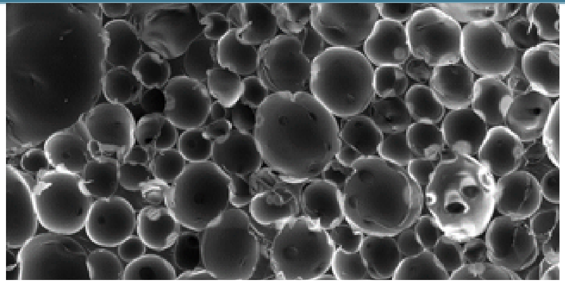
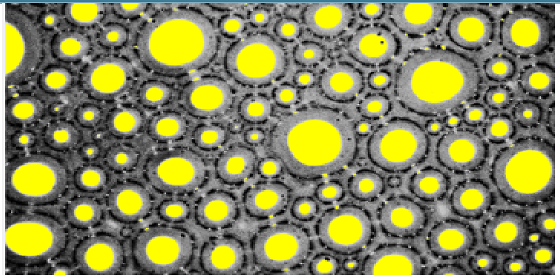
SAND2022-16022C

Sandia National Laboratories

Population Balance Modeling of Foams and Emulsions





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AIChE Annual Meeting 2022

Phoenix, AZ

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U.S. DEPARTMENT OF ENERGY NNSA

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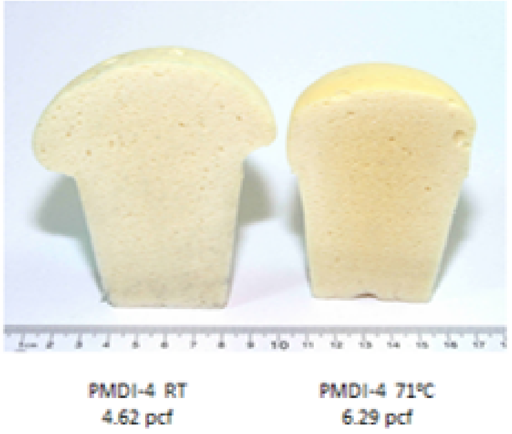
Motivation: Polyurethane Foams

- Polyurethane foams posses a variety of advantageous qualities including, durability, low thermal conductivity, a high strength-to-weight ratio, and are highly customizable
- Can be used to create almost any combination of shape and firmness
- Applications include: Insulation (buildings, electronics, appliances, etc.) and cushioning (vehicles, furniture, etc.)



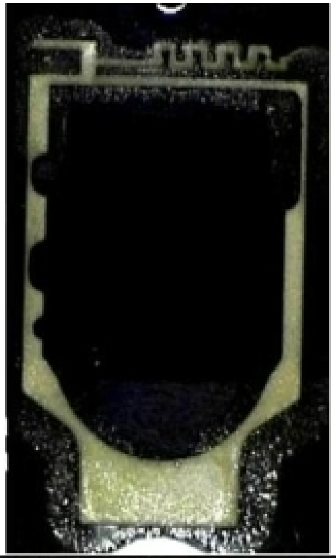
Goal: a computational model to optimize parts manufacturing and predict material properties

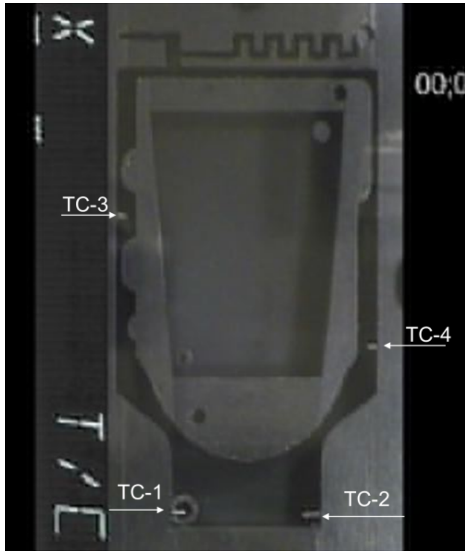
Cradle-to-Grave Model of PMDI Foam

Overarching Goal: **A computational model for foaming, vitrification, curing, 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

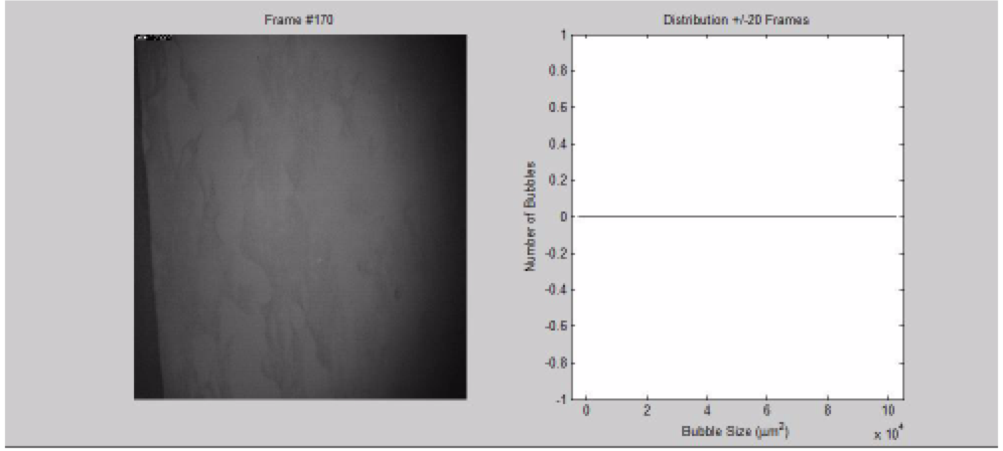




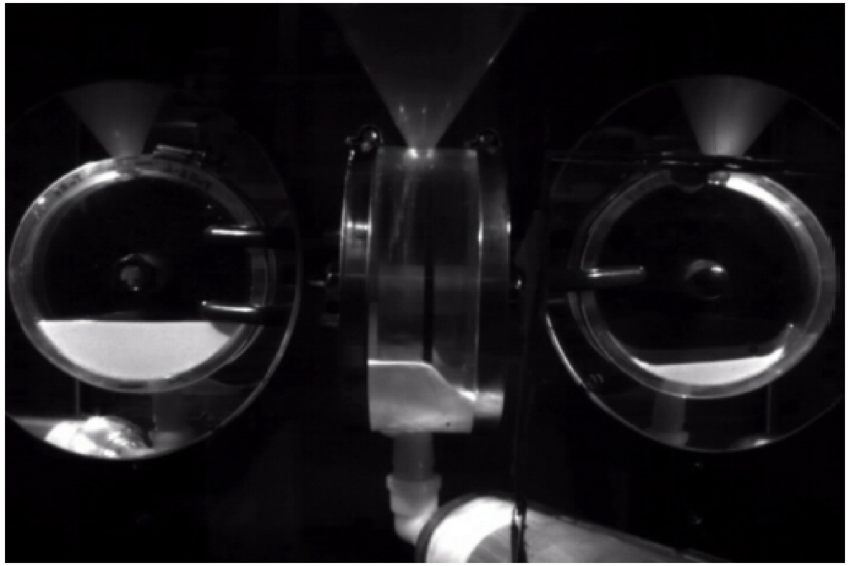
Remove from mold – predict cure and thermal stresses

Predict shape and size over years

Foam Filling is Complex



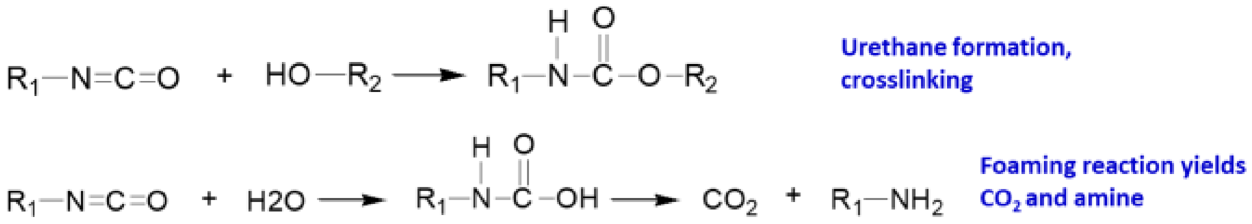
Foam front moving past camera, with bubble sizes at transparent wall determined with image processing.



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



$$R_1-N=C=O + HO-R_2 \rightarrow R_1-NH-C(=O)-O-R_2$$

$$R_1-N=C=O + H2O \rightarrow R_1-NH-C(=O)-OH \rightarrow CO_2 + R_1-NH_2$$

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

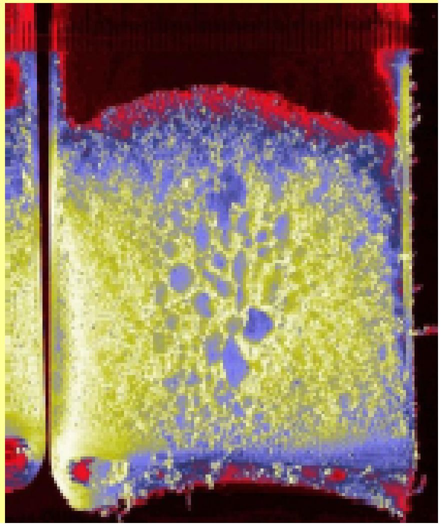
$$\frac{dC_{H_2O}}{dt} = -k_{H_2O} C_{H_2O}^n$$

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

$$C_{H_2O} = \frac{\rho_{foam} x_{H_2O}}{M_{H_2O}}$$

$$C_{CO_2} = \frac{\rho_{foam} x_{CO_2}}{M_{CO_2}}$$

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



NMR imaging shows coarse microstructure (Altobelli, 2006)

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

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

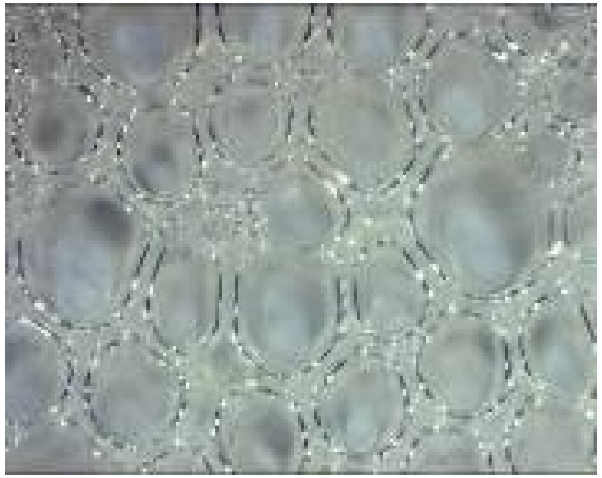
Foaming reaction predicts moles of gas from which we can calculate density

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

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

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

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

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

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

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

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

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

Population Balance Equation (PBE)

A continuity statement written in terms of a number density function (NDF), $n(t, \boldsymbol{x}, \xi)$ [5, 6]

$$\frac{\partial n}{\partial t} + \nabla_{\boldsymbol{x}} \cdot (n(\xi)\boldsymbol{u}_x) + \nabla_\xi \cdot (n(\xi)\boldsymbol{u}_\xi) = h(t, \boldsymbol{x}, \xi)$$

- Considered as a function of time t, physical space **x**, and **phase space** $\boldsymbol{\xi}$

- **Phase space** — a vector of intrinsic properties (e.g. mass, volume, velocity, etc.)

- Processes that impact *n(t, x,* ξ): growth, shrinkage, coalescence (aggregation), breakage, nucleation, evaporation

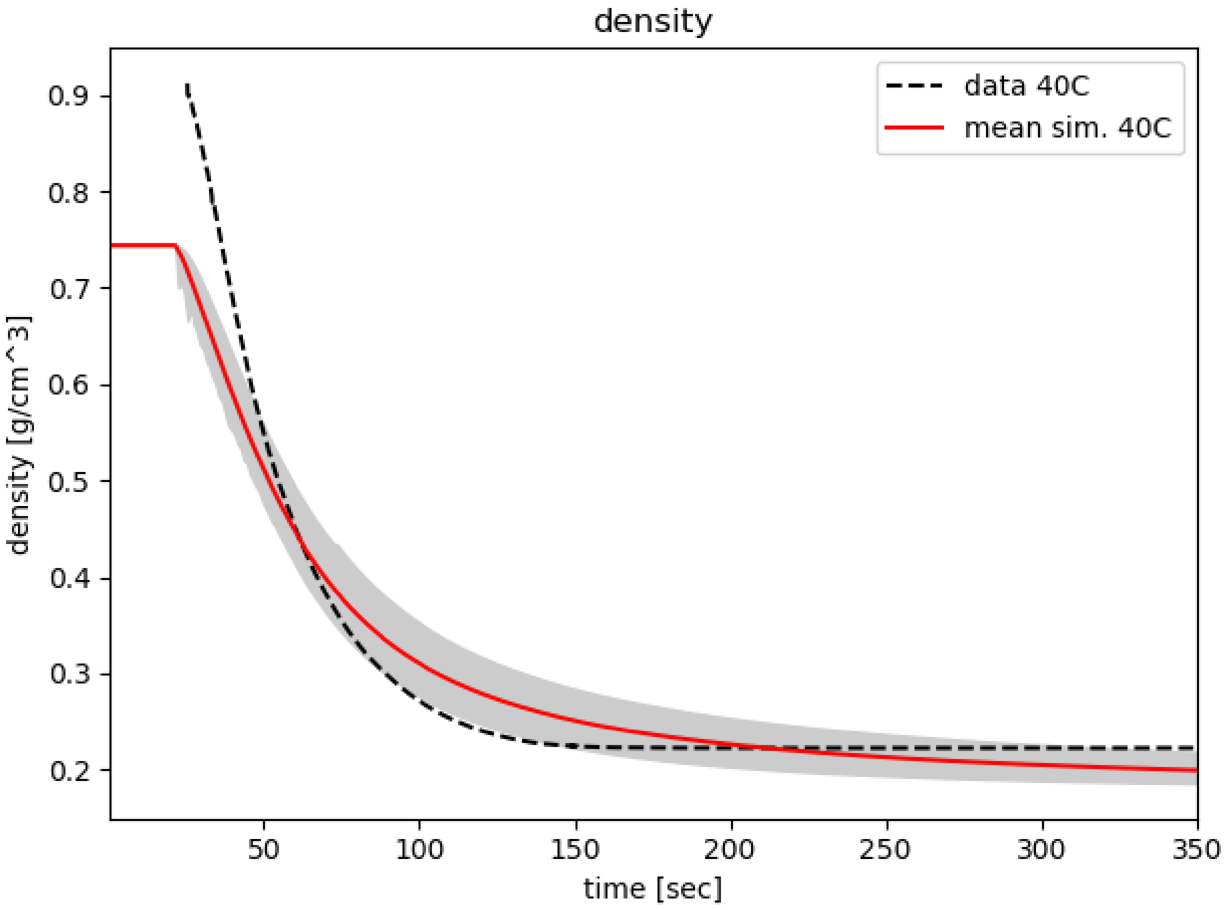
[5]Marchisio, Daniele L., and Rodney O. Fox. *Computational models for polydisperse particulate and multiphase systems*. Cambridge University Press, 2013

[6]Ramkrishna, Doraiswami. *Population balances: Theory and applications to particulate systems in engineering*. Elsevier, 2000.

Previous Work on PBE Modeling of Polyurethane Foam

- [4]Karimi et al baseline population balance equation modeling for polyurethane foams
- [2,3]Rao et al developed a kinetics based model which tracked the curing reaction through extent of reaction
- [1]Ortiz et al added a population balance equation to Rao et al's model to track bubble size, which included coalescence and growth

We build on this work by adding both nucleation and breakage to the population balance equation



[1]Ortiz, Weston, et al. "Population balance modeling of polyurethane foam formation with pressure- dependent growth kernel." AIChE Journal. 2022.

[2] Rao, Rekha, et al. "Density predictions using a finite element/level set model of polyurethane foam expansion and polymerization." Computers & Fluids 2018.

[3] Rao, Rekha, et al. "The kinetics of polyurethane structural foam formation: Foaming and polymerization." AIChE Journal, 2017.

[4]Karimi, Mohsen, and Daniele L. Marchisio. "A baseline model for the simulation of polyurethane foams via the population balance equation" Macromolecular Theory and Sim. 2015.

Included phenomena in PBE

— Model a continuous liquid phase with a gaseous disperse phase (bubbles) which cures over time

— Model **PMDI-10** filling a 3D cylindrical mold

— Phase space property: bubble volume, $\xi = \nu$

Consider the following PBE: $$\frac{\partial n(\nu)}{\partial t} + \nabla \cdot (n(\nu)\boldsymbol{u}) + \frac{\partial}{\partial \nu}\big(n(\nu)G(\nu)\big) = S(\nu, \nu') + \boldsymbol{B}(\boldsymbol{\nu}) + \boldsymbol{J}(\boldsymbol{t})$$

- Bubble size distribution n(ν) — distribution on bubble volume ν
- Growth term G(ν) — how bubbles of volume ν grow
- Coalescence term S(ν, ν') — how bubbles of volume ν and ν' form a bubble of volume $\nu + \nu'$
- **Breakage B(ν) term** — how bubbles of volume ν break
- **Nucleation term J(t)** — how new bubbles appear, separate from previous processes
- Bubble velocity **u** — assumed to be the same as the fluid velocity

Quadrature Method of Moments (QMOM)

Idea: *transform PBE to a discrete set of moment equations, and reconstruct the NDF from the moments*

Moment transformation:[8] $m_k = \int_0^\infty n(v) v^k dv, \quad k = 0, 1, 2, \ldots$

Apply moment transform to PBE: $\frac{\partial m_k}{\partial t} + \boldsymbol{u} \cdot \nabla m_k = k G_k + S_k + B_k + J_k \qquad k = 0, 1, 2, 3$

Physical meaning of key moments: $m_0 - \frac{\#\ bubbles}{liquid\ volume} \qquad m_1 - \frac{total\ bubble\ volume}{liquid\ volume}$

Estimate integrals with quadrature $(\boldsymbol{v}_i, \boldsymbol{\omega}_i)$

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

$$\bar{S}_k = \sum_{i=1}^{N} \sum_{j=1}^{N} \omega_i \omega_j \left[(v_i + v_j)^k - v_i^k - v_j^k \right] \beta_p(v_i, v_j)$$

$$\bar{B}_k = \sum_{i}^{N} \omega_i a(v_i) 2^{1-k} v_i^k - \sum_{i}^{N} \omega_i v_i^k a(v_i)$$

$$\bar{J}_k = 0^k J$$

kernels: rate at which the process takes place

[8]McGraw, Robert. "Description of aerosol dynamics by the quadrature method of moments" Aerosol Science and Technology. 1997.

[9]John V, Angelov I, Öncül A, Thévenin D. “Techniques for the reconstruction of a distribution from a finite number of its moments” Chem Eng Sci. 2007.

[10]Yuan, Cansheng, and Rodney O. Fox. "Conditional quadrature method of moments for kinetic equations" Journal of Computational Physics. 2011.

Kernels for PBE terms

Growth kernel:[1]

$$G_p(v) = C_0\left(\frac{P_{atm}^2}{(P-P_{ref})^2}\right)\frac{\eta_{ref}}{\eta}$$

Coalescence kernel:[4,1]

$$\beta_p(v,v') = \beta_0(v+v')$$

Breakage kernel:[7]

$$a(v) = a_0 v^{\alpha}$$

Fragment distribution : [7]

$$b(v|v') = \begin{cases} 2 & if \;\; v = \frac{v'}{2} \\ 0 & else \end{cases}$$

Nucleation term:

$$J = J_0 \max\left(0, \frac{w_c - w_{max}}{w_{max}}\right)$$

symbol	meaning
C_0	*growth rate constant*
P	*pressure*
P_{atm}	*atmospheric pressure*
P_{ref}	*reference pressure*
η	*viscosity*
η_{ref}	*reference viscosity*
β_0	*coalescence rate constant*
a_0	*breakage rate constant*
α	*breakage exponent*
J_0	*nucleation rate constant*
w_c	*current weight fraction of* CO_2
w_{max}	maximum weight fraction CO_2

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Modeling Polyurethane Foams

System of Equations:

$$\nabla \cdot \boldsymbol{u} = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial t} + \boldsymbol{u} \cdot \rho\right) \quad \text{(conservation of mass)}$$

$$\rho\left(\frac{\partial \boldsymbol{u}}{\partial t} + \boldsymbol{u} \cdot \nabla \boldsymbol{u}\right) = \nabla \cdot T_f + \rho \boldsymbol{g} + f_\Gamma \quad \text{(conservation of momentum)}$$

$$\frac{\partial \xi}{\partial t} + \boldsymbol{u} \nabla \xi - D_\xi \nabla^2 \xi = k(b + \xi^m)(1-\xi)^n \quad \text{(extent of reaction)}$$

$$\rho C_p\left(\frac{\partial T}{\partial t} + \boldsymbol{u} \cdot \nabla T\right) - \nabla \cdot \lambda \nabla T = \Delta H_{rxn} Y \rho \frac{\partial \xi}{\partial t} \quad \text{(conservation of energy)}$$

$$\frac{\partial C_{H_2O}}{\partial t} + \boldsymbol{u} \cdot \nabla C_{H_2O} - D_{H_2O} \nabla^2 C_{H_2O} = - k_{H_2O} C_{H_2O}^p$$

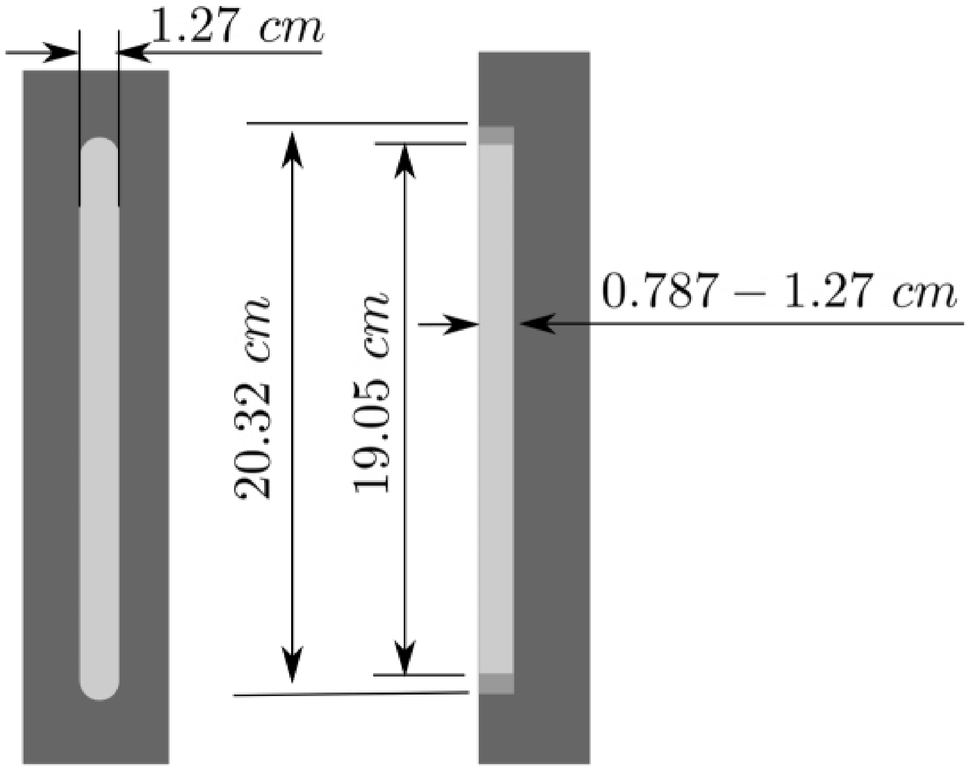
$$\frac{\partial C_{CO_2}^{liq}}{\partial t} + \boldsymbol{u} \cdot \nabla C_{CO_2}^{liq} - D_{CO_2}^{liq} \nabla^2 C_{CO_2}^{liq} = k_{H_2O} C_{H_2O}^p - \overline{G_1} \frac{P}{RT}$$

$$\frac{\partial C_{CO_2}^{gas}}{\partial t} + \boldsymbol{u} \cdot \nabla C_{CO_2}^{gas} - D_{CO_2}^{gas} \nabla^2 C_{CO_2}^{gas} = \overline{G_1} \frac{P}{RT} \quad \text{(conservation chemical species)}$$

symbol	meaning
ρ	*density*
$\boldsymbol{u}$	*mass-average fluid velocity*
T_f	*stress tensor*
f_Γ	*surface tension*
ξ	*extent of reaction*
k	*rate constant*
D_i	*diffusion coefficient for variable i*
b, m, n, p	*fitting parameters*
λ	*thermal conductivity*
T	*temperature*
Y	*liquid mass fraction*
H_{rxn}	*heat of reaction*
C_i	*concentration of variable i*
P	*pressure*
R	*universal gas constant*
$\overline{G_1}$	*growth of moment 1*

Summary of Numerical Methods

- Implemented in the open-source software Goma
- Arbitrary Lagrangian-Eulerian
- Implicit Euler time integration (except moment source)
- PBE solved via quadrature method of moments (QMOM)
- Nodes and weights found using the Adaptive Wheeler Algorithm[9]
- For *N*-node quadrature we only need 2*N* moment
- Initialize moments assuming log-normal NDF



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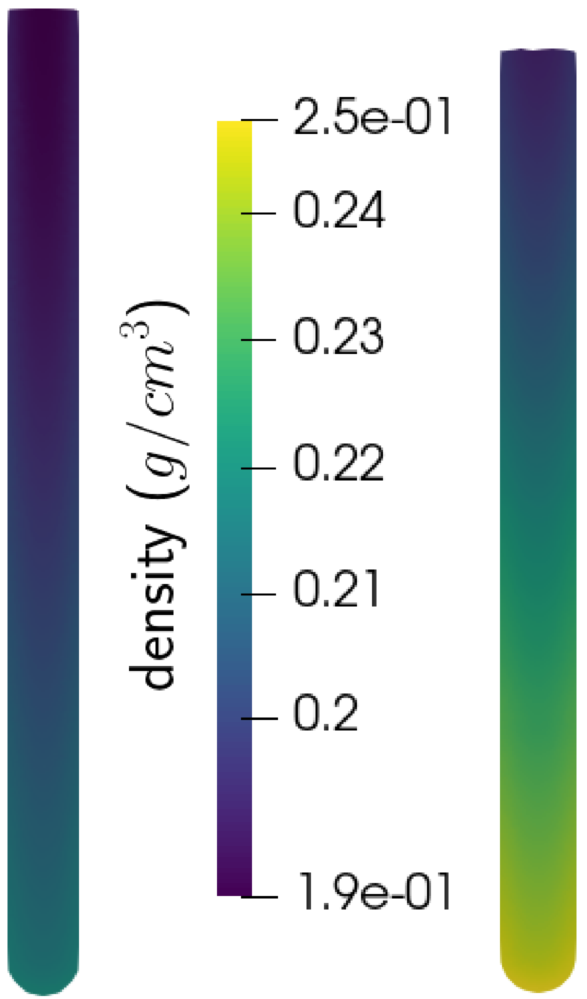
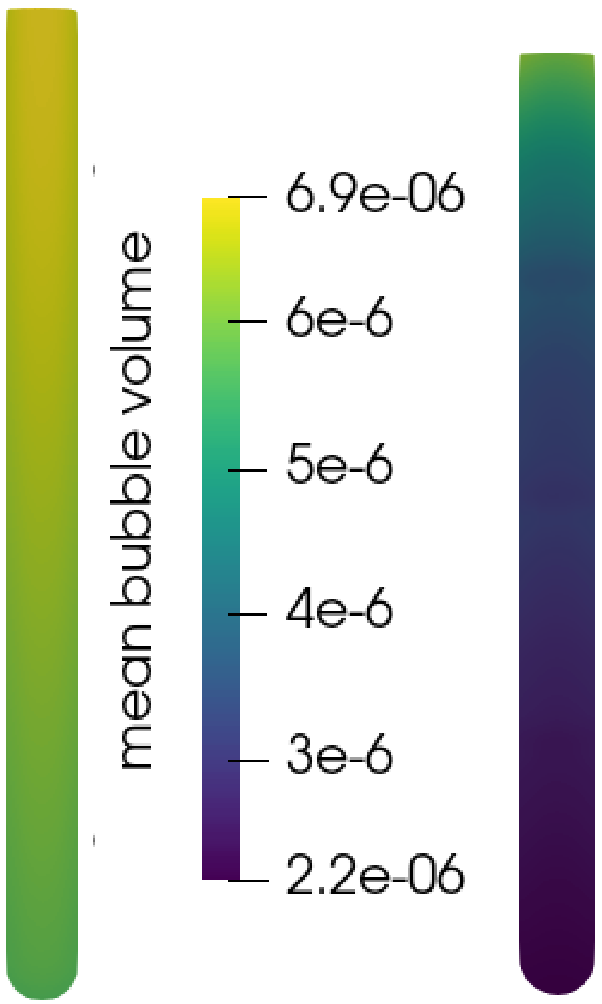
Results: bar at final time

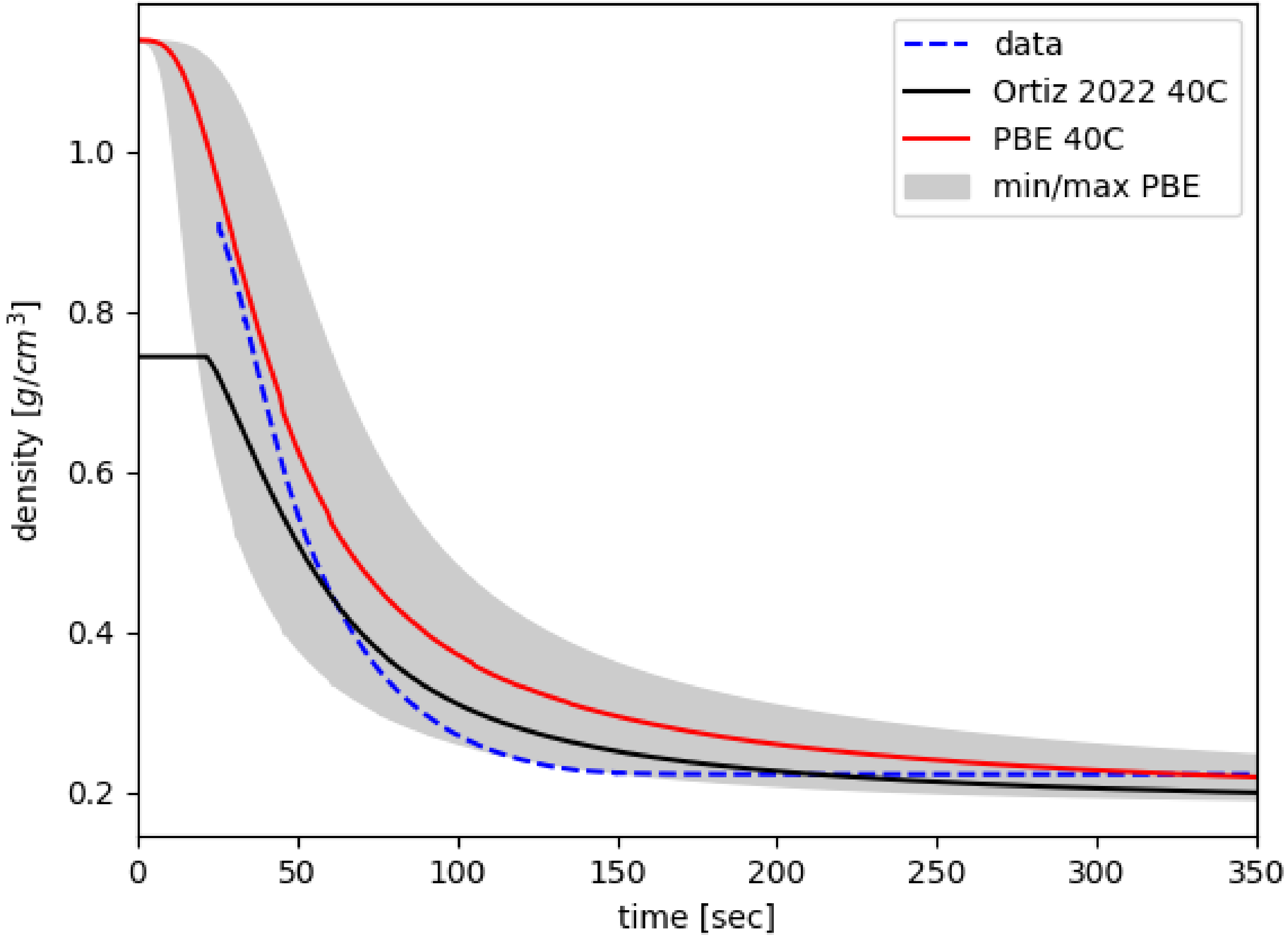
Left: Ortiz 2022 40C
Right: PBE 40C



Left: Ortiz 2022 40C
Right: PBE 40C



Results Continued

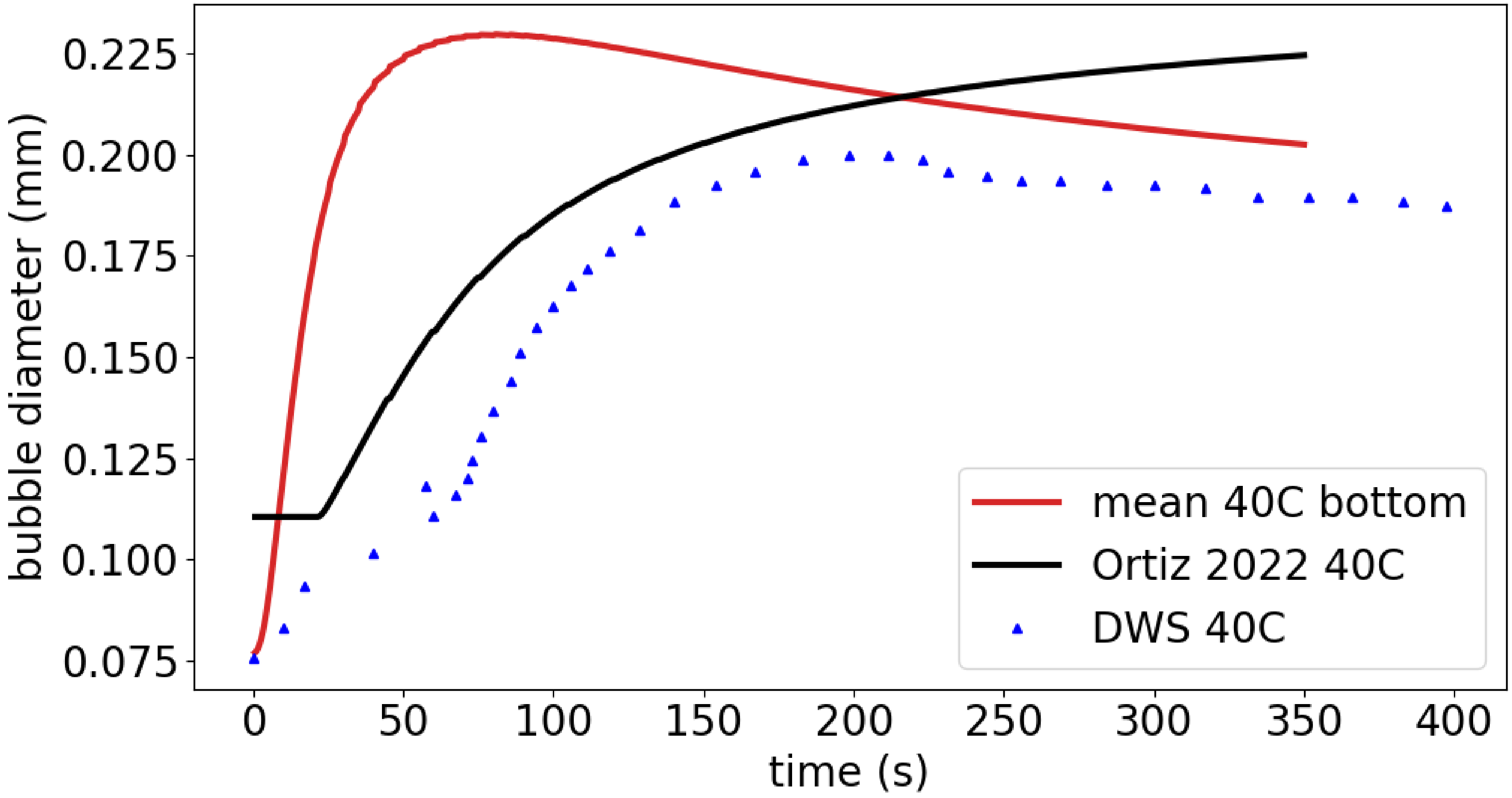


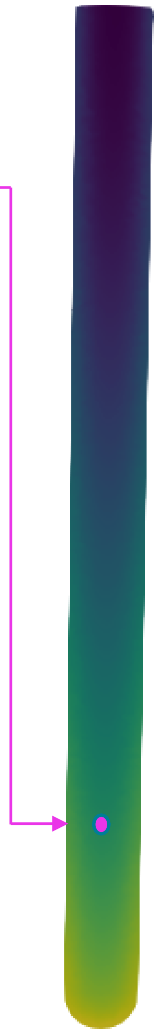
- Capturing early density well and producing similar shape to Ortiz 2022

Results Continued

DWS: Diffusion Wave Spectroscopy

Bottom: 2.5cm from base of mold





Summary and Future Work

Summary:

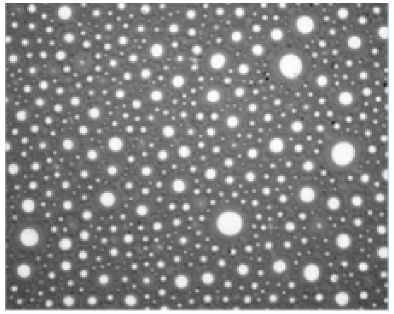
- Added nucleation and breakage to kinetics model with population balance modeling
- Obtaining a better picture of the underlying microstructure

Future work:

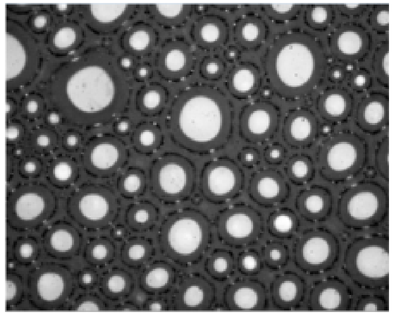
- Continue to modify and improve kernels
- Apply population balance model to **coarsening data**
- Working to implement this framework for polymer upcycling

Bubble coarsening :

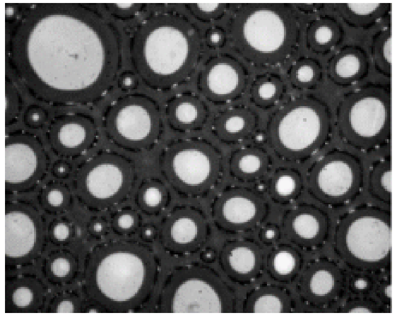
0 minutes



30 minutes



60 minutes



Works Cited

Texts:

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Images/photos:

US Korea Hotlink

https://www.buildinggreen.com/blog/epa-raises-health-concerns-spray-foam-insulation

PU Vacuum Foaming Molds | Refrigerator Door, Cabinet

Karimi, Mohsen, H. Droghetti, and Daniele L. Marchisio. "PUFoam: A novel open-source CFD solver for the simulation of polyurethane foams." Computer Physics Communications 217 (2017): 138-148.