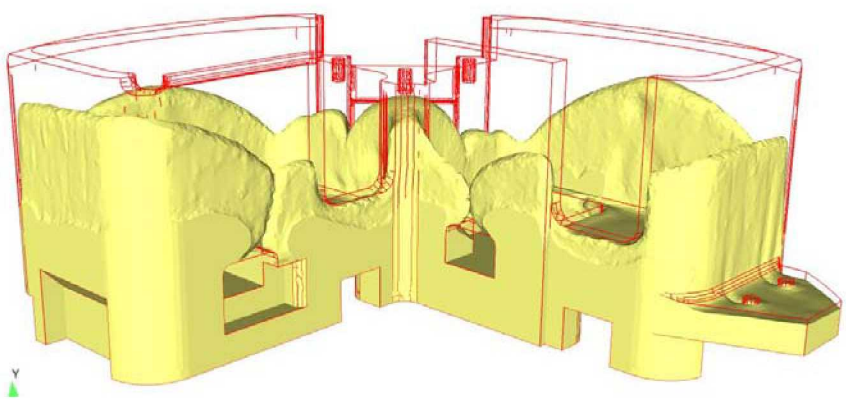
Compare Mold Front: Moderate Time

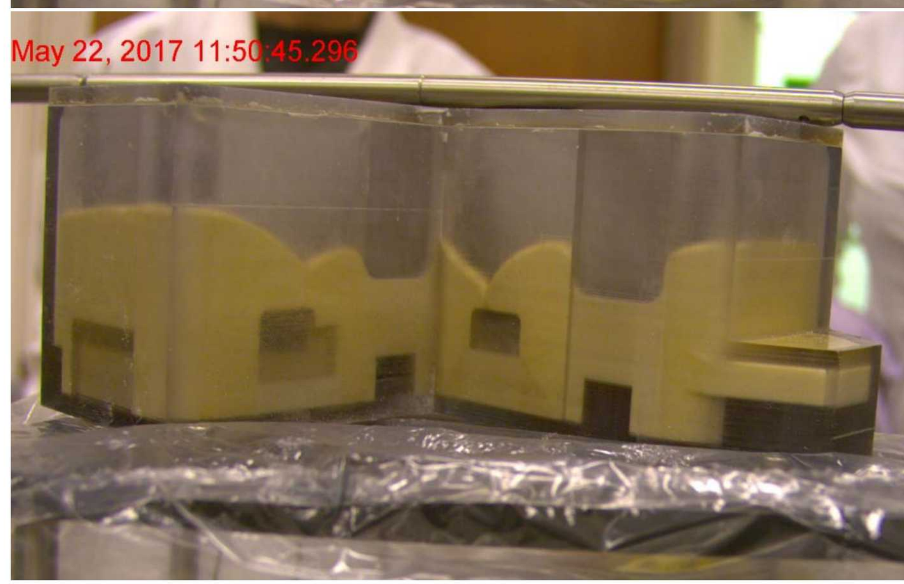
Time = 49.913



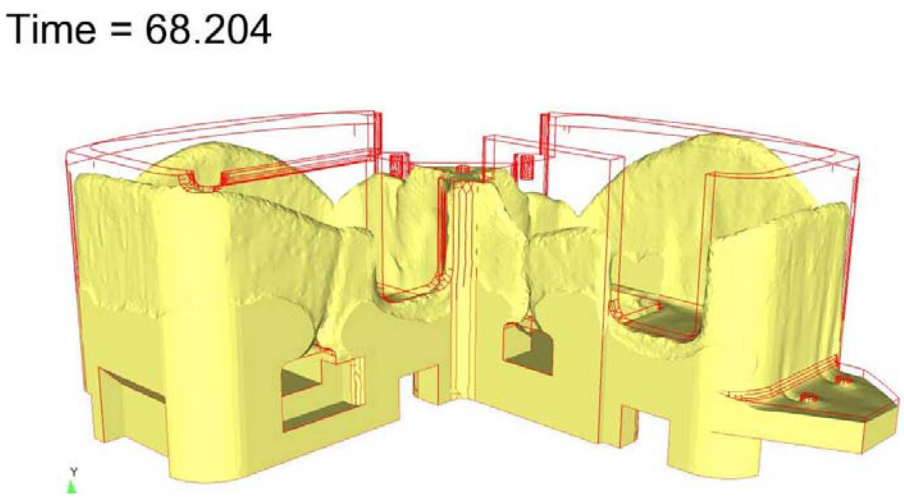


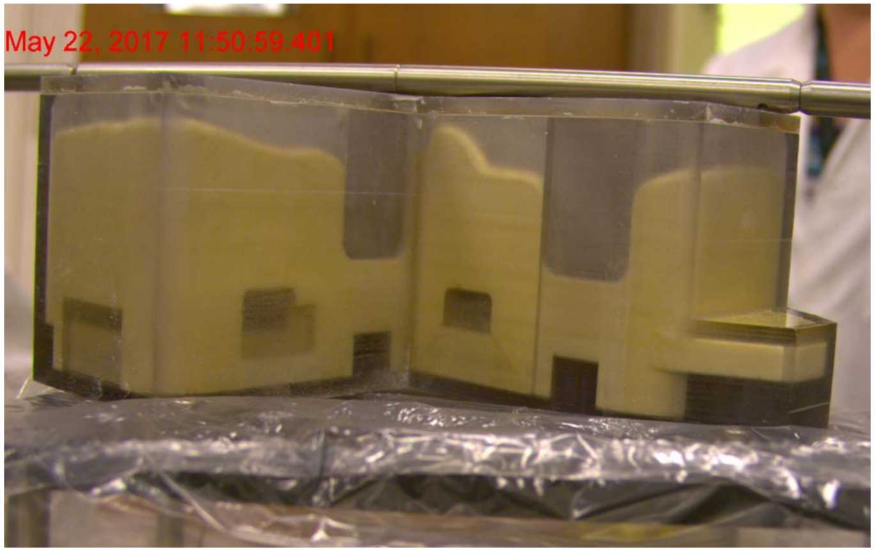
Time = 62.538





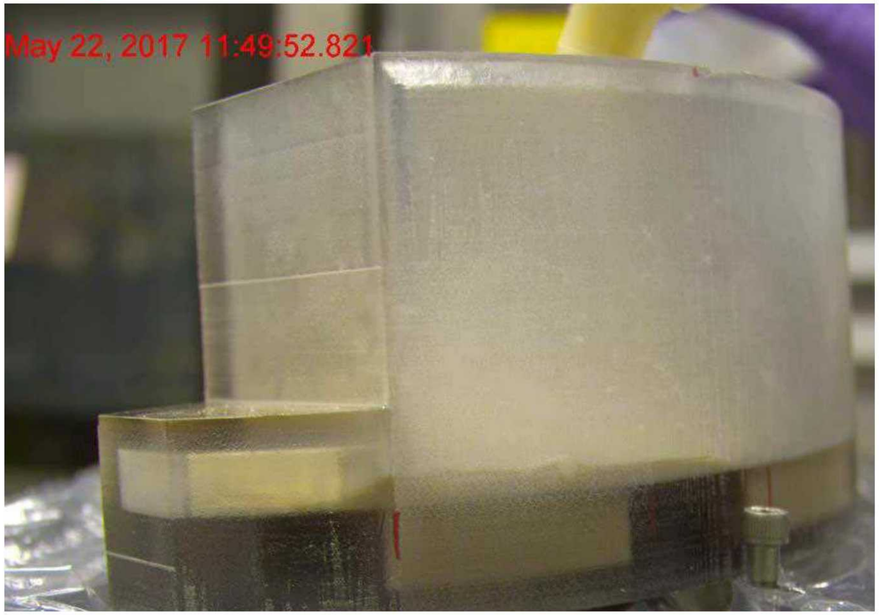
Compare Mold Front: Late Time

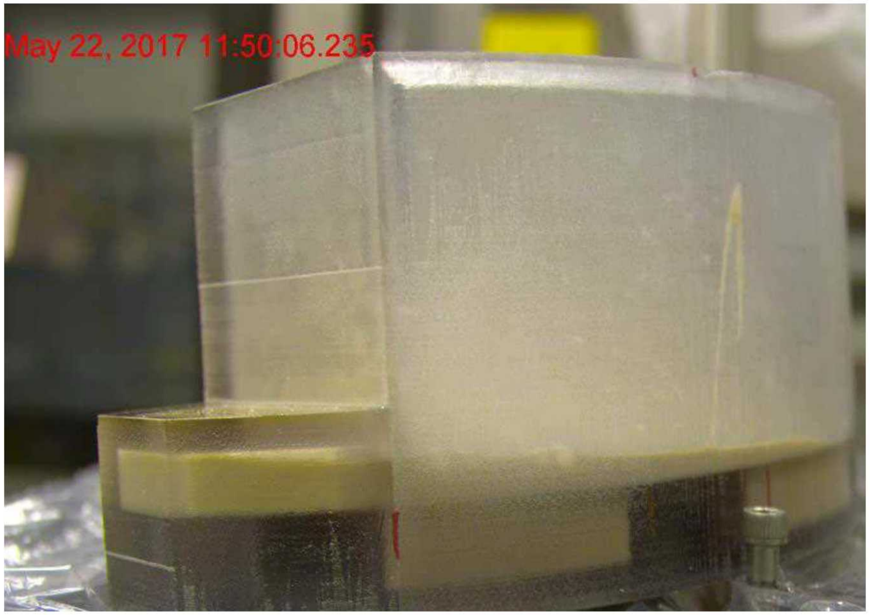


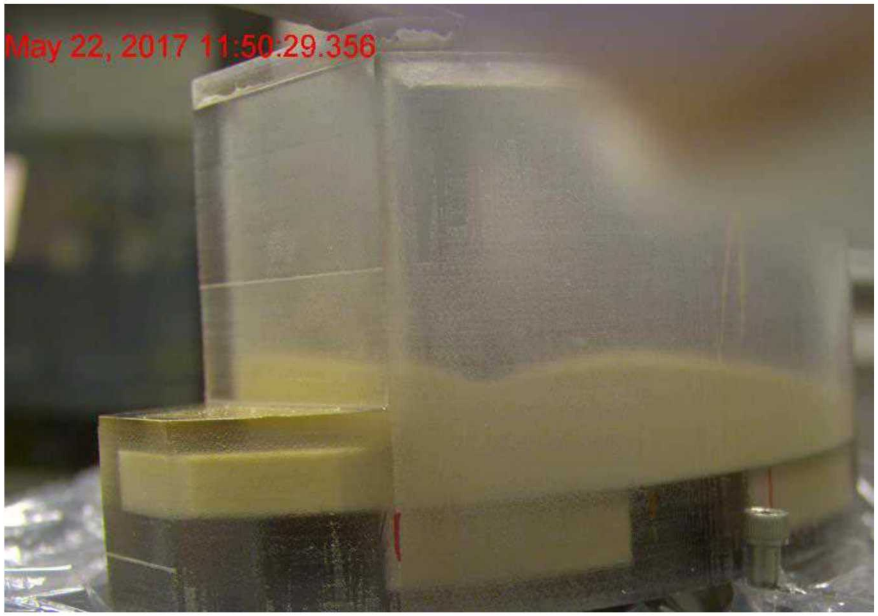


Shape of the model interface matches well with shape of experiment and the time-scale is similar

Shelf Feature Fills Well in Clear Mold





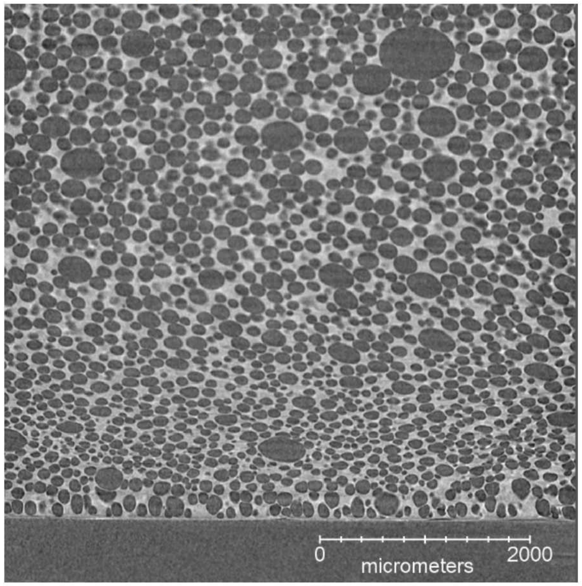


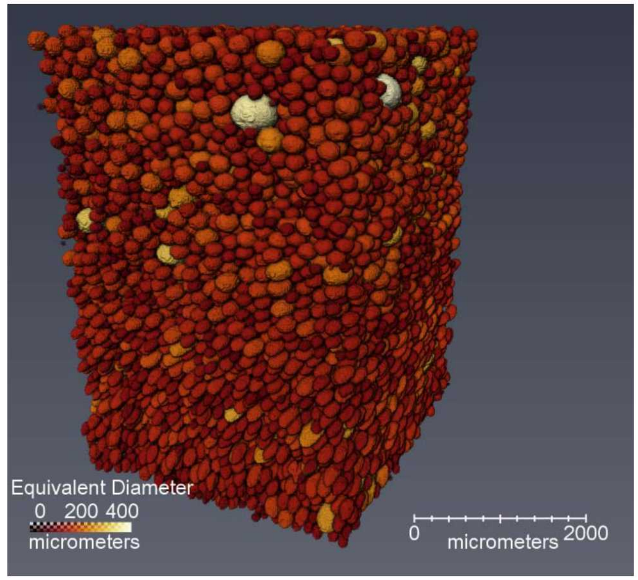
Experiment shows good filling of the shelf feature even at early times giving confidence in the foam model

Conclusions

- All simulations filled fairly well: Complex mold should fill with new shelf!
- Density of the shelf may be lower than nominal density
- Higher temperature increased void size due to ideal gas law, though it filled faster on average
- Vent on shelf did not change void content or density – this is probably due to coarse mesh. In real world, it should help
- Model follows free surface of foam fairly well
- Combination of experimental and computational work led to synergistic breakthroughs creating confidence in mold redesign
- Density and density gradients are still not quantitative and give direction for future work -> bubble-scale modeling

CT Microstructure of Bubbles from Large Complex Mold

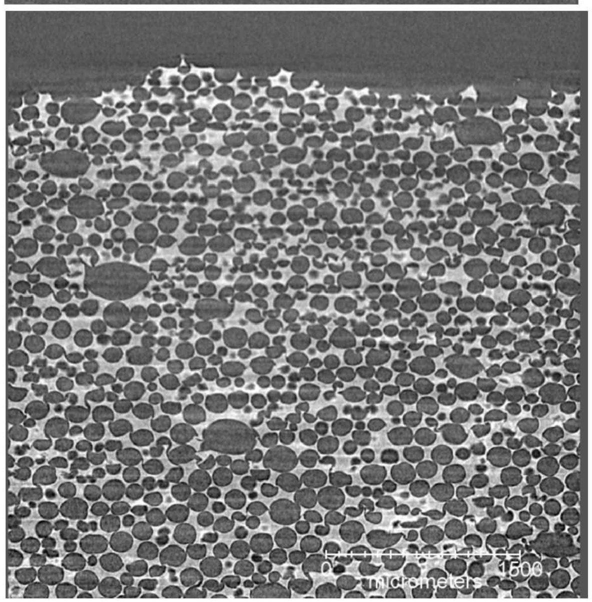


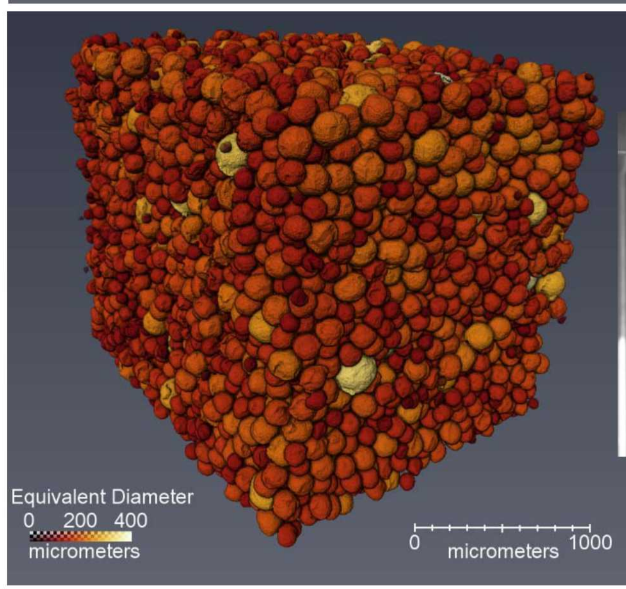


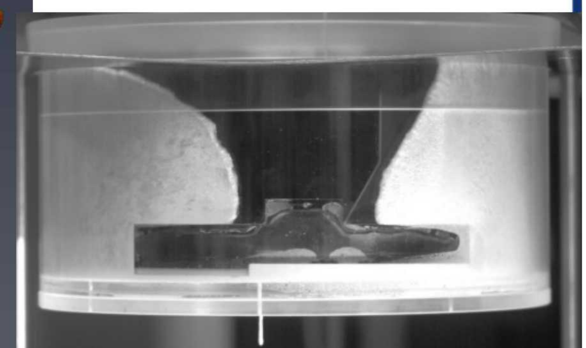
Sample 1 top

Foam microstructure

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



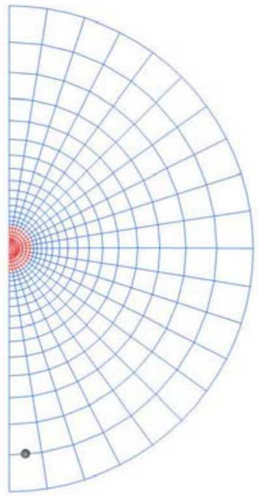




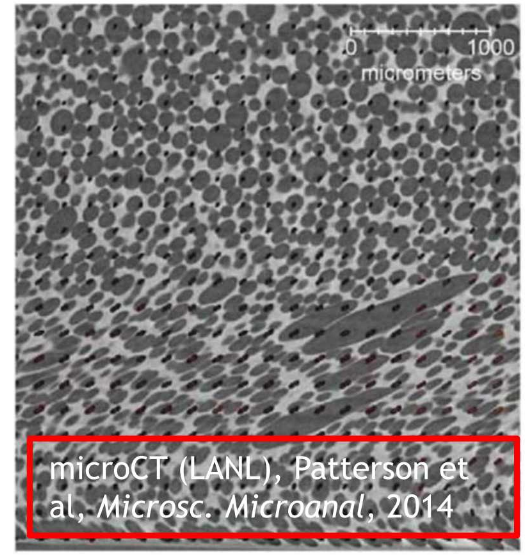
Sample 1 bottom

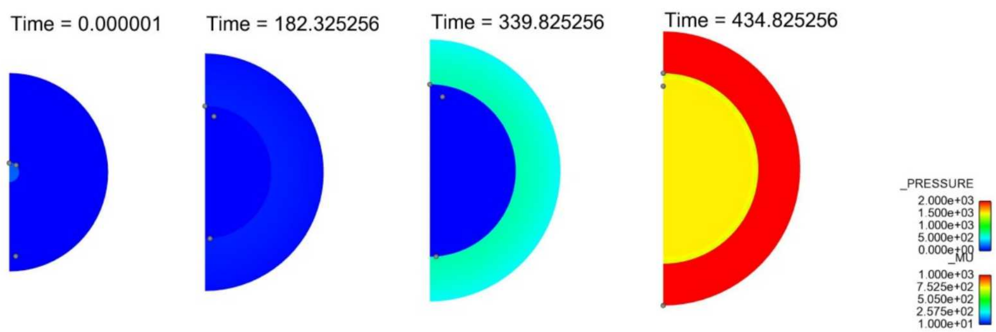
Brian M. Patterson (LANL)

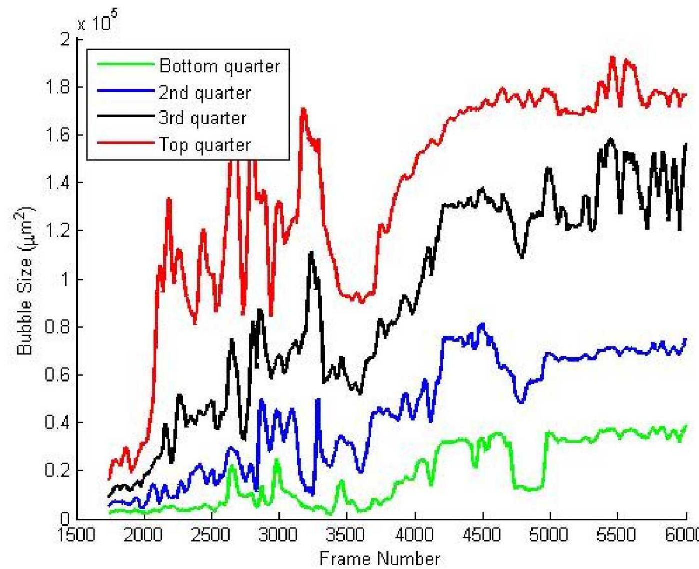
Bubble Expansion in a Polymerizing Fluid

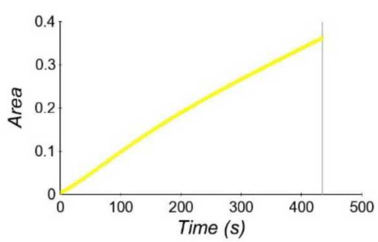


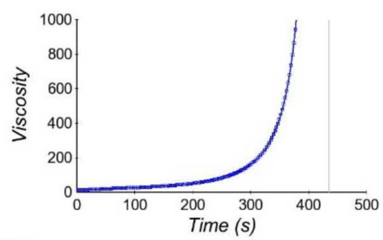
- Bubble grows as CO_2 enters the bubble (VLE model)
- Growth is halted abruptly once the polymer reaches the gel point and the viscosity diverges
- Post-gelation, bubble pressurization is observed
- ALE mesh is robust over shape change
- Data shows the correct trends when compared to experiment







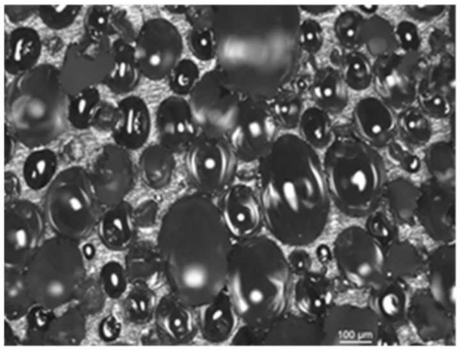


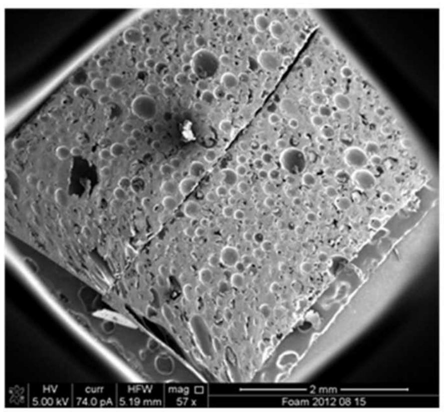


$$\rho\left(\frac{3}{2}\dot{R}^2 + R\ddot{R}\right) = p_{gas} - p_{liq} - 2\frac{\sigma}{R} - 4\eta_{polymer}\frac{\dot{R}}{R}$$

Future Work

SEM of foam showing polydispersity





Bubble at walls are elongated and show coarsening

- **Current model is adequate for production calculation**
- **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