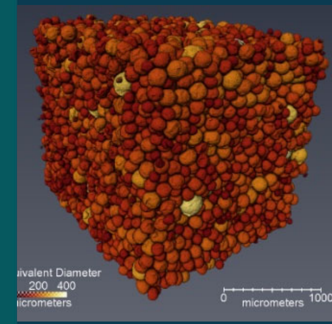
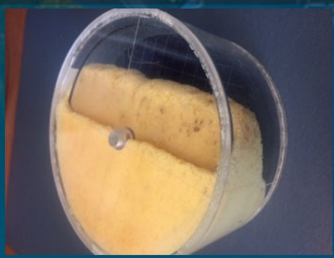
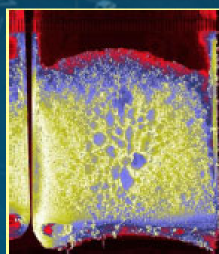
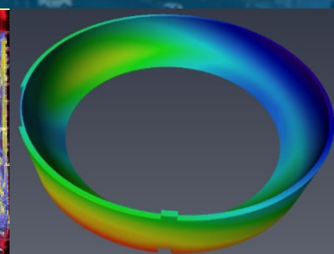
SAND2022-7186C

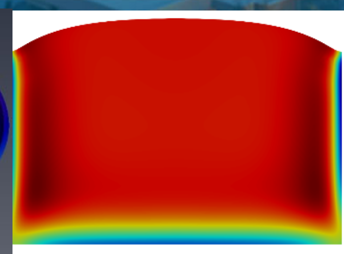
Multiphysics Modeling of Chemically Blown Polyurethane Foams During Manufacturing











SAND2022-????

PRESENTED BY

Rekha Rao, Sandia National Laboratories

Albuquerque, NM

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

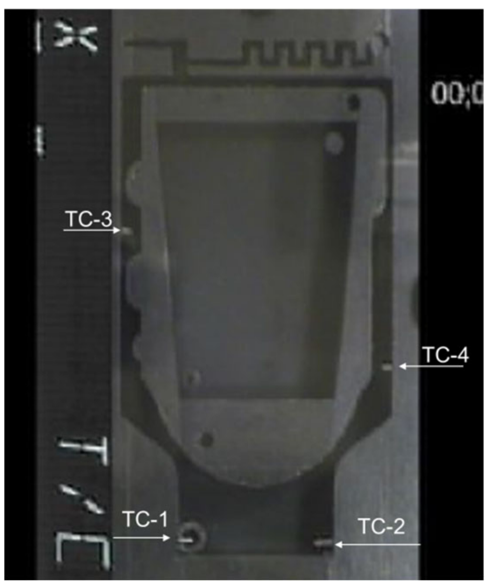
Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

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

Cradle-to-Grave Modeling of Foam Parts

Sierra Mechanics FEA Code Suite

Kinetics and species balances for CH20 and YRCT were developed and coupled to the solid mechanics FE code through an ALE formulation in the thermal-fluid FE code

Thermal-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

Thermal-Fluid/Solid Mechanics

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

Once the polymer vitrifies, further gas production causes bubble pressurization without volume increase

Thermal-Fluid/Solid Mechanics

Vitrified and Released
(10^4 + seconds)

Residual stresses, density, and properties vary spatially

Water uptake/swelling and post-cure shrinkage reactions

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

Foaming and Filling — Primary Cure — Demolding

t = 1 - 15 minutes — t = 3 hours — t = 1- 30 years

Manufacturing — Service Life

Why Are Polyurethane Structural Foams Difficult?

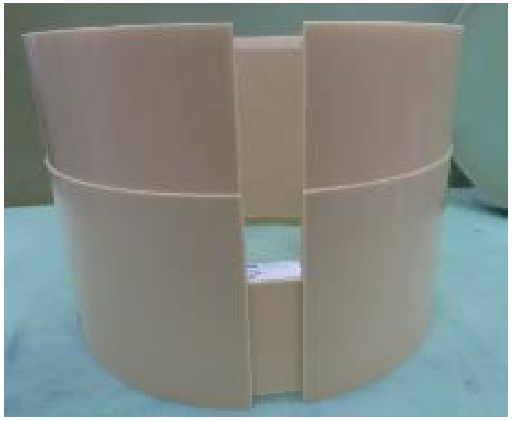
Polyurethane (PMDI) is used as an encapsulant for electronic components, to mitigate against shock and vibration, and for light-weight structural parts.

High-fidelity cradle-to-grave foam models for structural polyurethane for part design.

- Filling profile for vent and gate locations
- Density and density gradient predictions for initializing structural mold, including pressurization and compressibility effects
- Polymerization chemistry for gelation and vitrification
- Manufacturing stresses
- Dimensional stability during manufacturing and aging

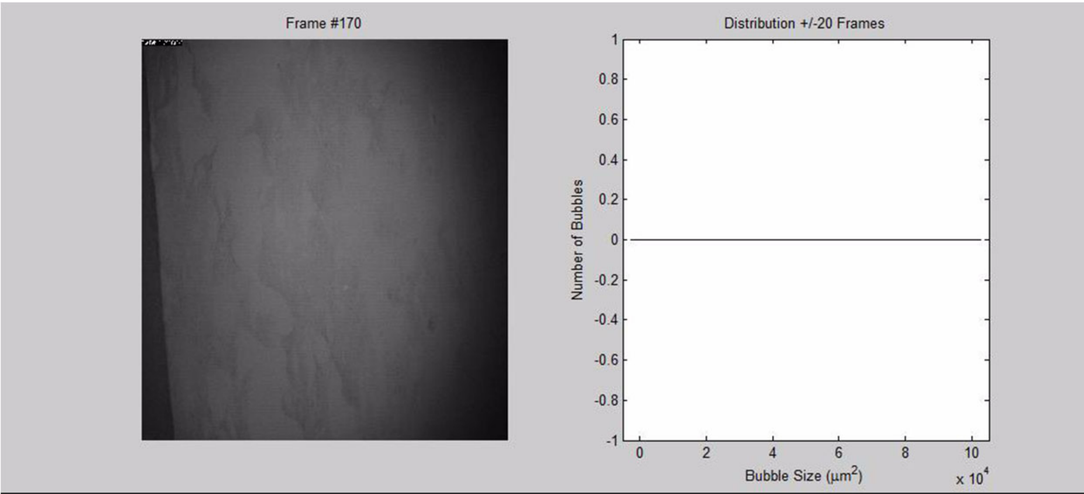
Customer asked us to "use" the model to support mold design – while the model was still under development.

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

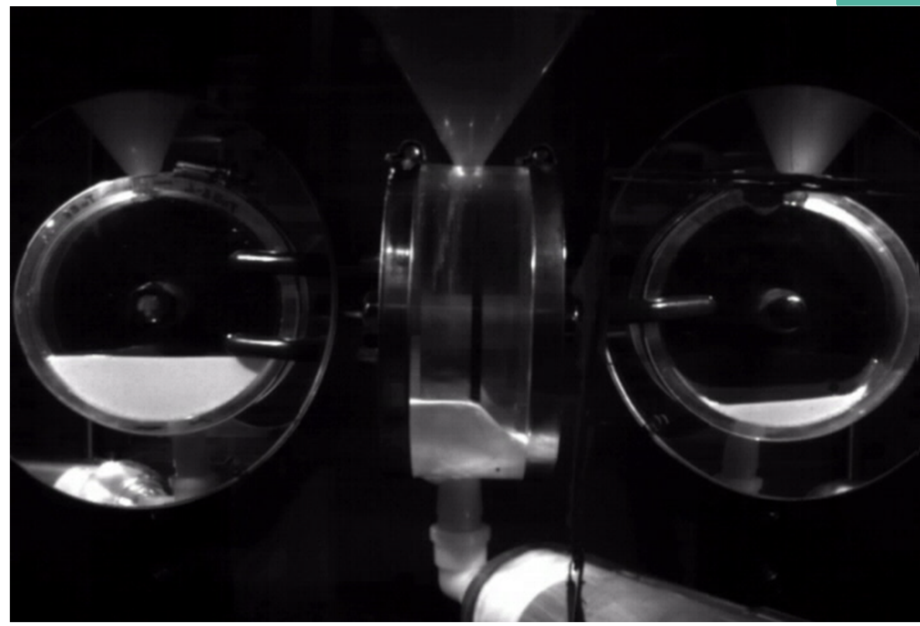


Support A-4 PMDI Structural Part

Foam Filling is Complex



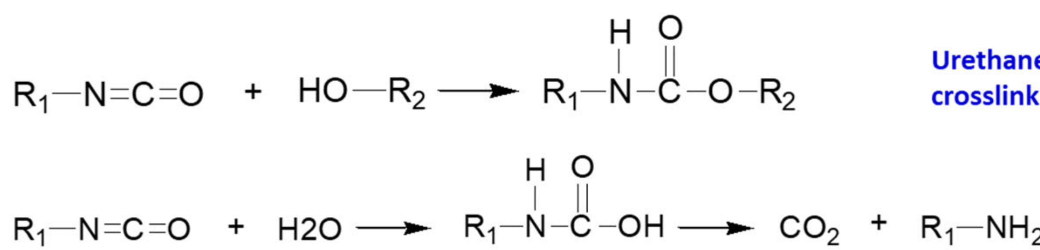
Foam front moving past camera, with bubble sizes at transparent wall determined with image processing.



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

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

Two key reactions: **Isocyanate reaction with polyols and water**



Urethane formation, crosslinking

Foaming reaction yields CO_2 and amine

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

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

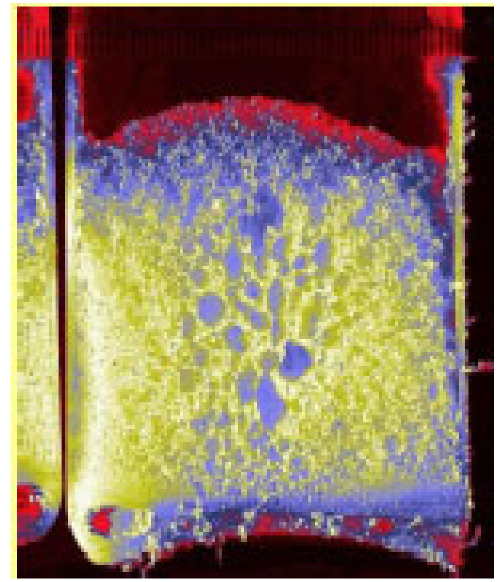
Extent of reaction equation for polymerization: condensation chemistry

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

Molar concentration equations for water and carbon dioxide

$$\frac{dC_{H_2O}}{dt} = -k_{H_2O} C_{H_2O}^n \qquad C_{H_2O} = \frac{\rho_{foam} x_{H_2O}}{M_{H_2O}} \qquad k_{H_2O} = A_{H_2O} \exp(-E_{H_2O} / RT)$$

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



NMR imaging shows coarse microstructure (Altobelli, 2006)

Rao et al., "Polyurethane kinetics for foaming and polymerization" , *AICHE Journal*, 2017

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

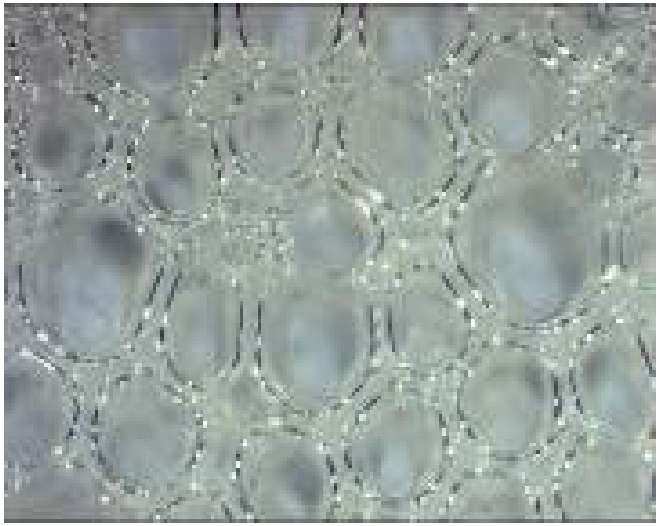
Foaming reaction predicts moles of gas from which we can calculate density

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

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

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

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

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

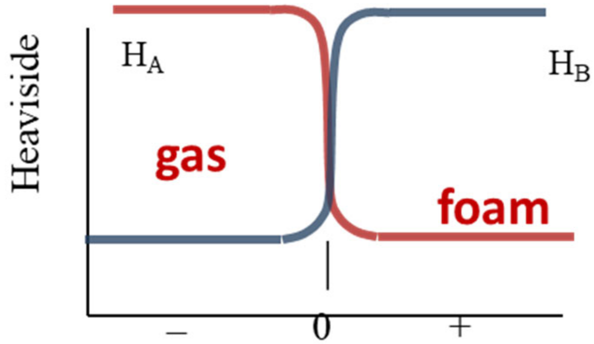
$$\lambda = \frac{4}{3}\mu_0 \frac{(\phi_v - 1)}{\phi_v}$$

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

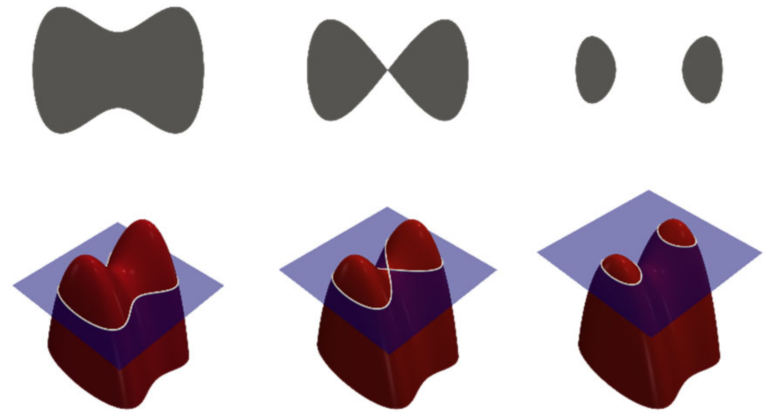
- Experiments to determine foaming and curing kinetics as well as parameters for model

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

Coupled Finite Element Method/Level Set to Solve Foam Dynamics



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



Nicoguaro [CC BY 4.0 (https://creativecommons.org/licenses/by/4.0)], from Wikimedia Commons

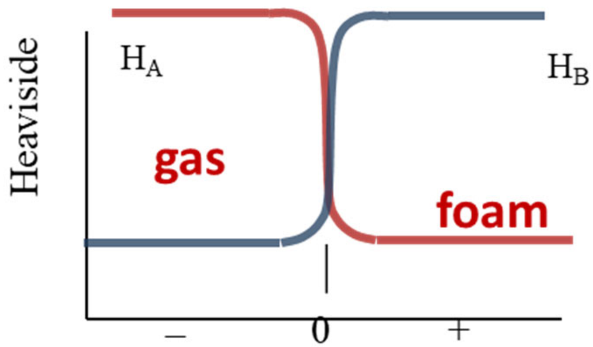
$$H(\phi) = \frac{1}{2}\left(1 + \frac{\phi}{2} + \frac{\sin(\frac{\pi\phi}{\alpha})}{\pi}\right), \ -\alpha < \phi < \alpha$$

- Level set advects with the fluid velocity
- Renormalize periodically to maintain the distance function using a mass conserving Huygens algorithm
- Properties vary with the level set based on the level set and modulated using the Heaviside

$$\eta(\phi) = (\eta_{gas} - \eta_{foam})H(\phi) + \eta_{foam}$$
$$\kappa(\phi) = (\kappa_{gas} - \kappa_{foam})H(\phi) + \kappa_{foam}$$
$$\rho(\phi) = (\rho_{gas} - \rho_{foam})H(\phi) + \rho_{foam}$$

RR Rao et al, C&F, 2018

Coupled Finite Element Method/Level Set to Solve Foam Dynamics



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

- Momentum and Continuity shown for an example. Energy is similar

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

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

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

$$\frac{dC_{H_2O}}{dt} = -(k_{H_2O} C_{H_2O}^n) H_B$$

$$\frac{dC_{CO_2}}{dt} = +(k_{H_2O} C_{H_2O}^n) H_B$$

- Equations discretized with bilinear FEM, pressure stabilized and upwinded
- Equations solved in a segregated manner with momentum and pressure in one block, level set in another, and energy and reactions in the third
- Each block solved with Krylov-based iterative solvers

RR Rao et al, C&F, 2018

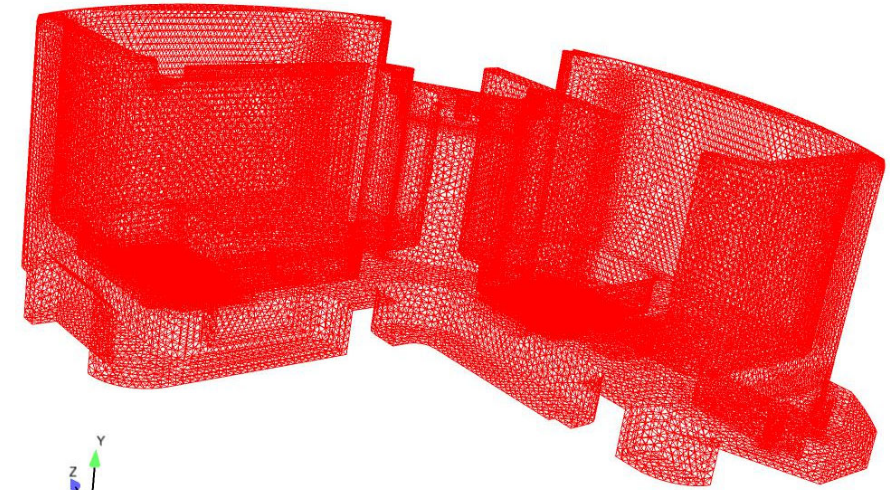
Simulations & Experiments

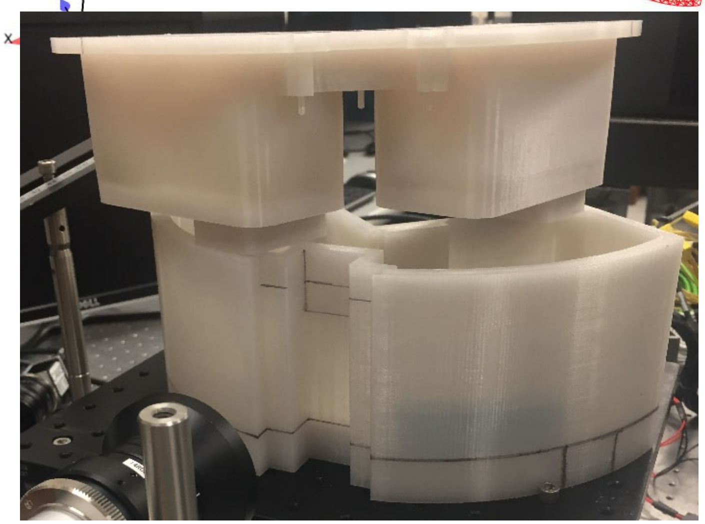
Simulations

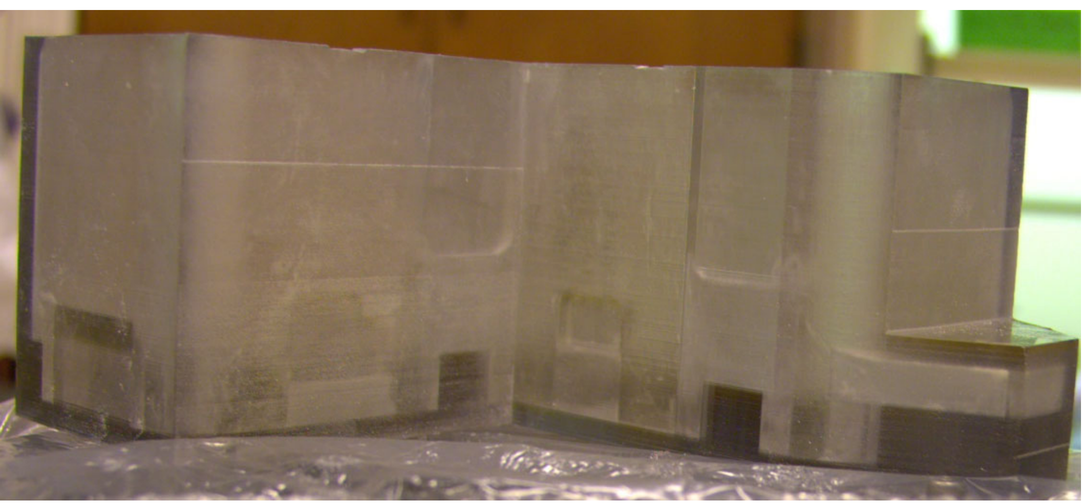
- Flat configuration
- 5^{o} tilt
- 20^{o} tilt
- 20^{o} tilt toward the shelf feature
- Study of vent locations

Experiments

- Flow visualization experiments
- Additive manufacture mold

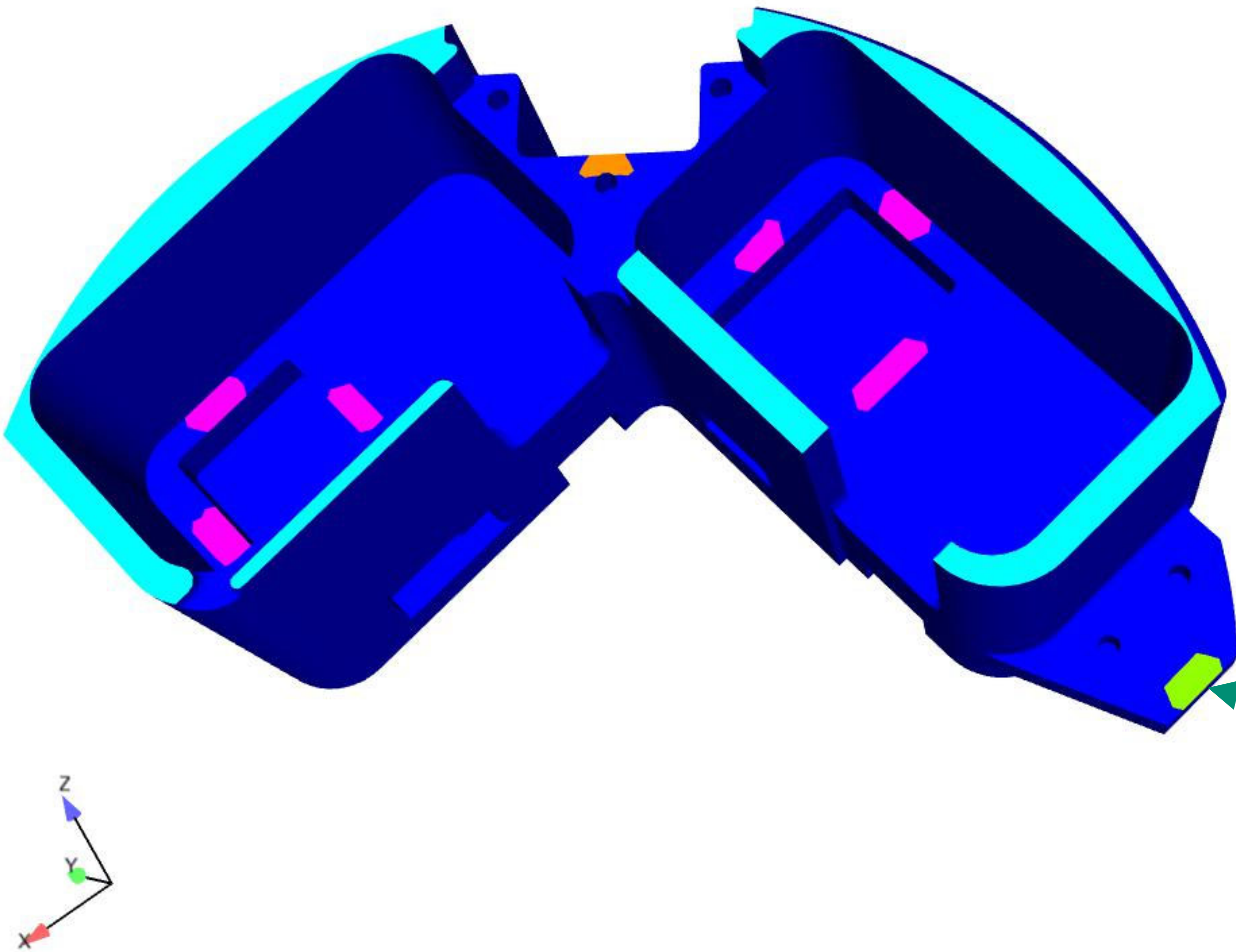






Goal: Use foaming and filling modeling and flow visualization experiments to develop confidence in foam model

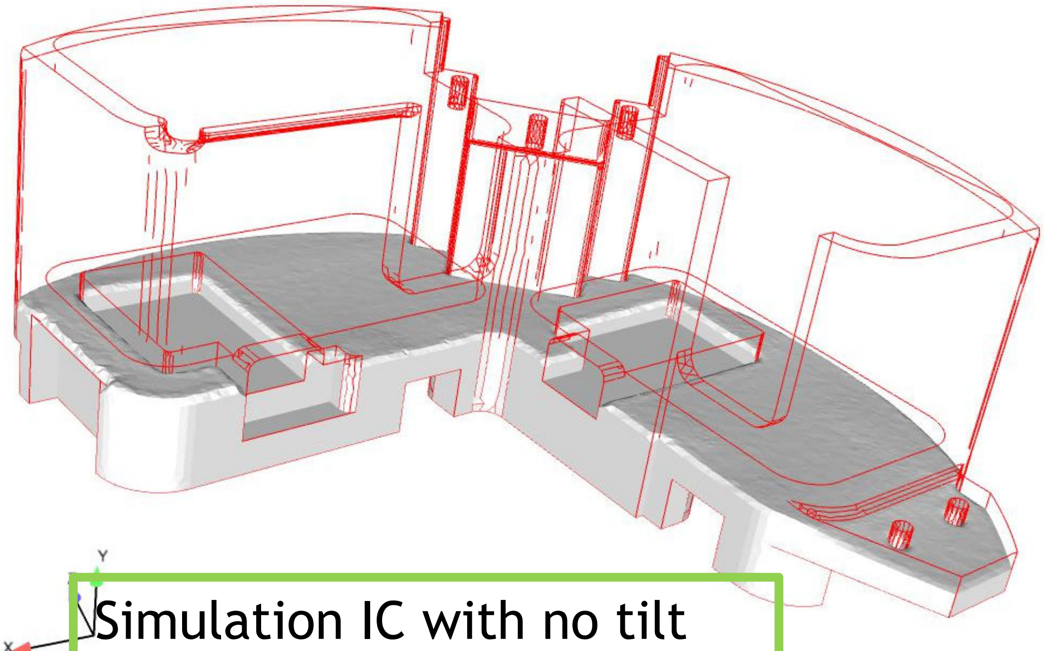
These Vent Locations Seem Representative of a Foaming Process



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



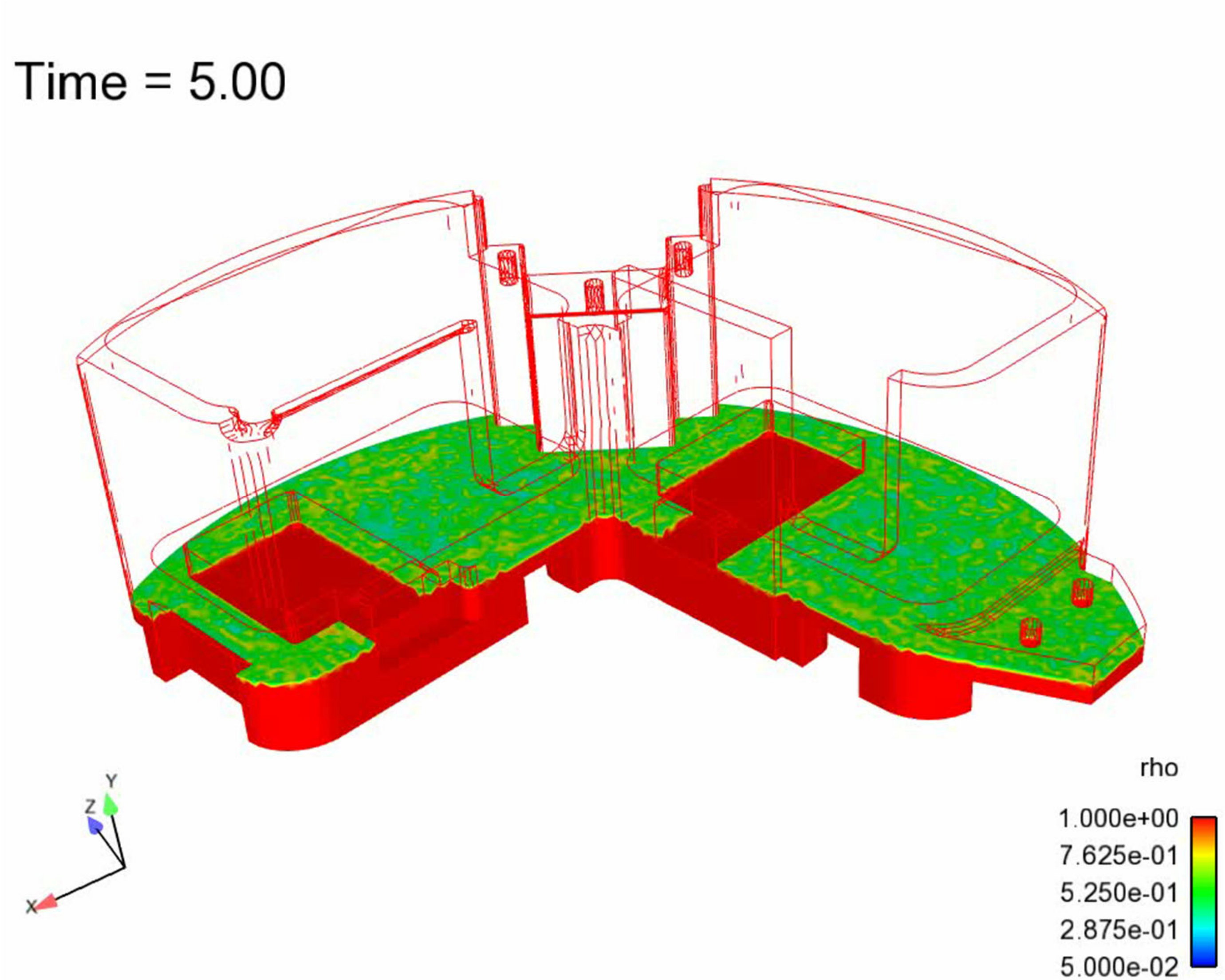
Flow visualization verifies initial condition:

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

Simulation IC with no tilt

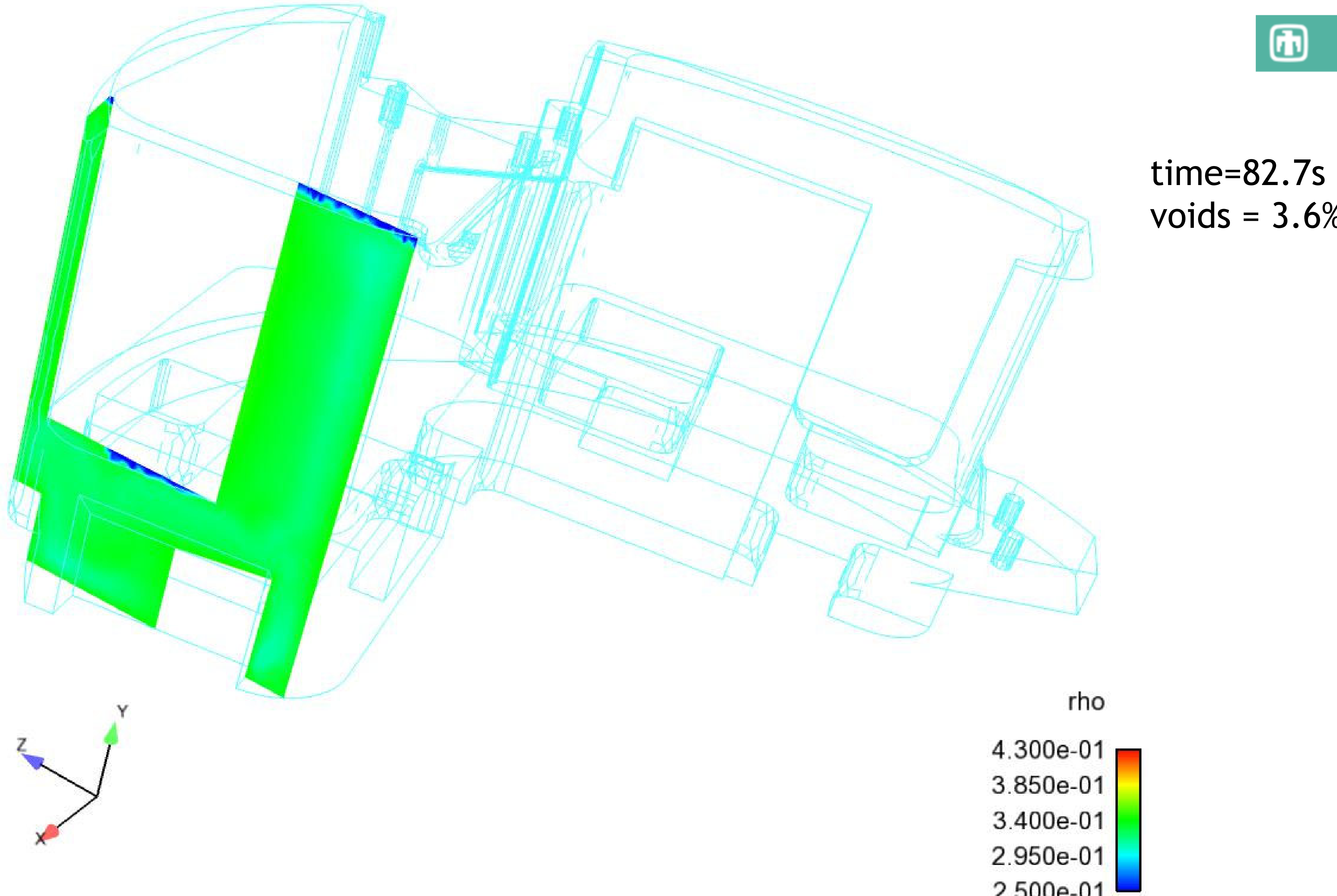
- Shelf is half-filled at start of the simulation

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

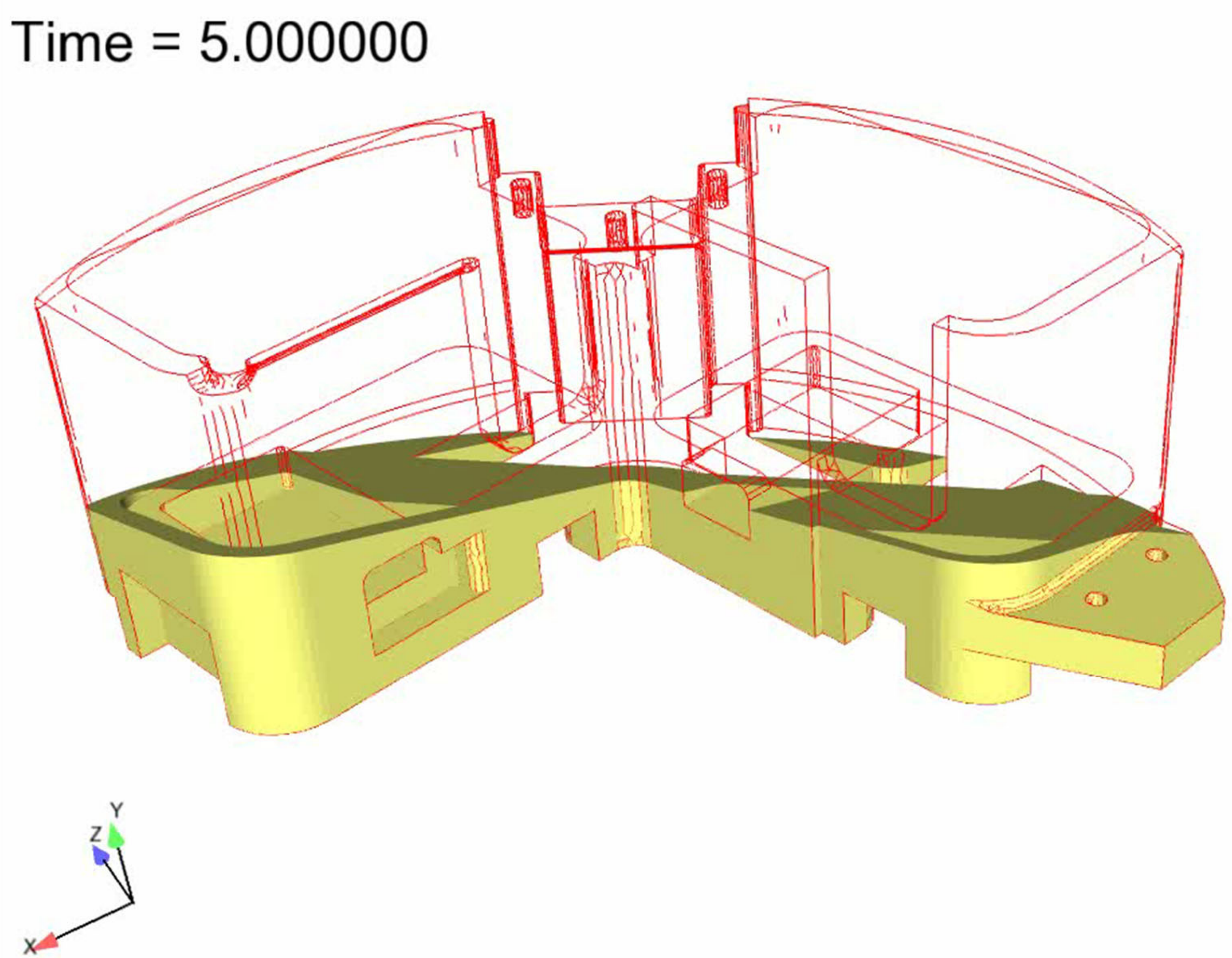


Density Variations at Different Locations: Flat Mold with Shelf Vent

Dynamics of Filling with 20o Tilt Angle

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

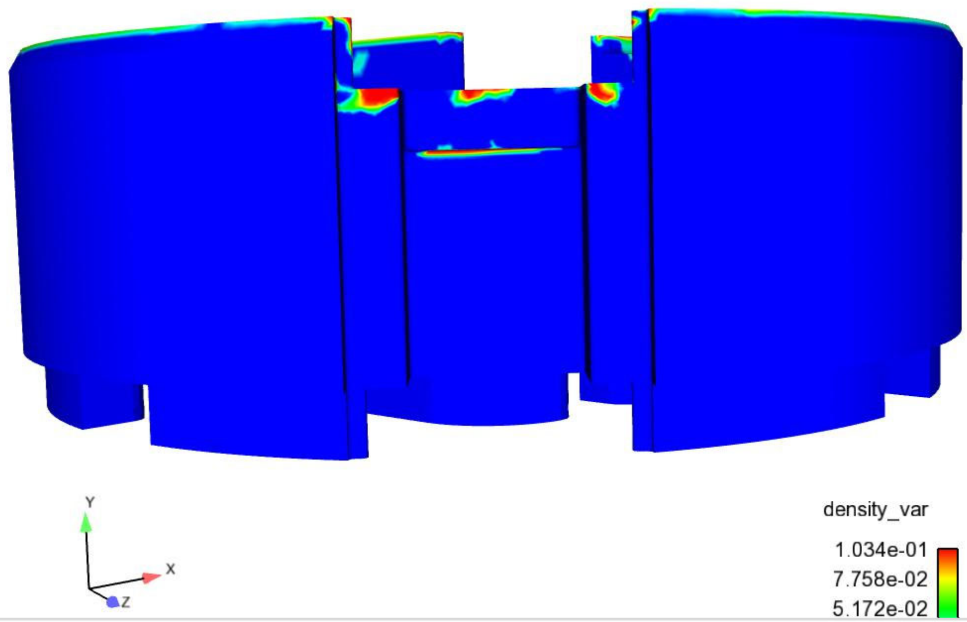
- Initial condition has a tilt forward for foam position and a flat interface
- Gravity vector is also tilted



Density Variations: Back View

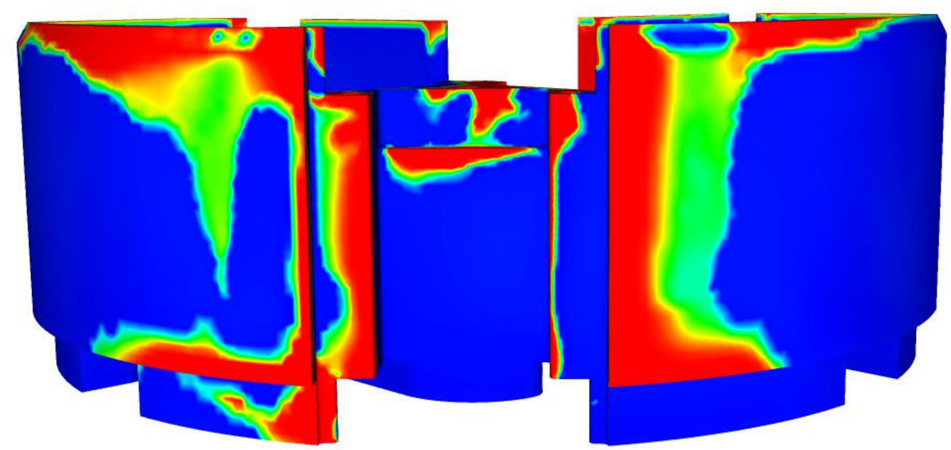
Time = 82.737

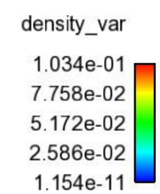
FLAT FILL



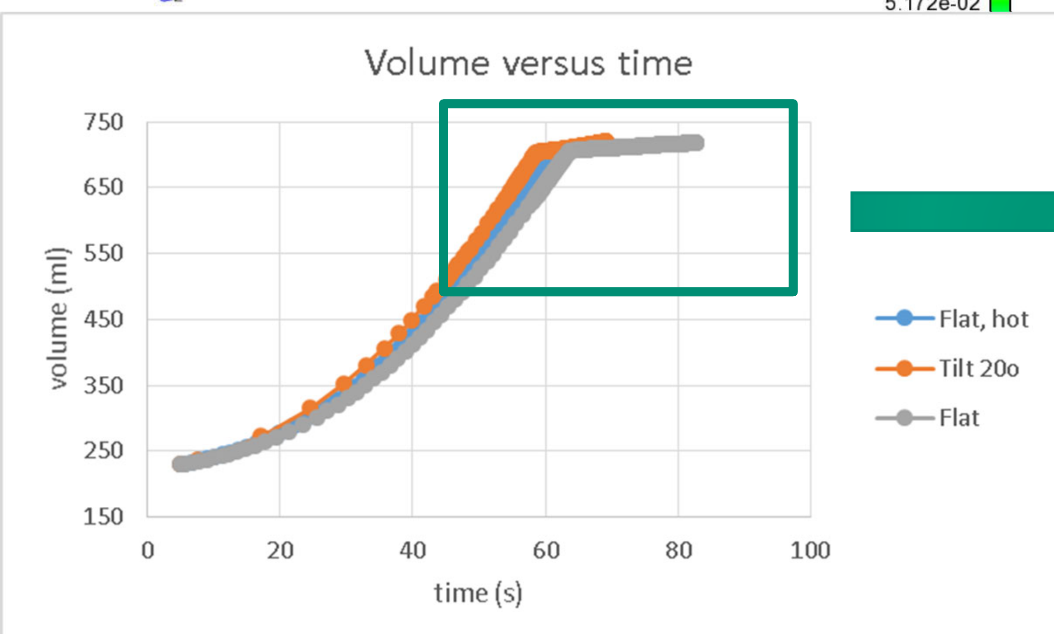
Time = 71.091

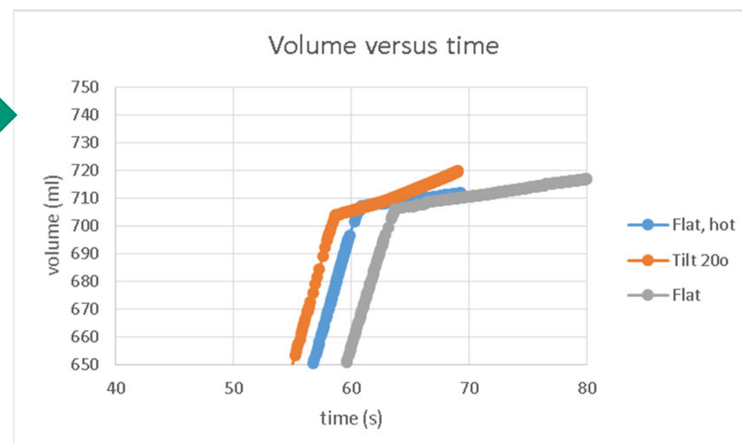
TILT 20 DEGREES FILL



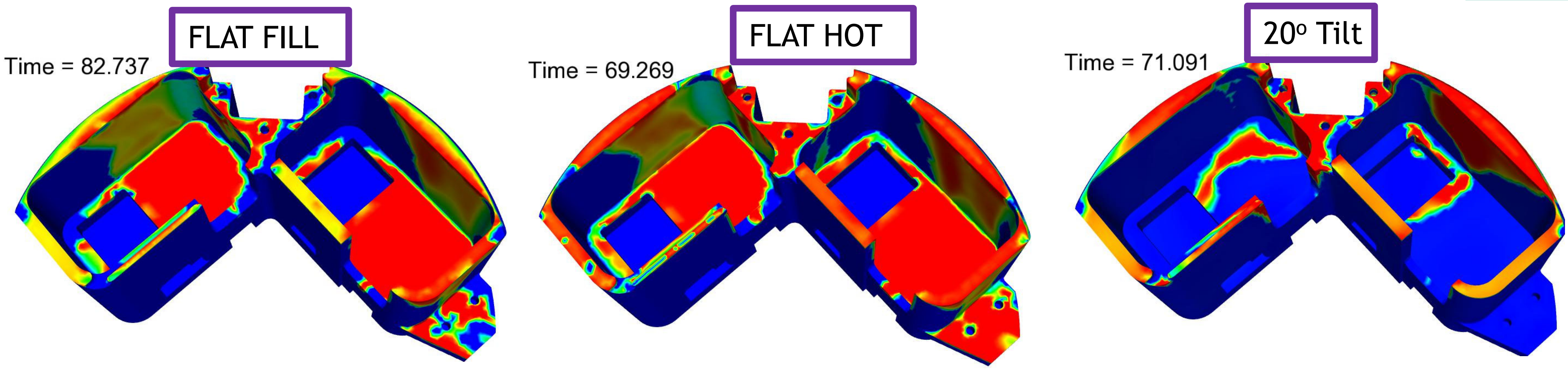


- Forward tilt moves defects to the back part of the mold
- Tilt fills faster than flat

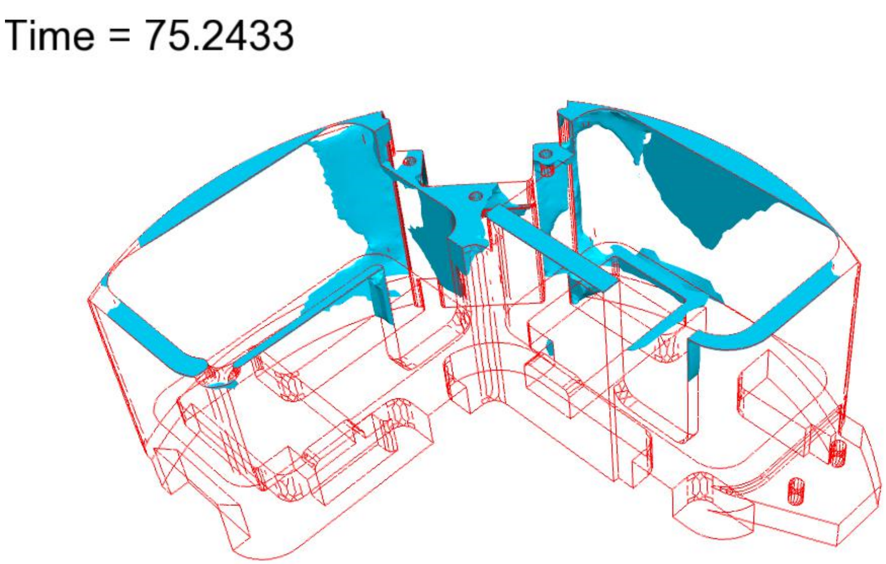




Computational Models of Foam



Density variations for three cases of interest



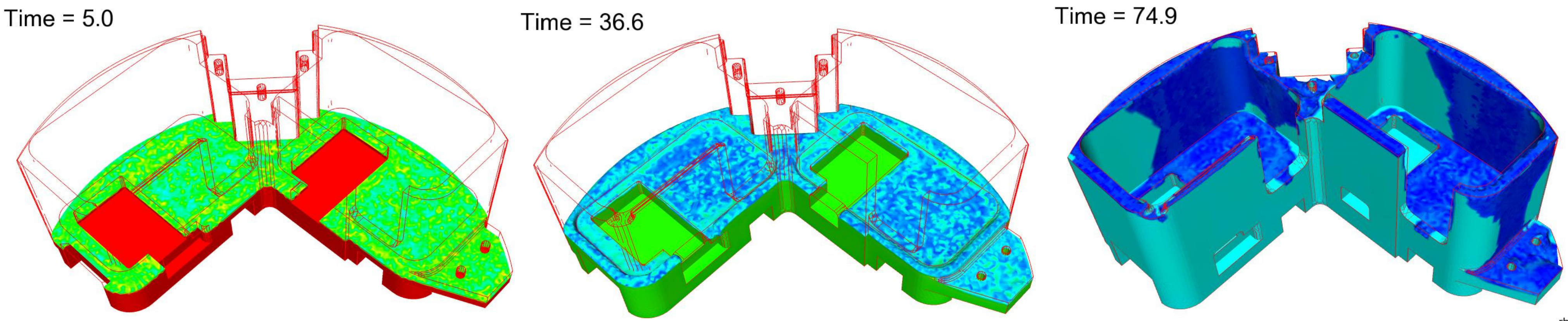
Foam filling for 20º tilt: the angled fill reduces voids on the new shelf

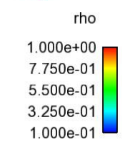
Case	Flat	Flat Hot	20º Tilt
Max. Time (s)	83s	70s	71s
Voids	3.6%	4.4%	2.9%
Density variation	2.8	2.9	3.6

All cases fill well!

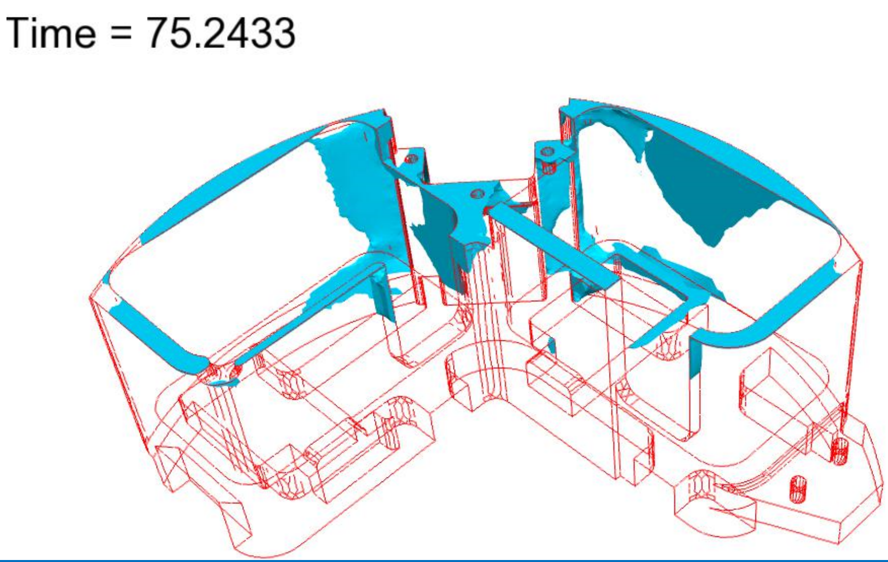
- Model over-predicts voids, but predictions are small
- Density variation greater with tilt

Computational Models of Foam

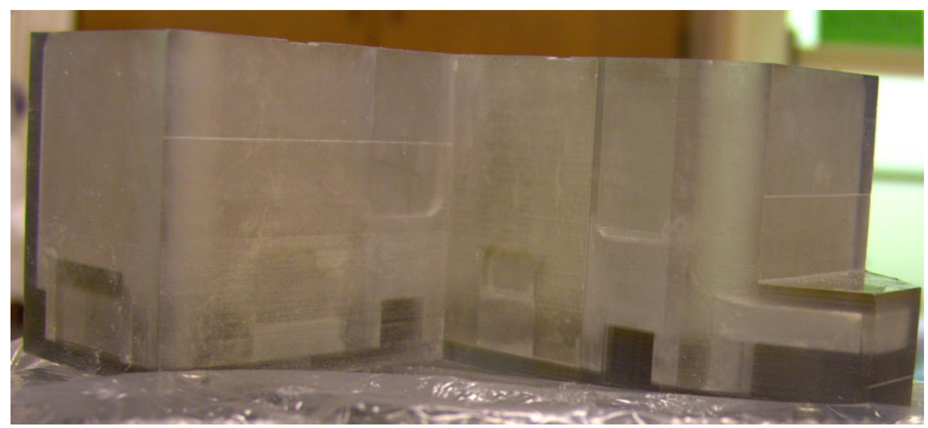




Evolution of density for flat mold with vent on the shelf feature

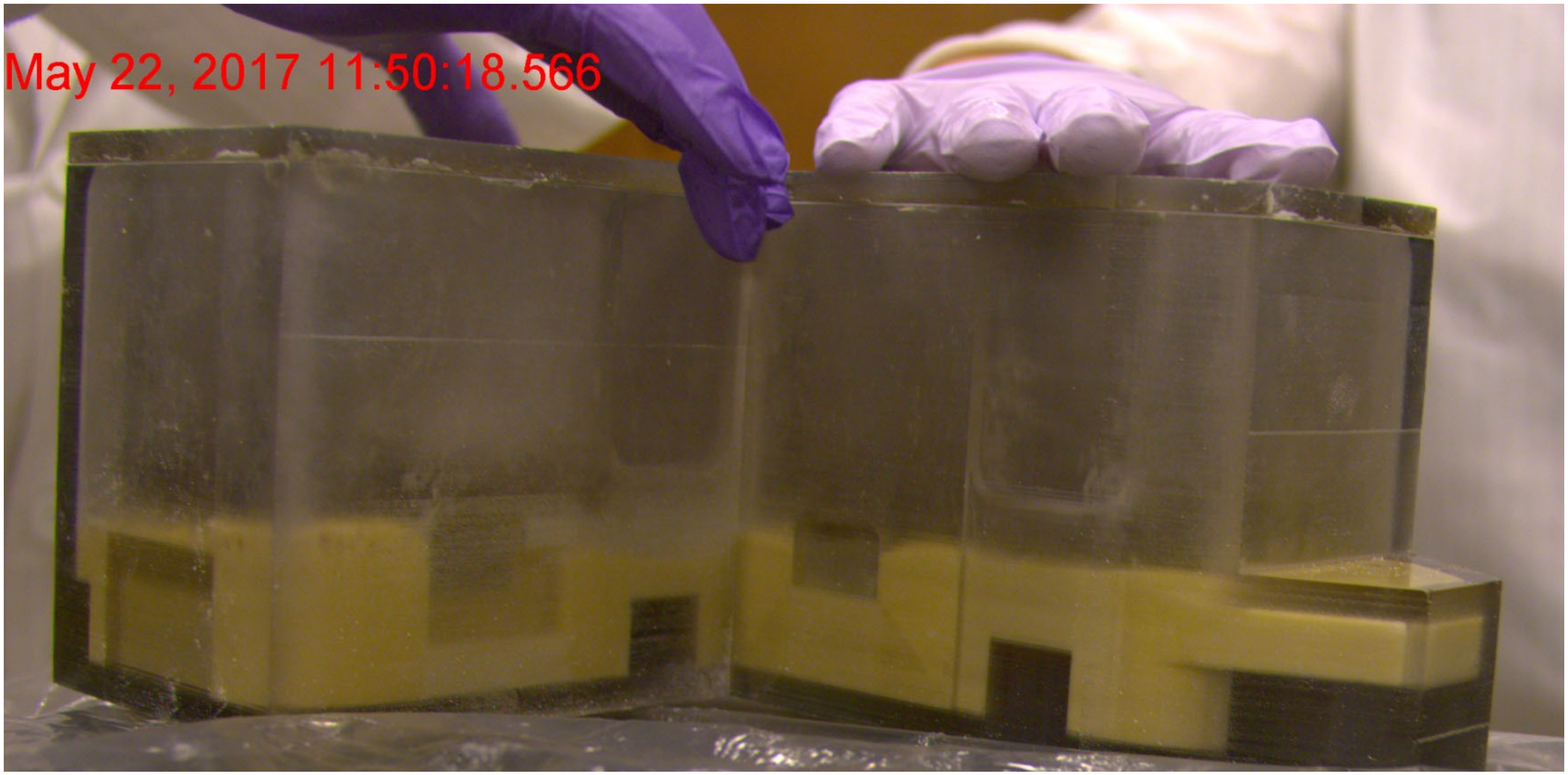


Flow visualization study supports computational conclusions



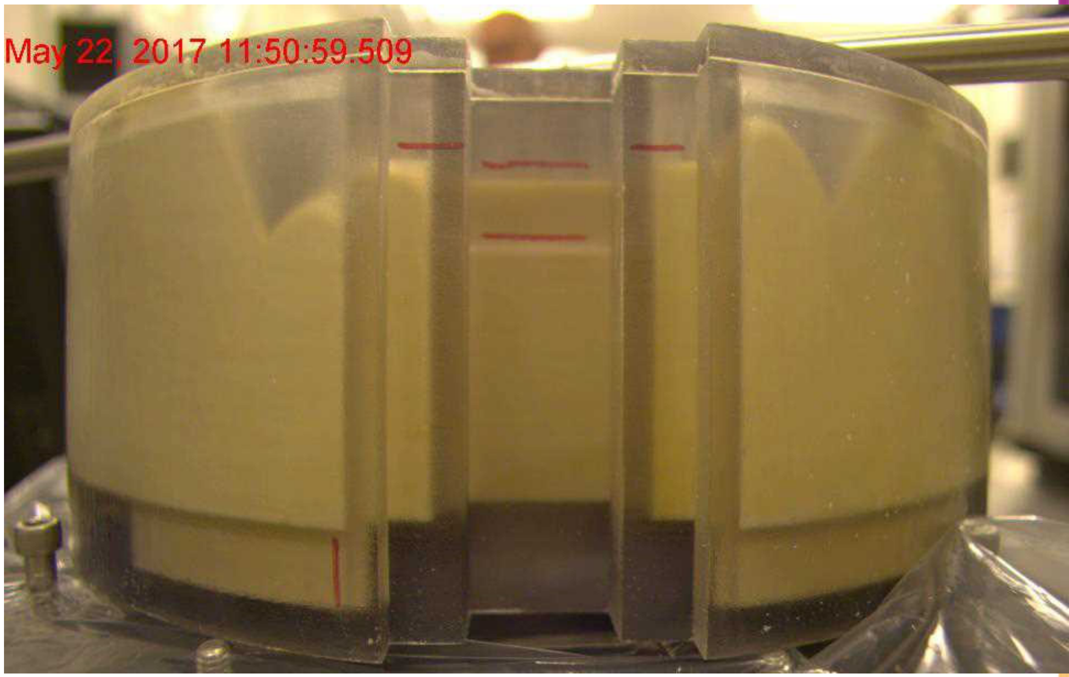
Foam filling for 20º tilt: the angled fill reduces voids on the new shelf

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



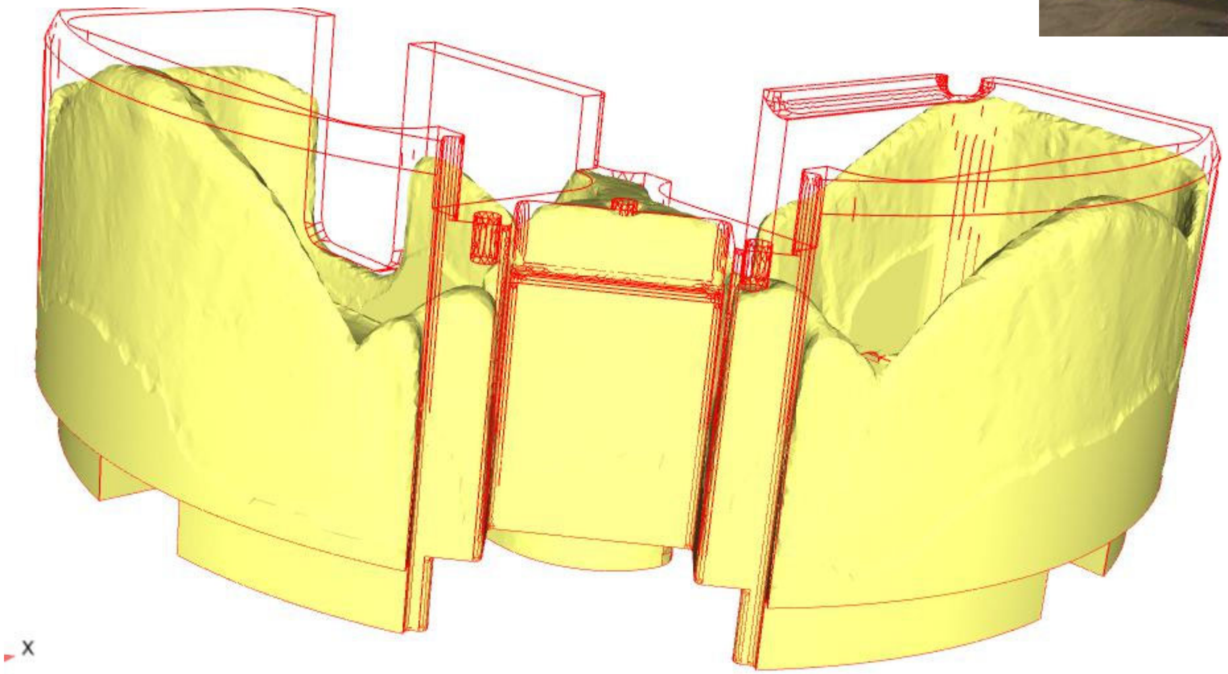
- New experiment using clear mold
- Room temperature mix of foam, which heats up to 24^{o}C
- Mold stays roughly 22^{o}C
- 5 degree tilt towards the front of the mold

Experimental Conditions: Back of Mold



Run model with similar initial conditions:

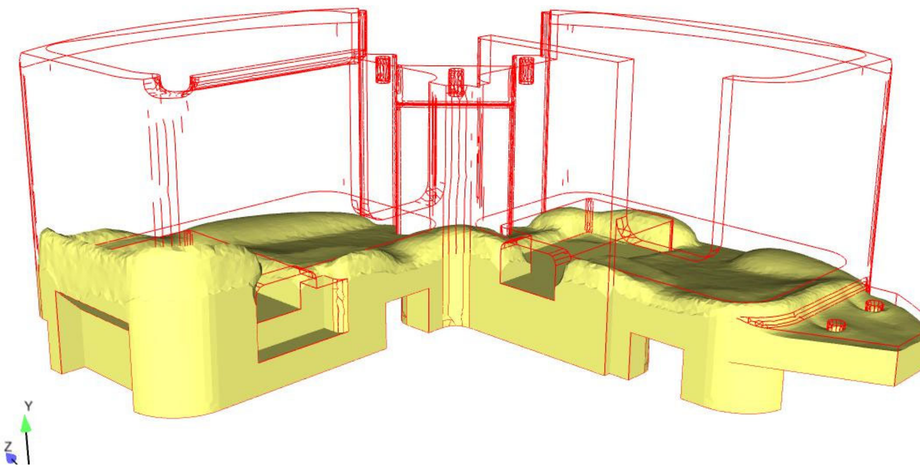
- 240g material
- 4 degree tilt
- Room temperature mold and foam

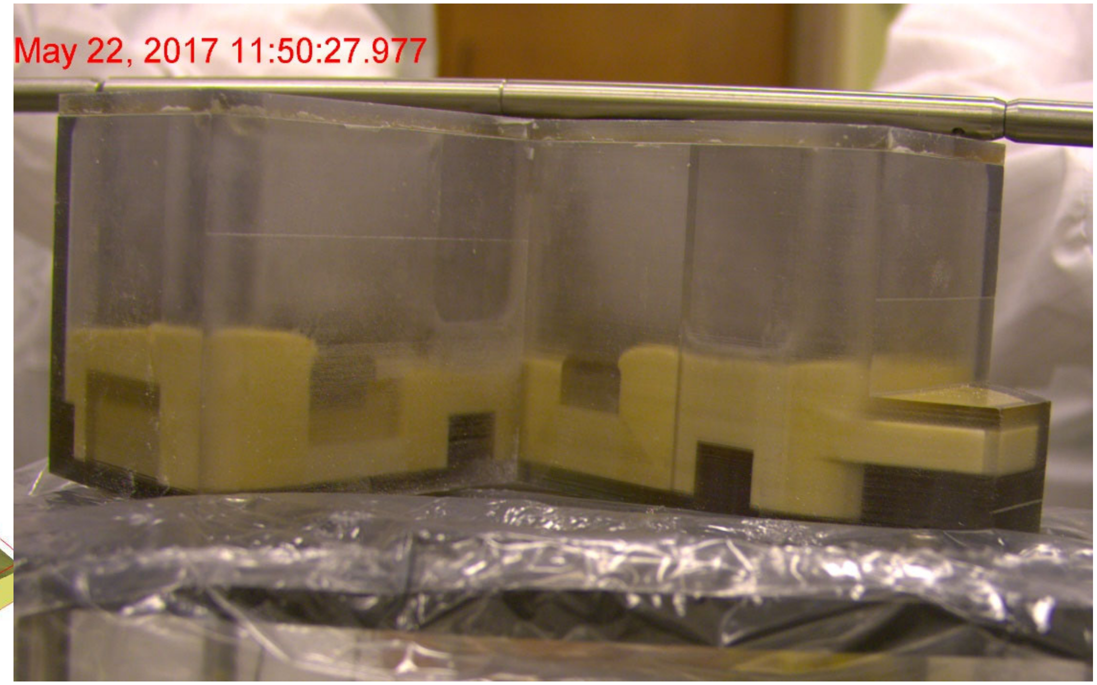


Shape of the model interface matches well with shape of experiment thought model fills back feature faster

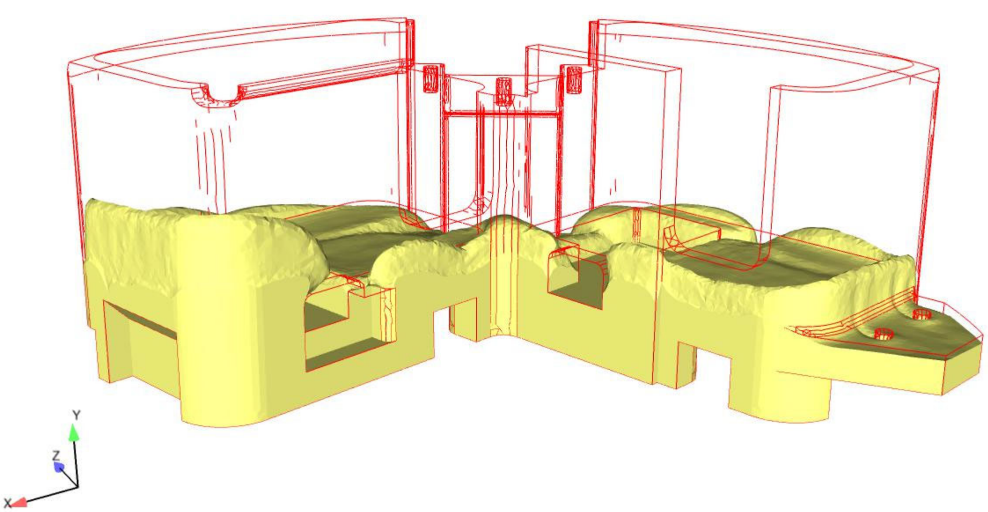
Compare Mold Front: Early Times

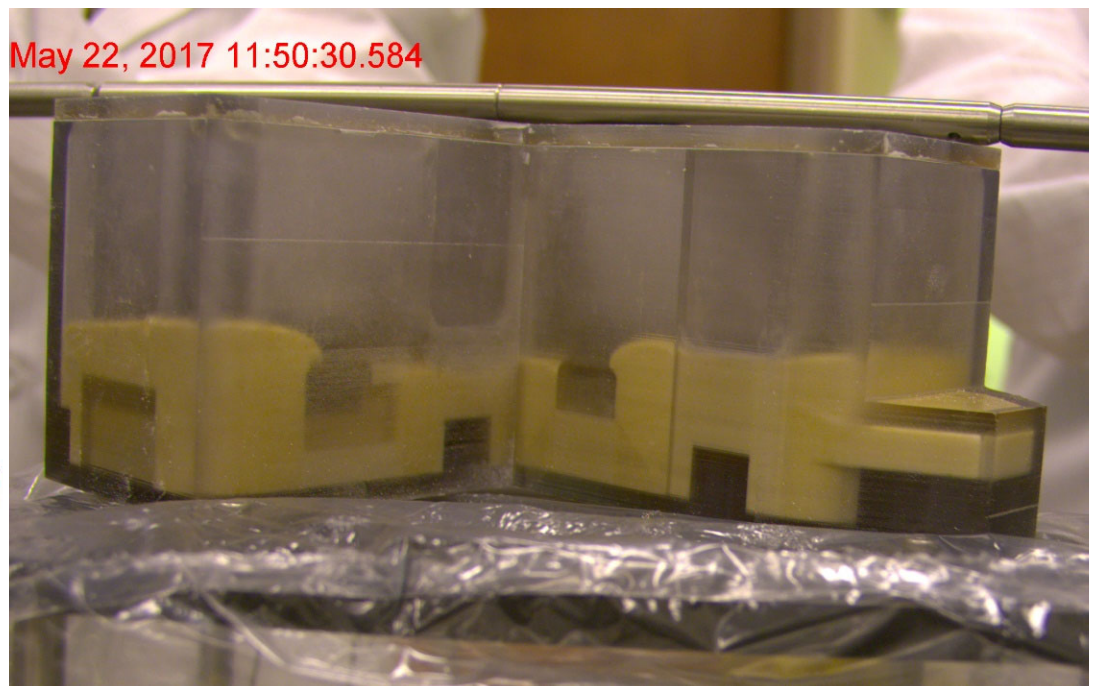
Time = 34.184





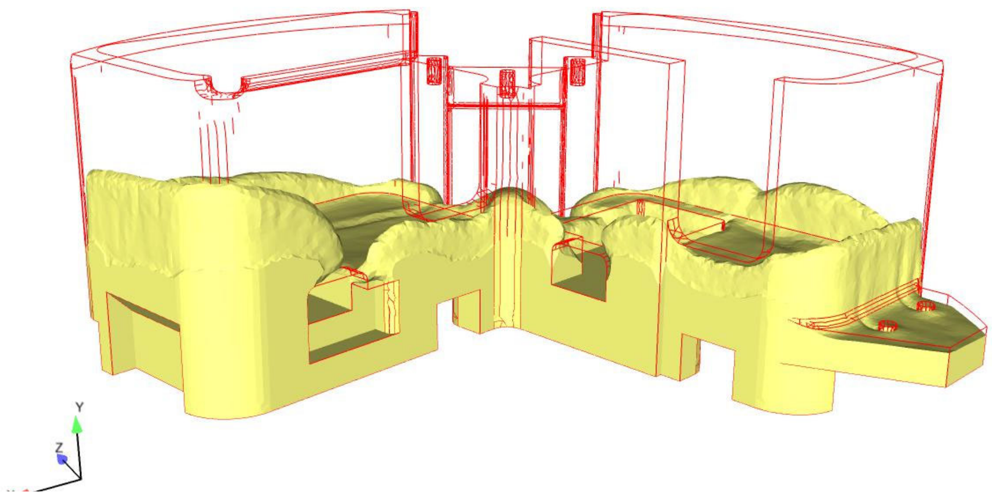
Time = 44.617



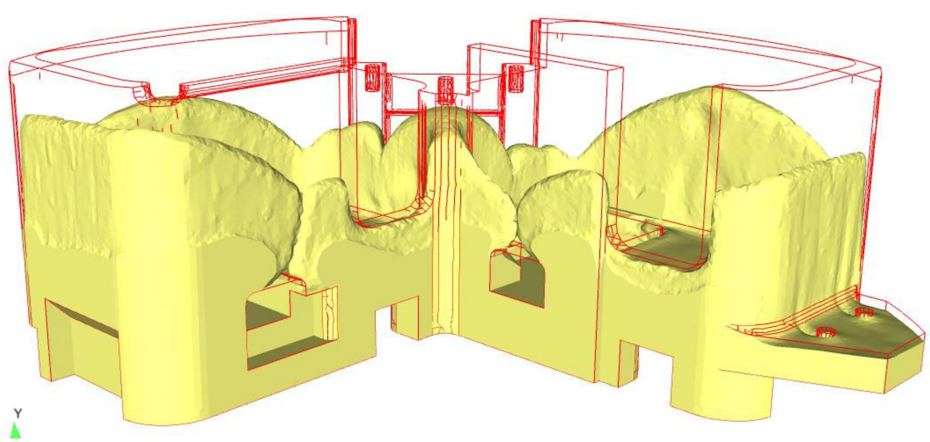


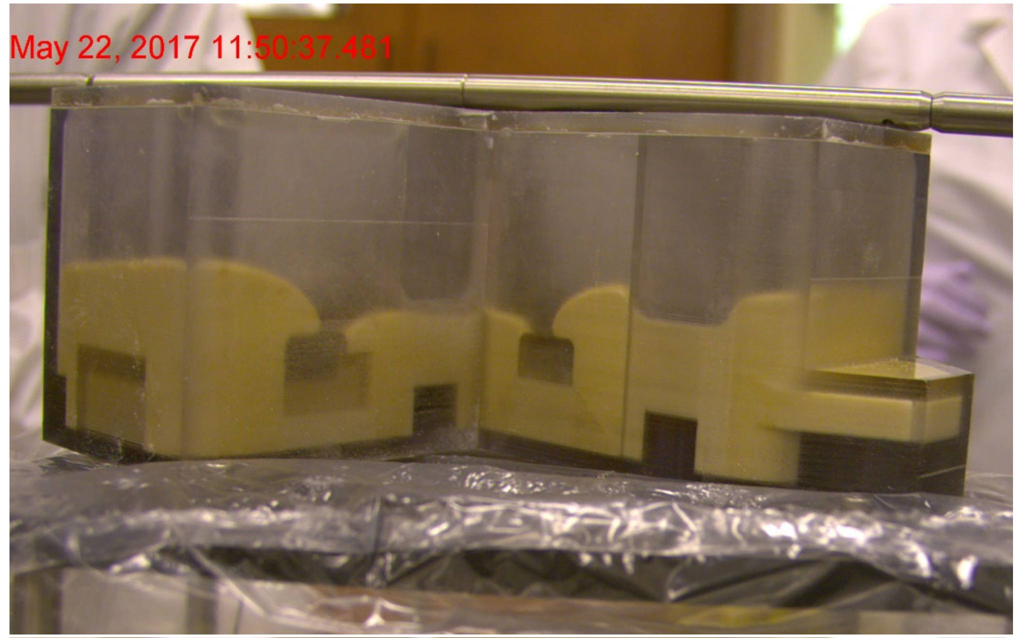
Compare Mold Front: Moderate Time

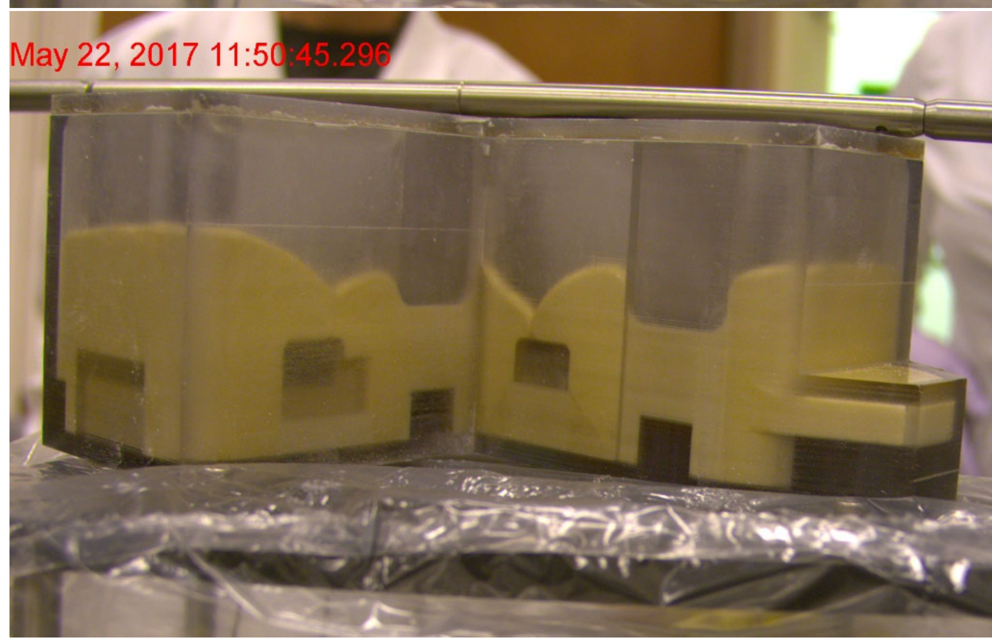
Time = 49.913



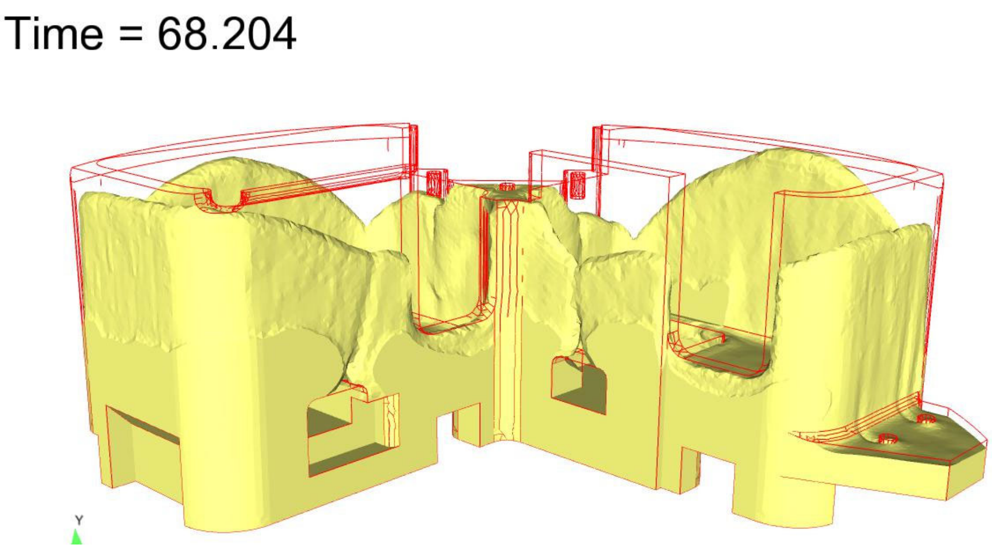
Time = 62.538

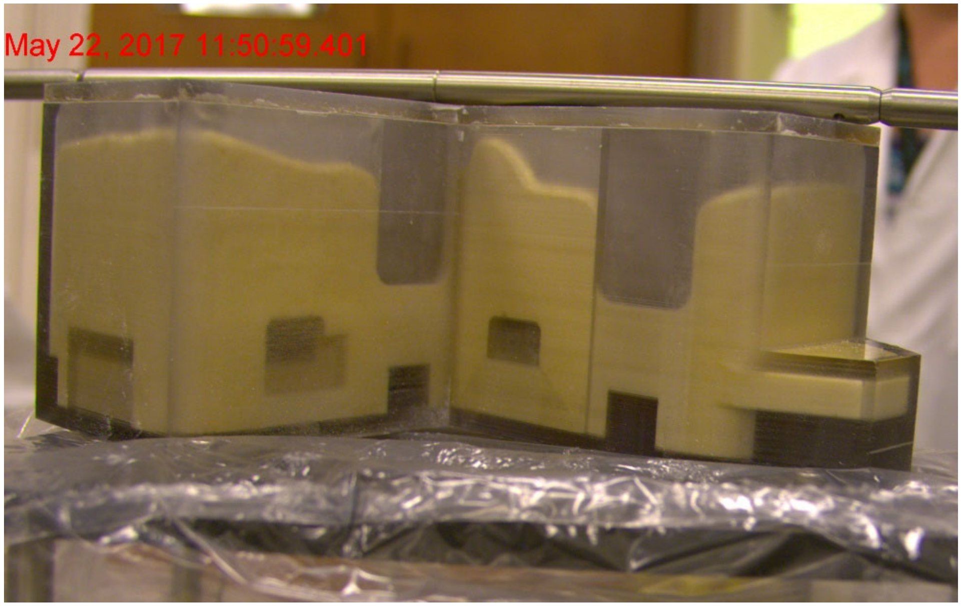






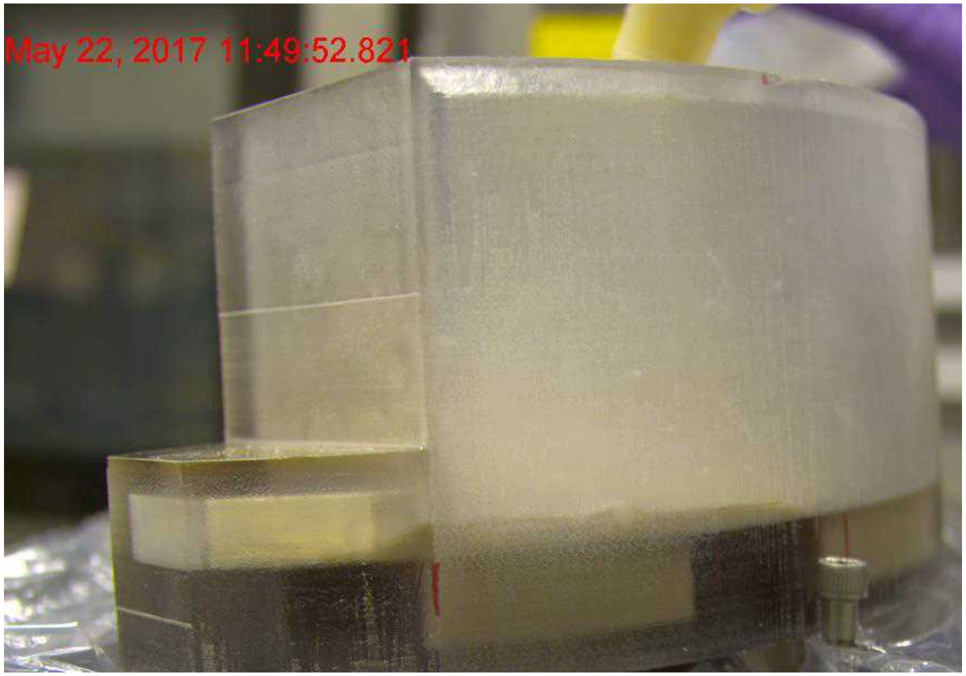
Compare Mold Front: Late Time

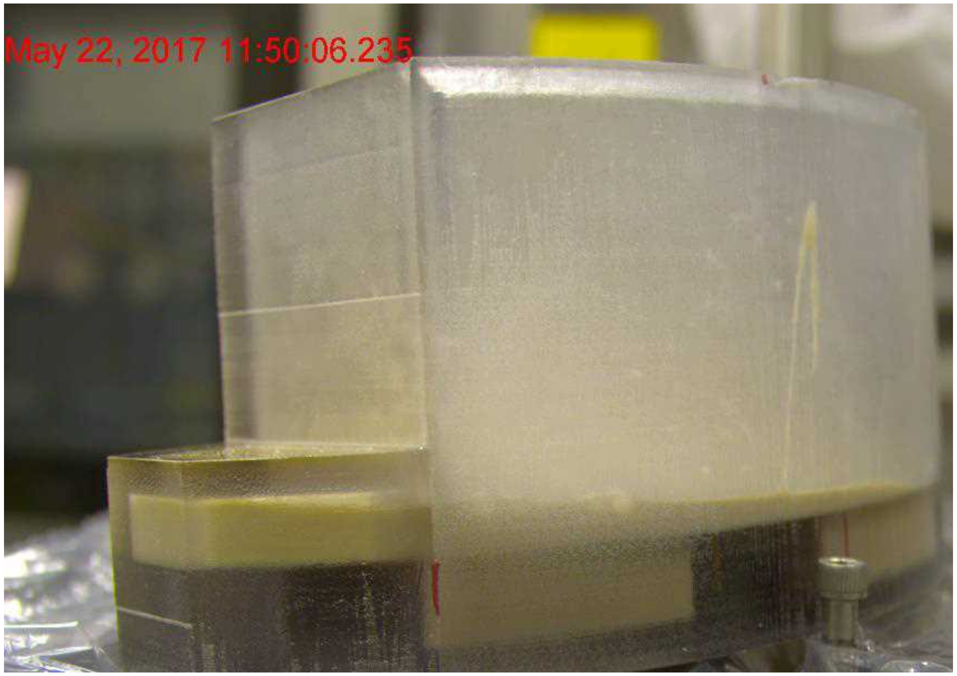


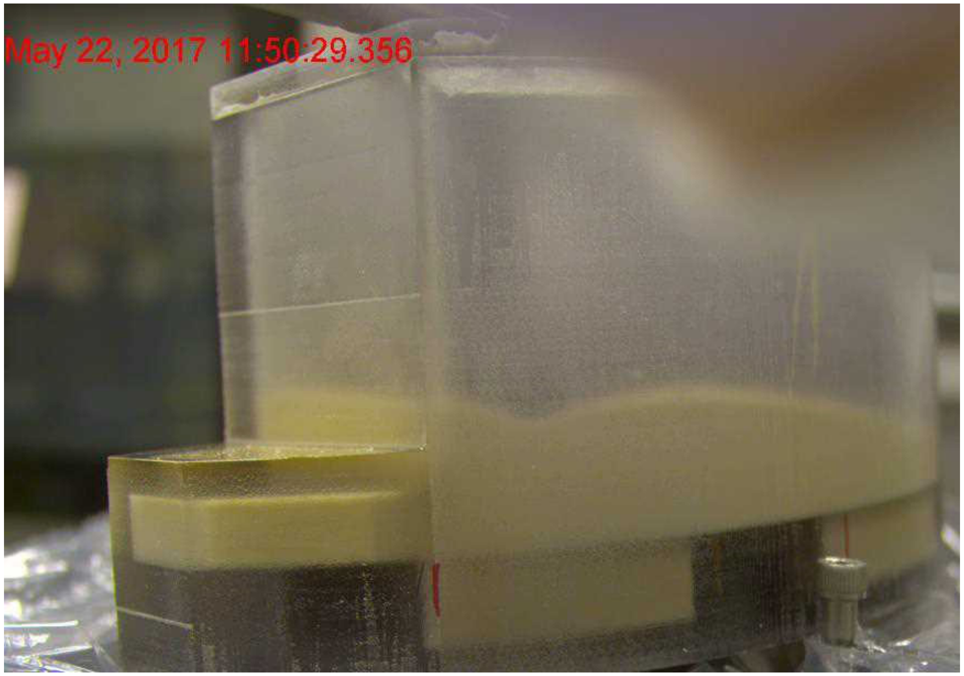


Shape of the model interface matches well with shape of experiment and the time-scale is similar

Shelf Feature Fills Well in Clear Mold

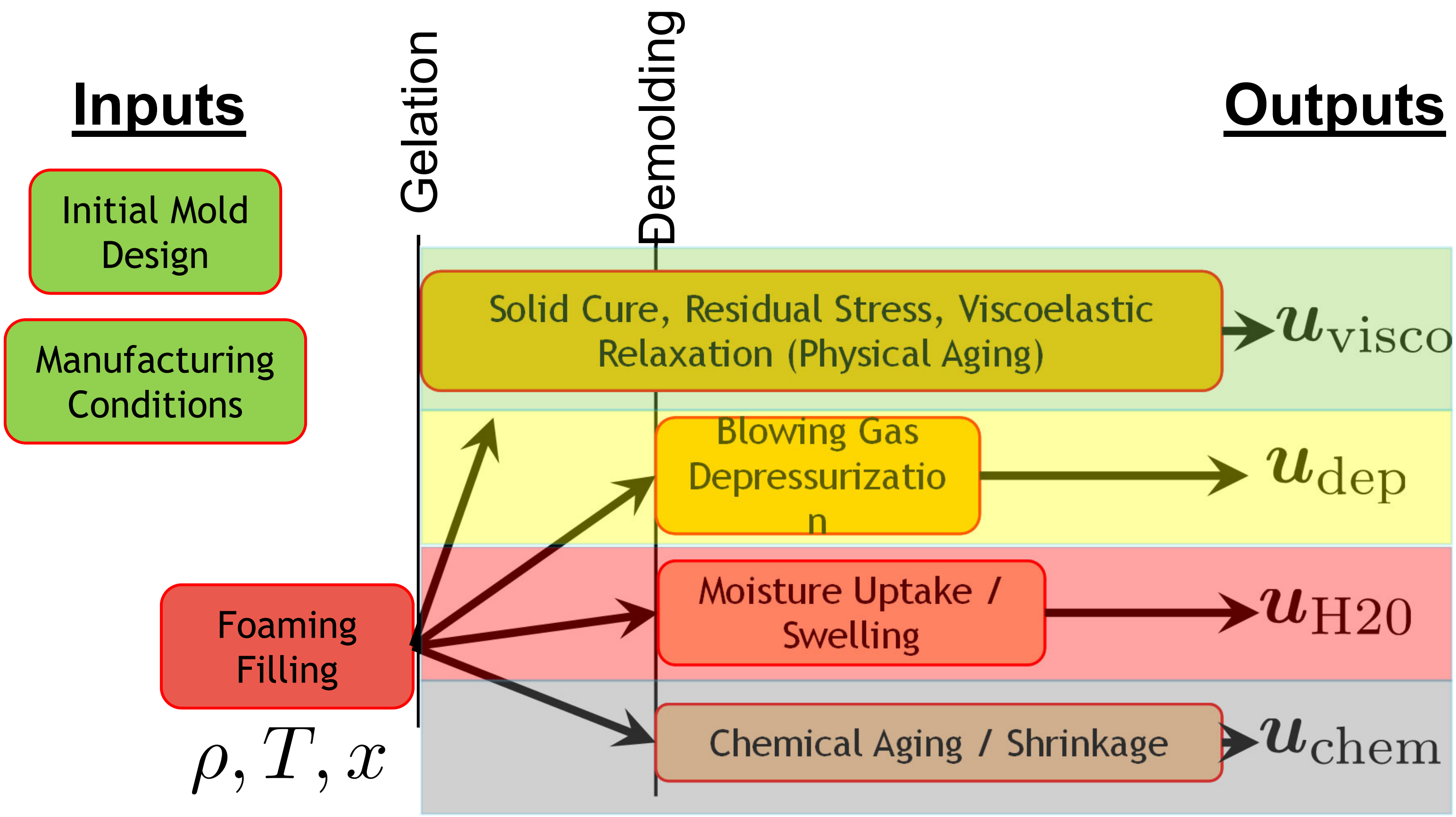






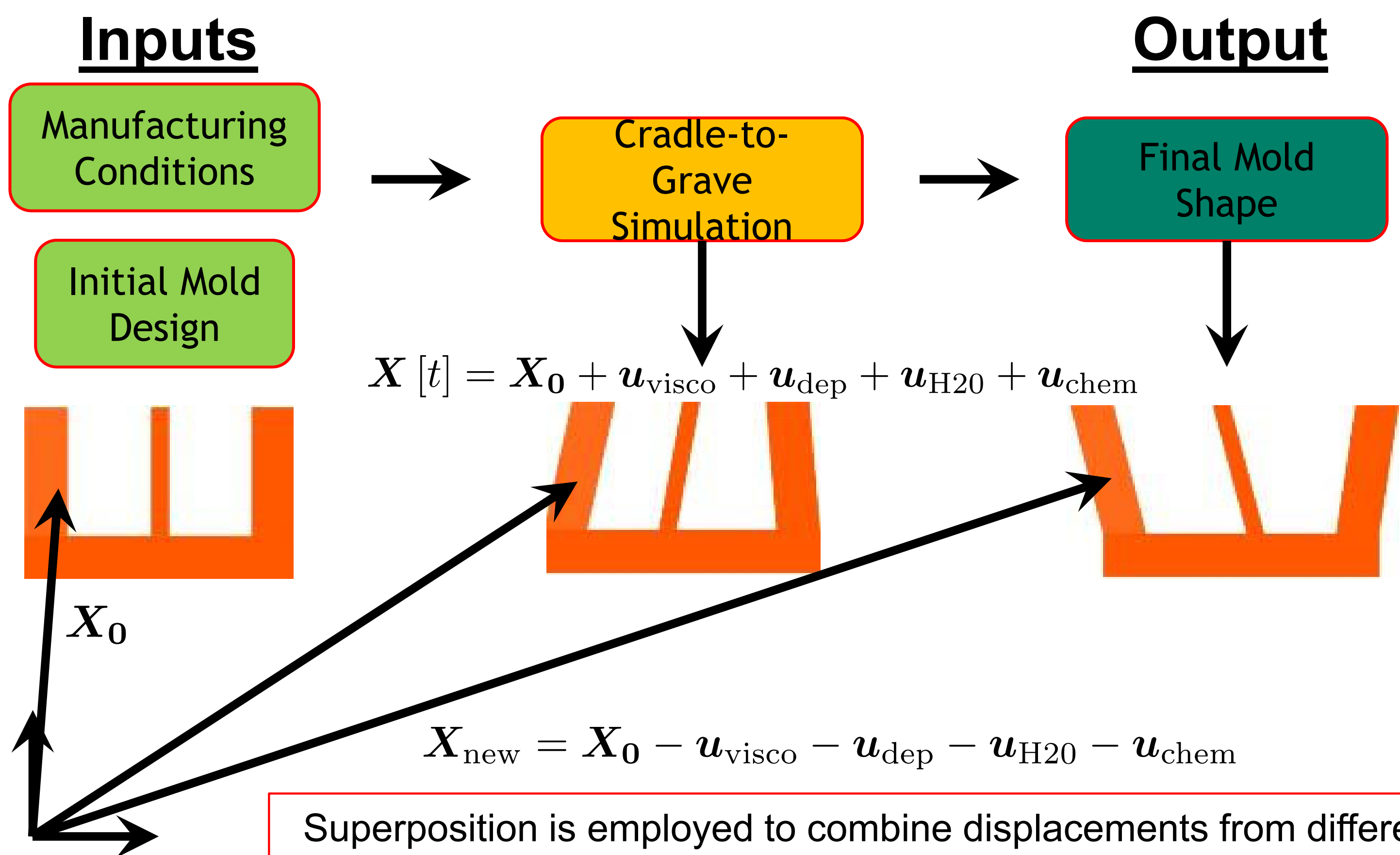
Experiment shows good filling of the shelf feature even at early times giving confidence in the foam model

Develop an engineering-scale model framework for manufacturing and in-service aging for Rigid PMDI Foams



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

A Key Model Target: Inverse mold design for manufacturing/age aware shrinkage mitigation



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

Non-Linear Curing Viscoelastic Solid Modeling

Balance Laws and Solution Fields:

- Mass + Momentum (*Displacements*) ← Lagrangian FEM
- Species Balance (*Chemical Reaction Extent*) ← ALE FEM
- Energy (*Temperature*) ← ALE FEM

Solid State Non-Linear Viscoelastic (NLVE) Model Initial Conditions

- Initialize *temperature, foam density, and reaction extent* from simulation stage 1
- Directly initialize the stress-free reaction and temperature (expansion free)
- Assume the NLVE viscous stresses are initially zero

Stress prediction based on the universal curing model developed at SNL

DB Adolf and RS Chambers, "A thermodynamically consistent, nonlinear viscoelastic approach for modelling thermosets during cure," J. Rheology, 2007.

Cauchy Stress: SNL Non-linear Viscoelastic Curing Model (Adolf & Chambers 2007)

$$\underline{\underline{\sigma}} = \underline{\underline{\sigma}}\left[\log \underline{\underline{U}},\ T,\ x,\ \text{histories}\right]$$

Logarithmic Strain — Temperature — Extent of matrix cure

Material and Laboratory Time Relation

$$dt^* = \frac{dt}{a[t]} \qquad \log a = -\hat{C}_1\left(\frac{N}{\hat{C}_2 + N}\right)$$

Density Scaling

$$\psi[\rho_0] = \left(\frac{\rho_0}{\rho_{ref0}}\right)^p \psi[\rho_{ref0}] \quad \text{Free Energy}$$

$$\underline{\underline{\sigma}}[\rho_0] = \left(\frac{\rho_0}{\rho_{ref0}}\right)^p \underline{\underline{\sigma}}[\rho_{ref0}] \quad \text{Cauchy Stress}$$

Curing NLVE Model Continued

Relaxation behavior and mechanical properties depend on the *temperature, extent of cure, and histories of deformation*

Material Time Dependencies

Thermal

Pressure

$$N=\left\{\left[T(t)-T_{ref}\right]-\int_0^t ds\ f_1\left(t^*-s^*\right)\frac{dT}{ds}(s)\right\}+C_3\left\{I_1(t)_{ref}-\int_0^t ds\ f_1\left(t^*-s^*\right)\frac{dI_1}{ds}(s)\right\}$$

$$+C_4\left\{\int_0^t\int_0^t ds\,du\,f\left(t^*-s^*,t^*-u^*\right)\frac{d\underline{\underline{\varepsilon}}_{dev}(s)}{ds}:\frac{d\underline{\underline{\varepsilon}}_{dev}(u)}{du}\right\}+C_5\left(x(t)\right)\left\{\left[x(t)-x_{ref}\right]-\int_0^t ds\ f_1\left(t^*-s^*\right)\frac{dx}{ds}(s)\right\}$$

Shear Deformation

Matrix Cure

Glass Transition Evolution

$$T_{ref}(x)=T_{ref}-\frac{\left[C_3\beta_\infty+C_5\left(x(t)\right)\right]\left(x(t)-x_{ref}\right)}{\left(1+C_3\alpha_\infty\right)}$$

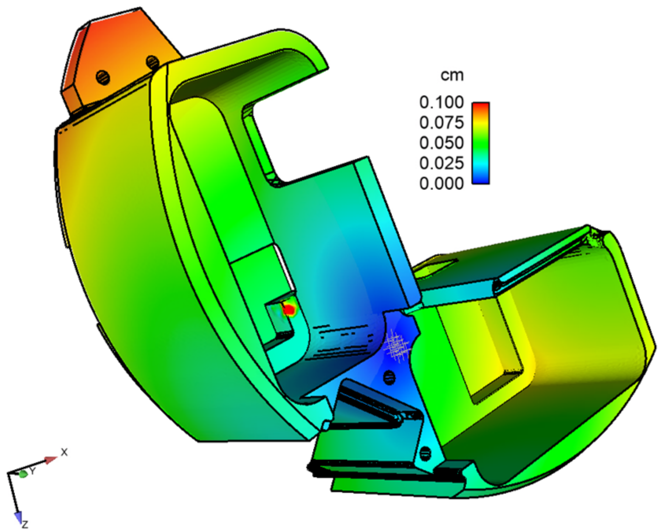
$$C_5\left(x(t)\right)\equiv C_{5a}+C_{5b}\,x$$

Shear Modulus

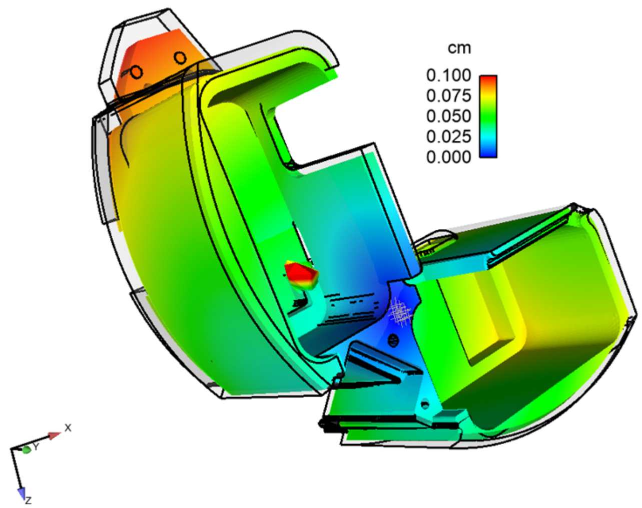
$$G_g(T)=G_{gref}+\frac{\partial G_g}{\partial T}(T-T_{ref})+\frac{\partial G_g}{\partial x}(x-x_{ref})$$

$$G_\infty(T)=\left\{G_{\infty ref}+\frac{\partial G_\infty}{\partial T}(T-T_{ref})\right\}\left[\frac{x^m-x_g^m}{x_{ref}^m-x_g^m}\right]^n$$

Contour Plots of Displacements: Manufacturing + Viscoelasticity

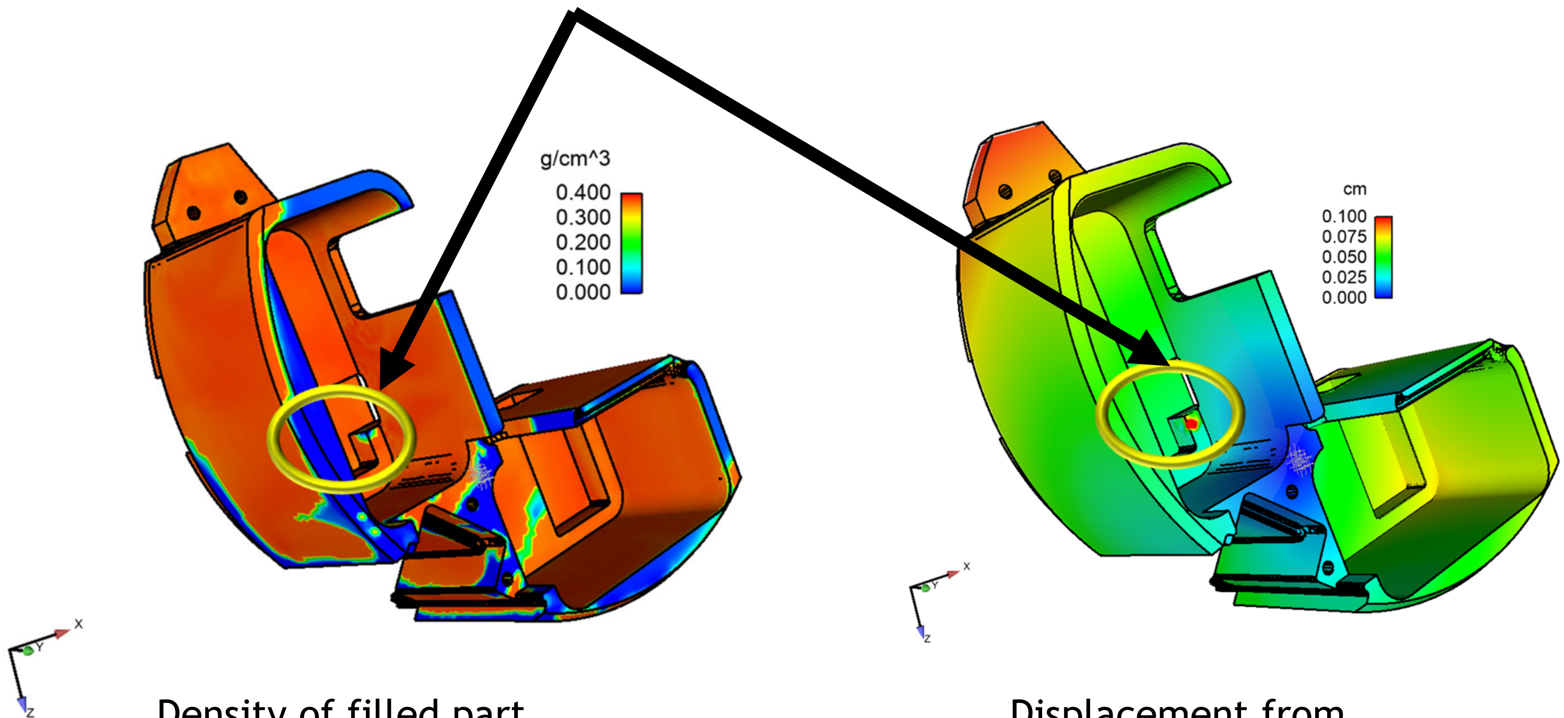


Deformed shape shown to scale



Deformed shape magnified 10x

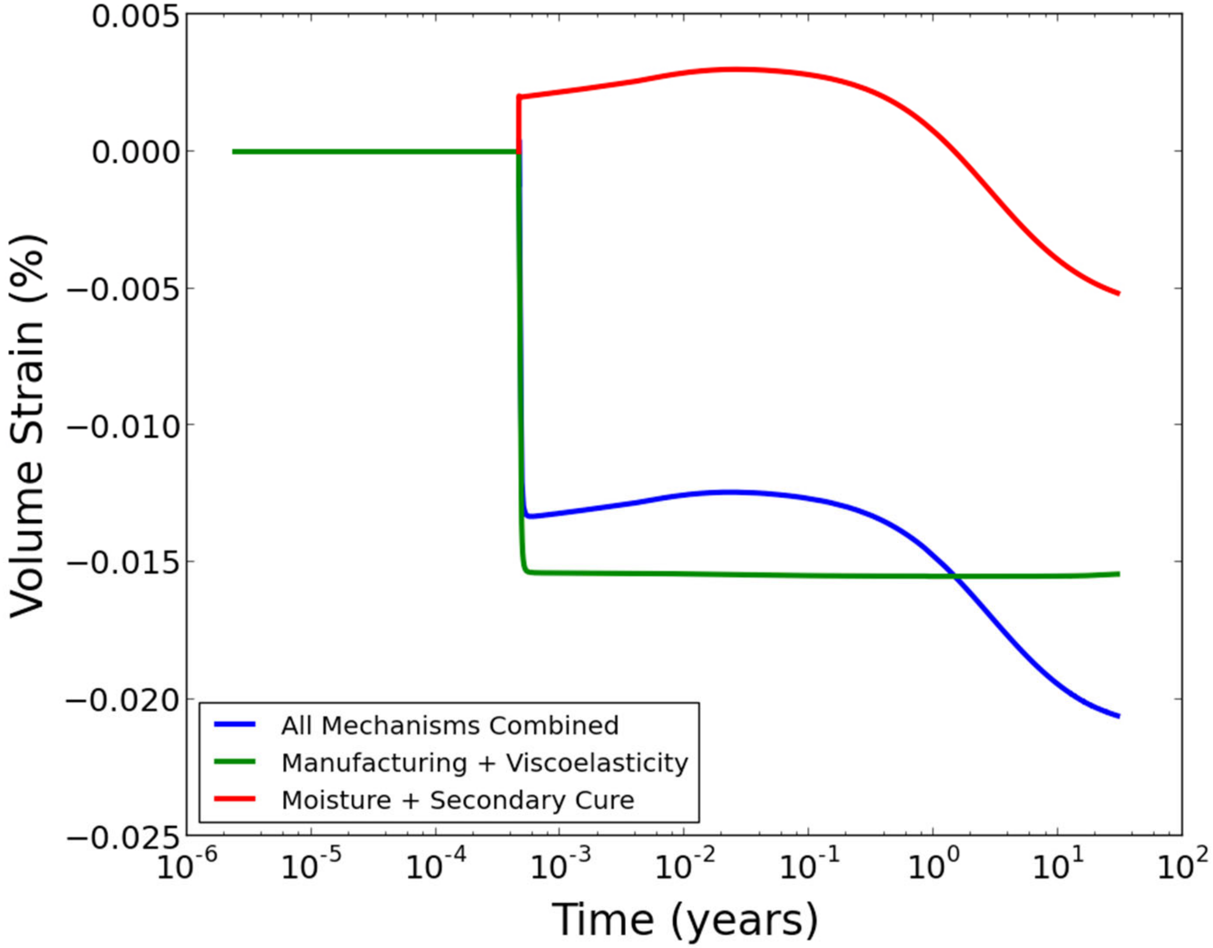
Poor fill quality leads to large, local deformations



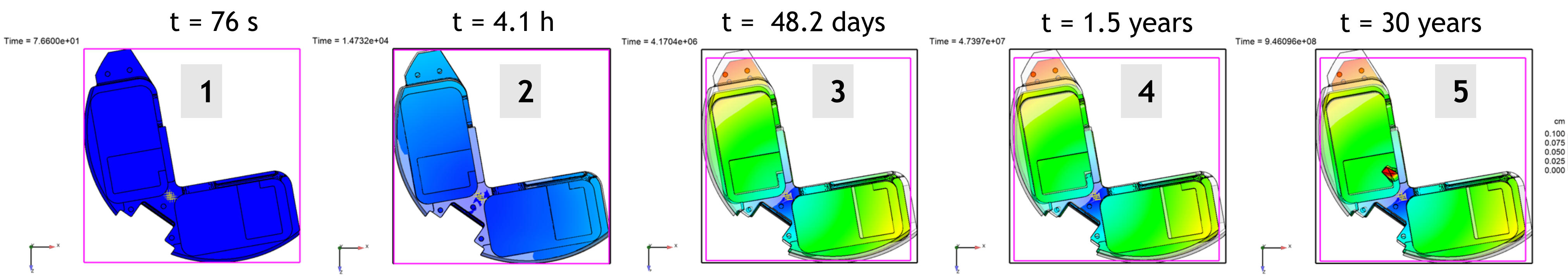
Density of filled part

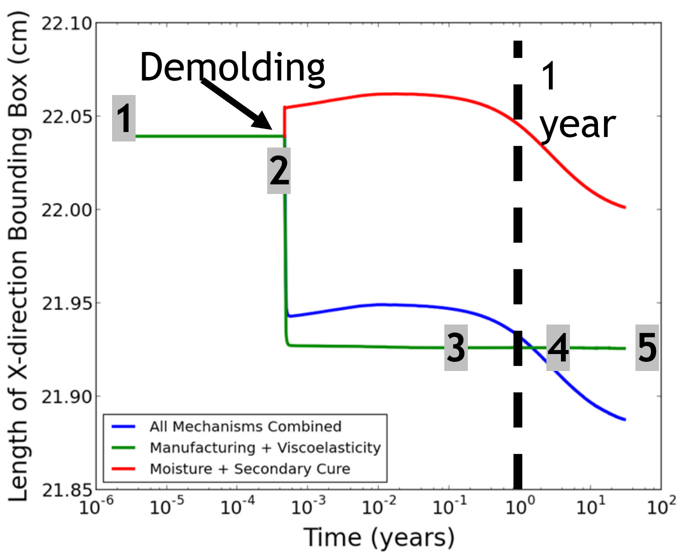
Displacement from Manufacturing + Viscoelasticity, Deformed shape shown to scale

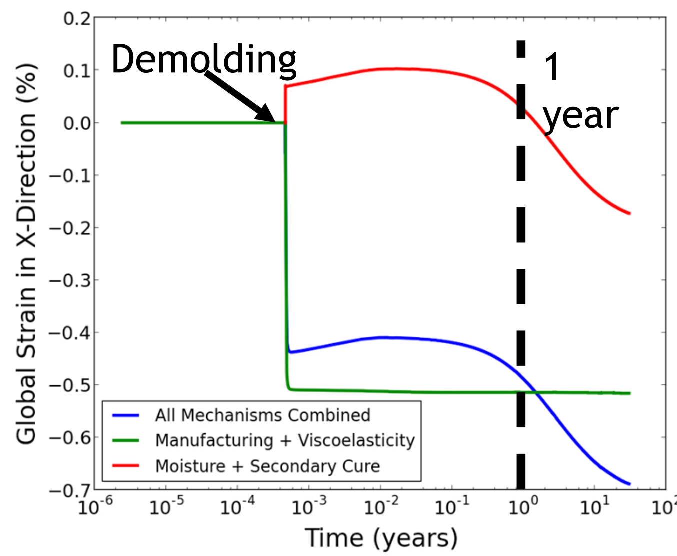
Volume Strain as a Function of Time



Change in Bounding Box Length—X Direction

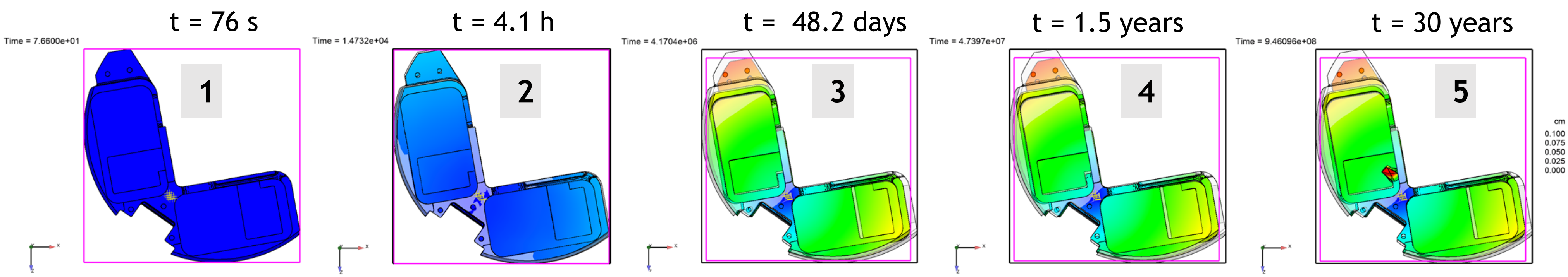


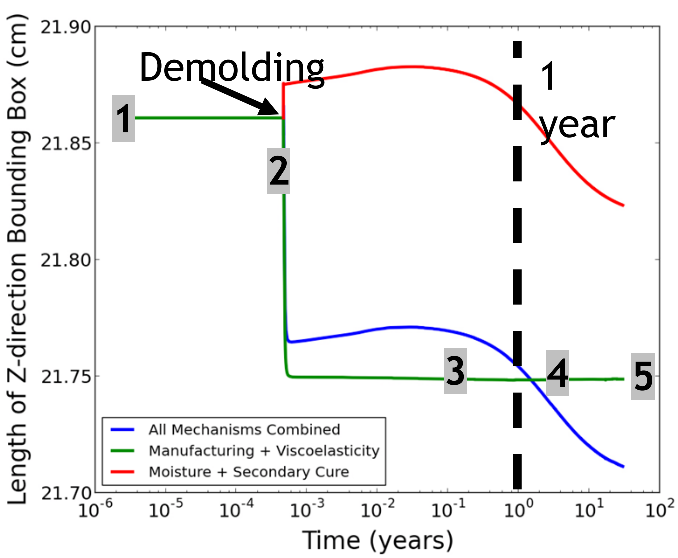


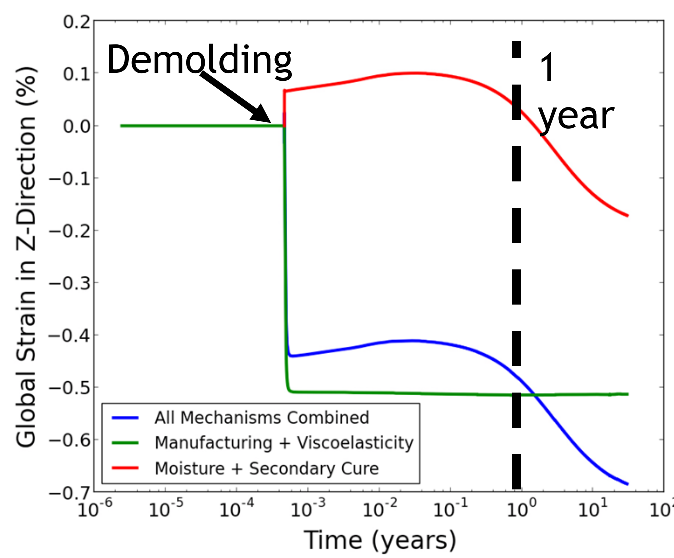


Contours show Manufacturing + Viscoelasticity

Change in Bounding Box Length—Z Direction







Contours show Manufacturing + Viscoelasticity

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
- Multiphysics models allows prediction of shape change during manufacturing and viscoelastic relaxation over 30 years of storage