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Experimental Characterization of Polyurethane Foam Processing

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PROBLEM

- Polyurethane (PU) foam is used as an encapsulant and structural support for components, to mitigate against shock and vibration.
- PU foam starts as a two-part liquid kit (resin & curative), that once mixed reacts to produce gas and polymerize to a solid.
- PU has a short pot life and can cure quickly, freezing in defects.
- We are developing a computational model to help us understand foam expansion for manufacturing applications.
- Challenges to develop the model and populate parameters include complex, multiphase materials with ongoing chemical reactions.
- Solve momentum, energy, and mass balances. Rate of polymerization (blue) drives heat generation, affects rheology, and rate of gas formation determines density ρ and also affects rheology. Parameters (red) must be determined.

$$\rho\frac{\partial \mathbf{v}}{\partial t} = -\rho\mathbf{v}\bullet\nabla\mathbf{v} - \nabla p + \nabla\bullet(\eta_f(\nabla\mathbf{v}+\nabla\mathbf{v}')) - \nabla\bullet\lambda(\nabla\bullet\mathbf{v})I + \rho\mathbf{g}$$

From foaming kinetics

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

Rate of polymerization reaction

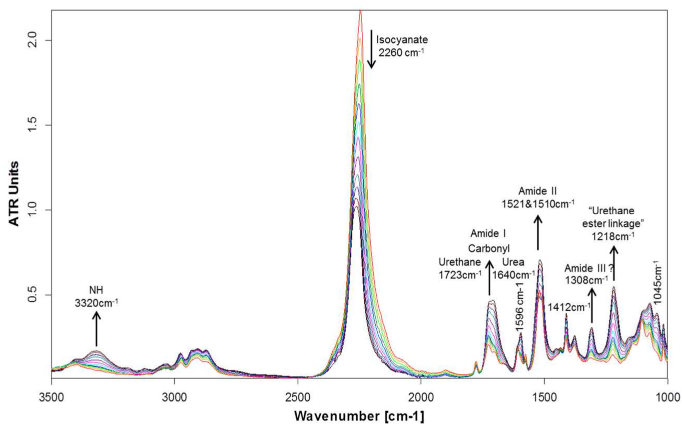
$$\nabla\bullet\mathbf{v} = -\frac{1}{\rho}\left(\frac{\partial\rho}{\partial t} + \mathbf{v}\bullet\nabla\rho\right)$$

MODEL REQUIRES REACTION KINETICS

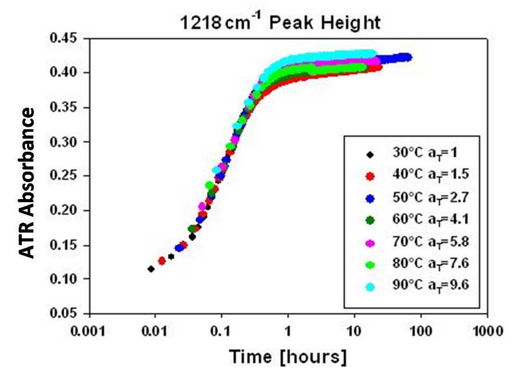
- We use IR spectroscopy to track reaction rates in several isothermal experiments at different temperatures to understand polymerization.

$$\frac{d\xi}{dt} = k_0 e^{\Delta E/RT}(1-\xi)^q(A+\xi^p)$$

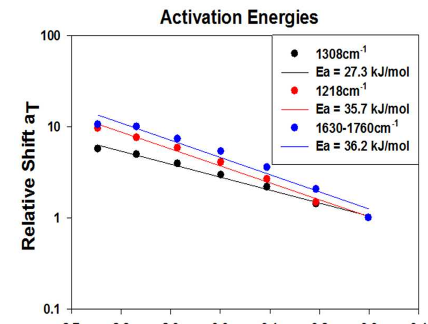
IR data leads to an equation for extent of reaction



IR-spectra at various times showing the isocyanate peak decreasing as the urethane band and others increase

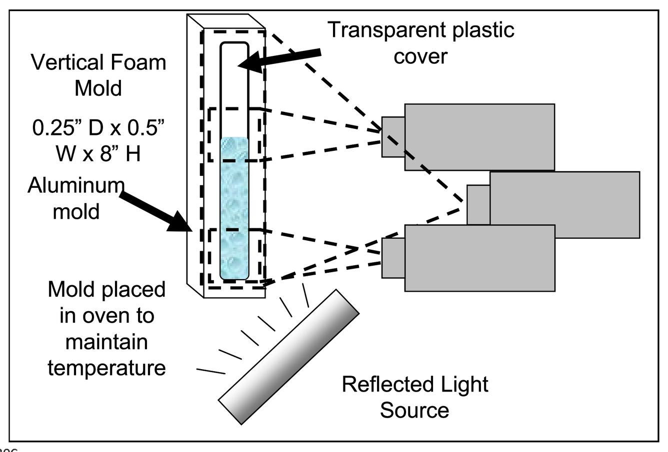


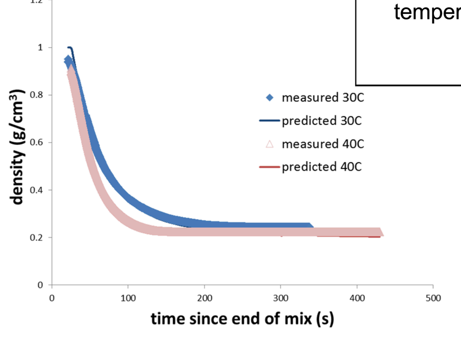
Typical shifted plot for PMDI-10 structural foam, with shift factors a_T noted.



Activation energies as predicted by three IR peaks.

- Gas generation measured by free rise height and foam temperature and pressure since IR does not provide a clear signal for the foaming reaction.





$$\frac{d\alpha}{dt} = \frac{Nk(1-\alpha)^n}{(1-\alpha)^m + M}$$

$$k = A_1\exp(-E_1/RT)$$

$$M = A_2\exp(-E_2/RT)$$

$$N = 0.5\,(1+\tanh\,(t-t_{nucleation}))$$

$$\phi(t) = \frac{n_{CO_2}MW_{CO_2}/\rho_{CO_2}}{n_{CO_2}MW_{CO_2}/\rho_{CO_2} + V_{liquid}}$$

$$\rho_{foam} = (\rho_{CO_2} - \rho_{liquid})\phi(t) + \rho_{liquid}$$

Kinetics for gas generation reaction leads to density prediction. Time to nucleate needed.

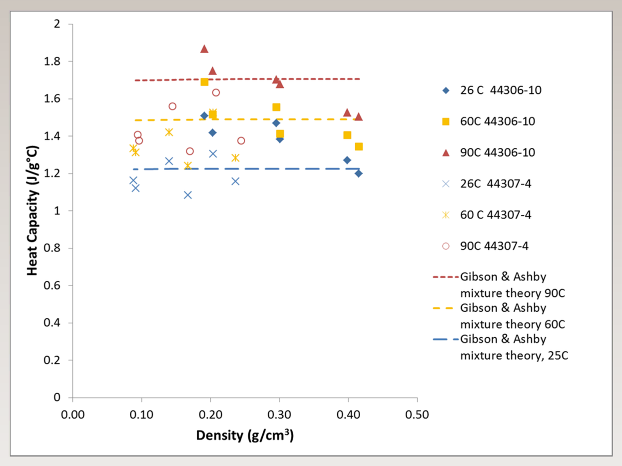
EXPERIMENTS FOR MATERIAL PARAMETERS

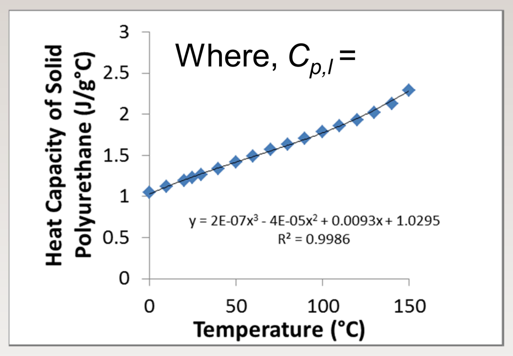
- Thermal properties

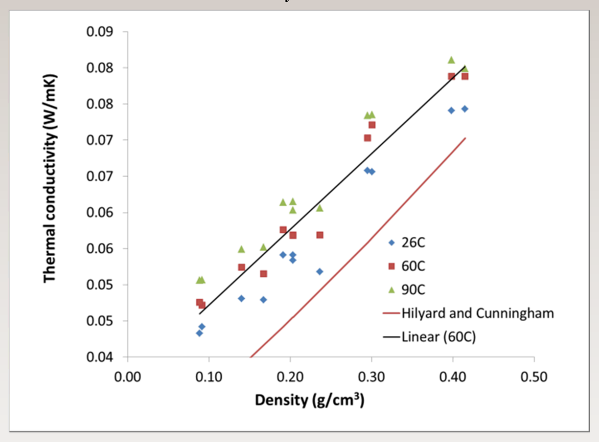
$$C_p = \frac{\hat{c}_{p,l}\rho_l(1-\phi_g) + \hat{c}_{p,g}\rho_g\phi_g}{\rho}$$

$$\phi_g = (\rho_{foam} - \rho_l)/(\rho_g - \rho_l)$$

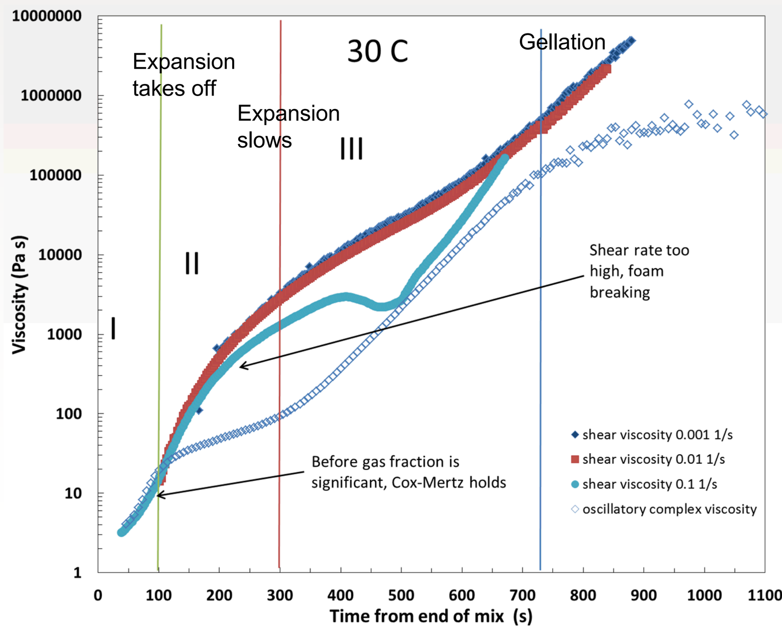
$$k = \frac{\phi_g^{2/3}k_g + k_l\left(1-\phi_g^{2/3}\right)}{\left(\phi_g^{2/3}-\phi_g\right)\frac{k_g}{k_l} + \left(1-\phi_g^{2/3}+\phi_g\right)} + k_r$$





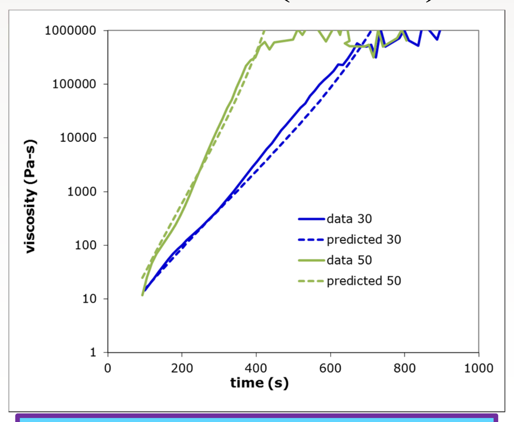


- Rheology is complex

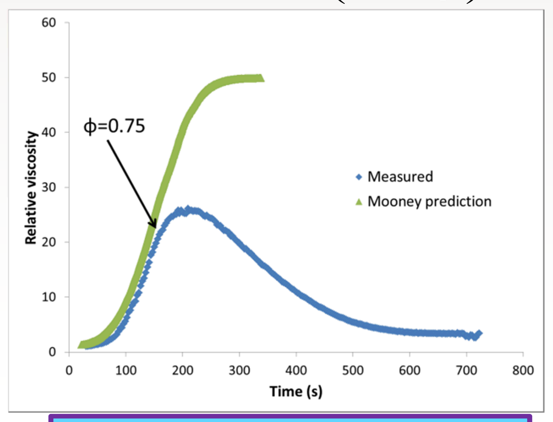


$$\eta = \eta_0\, e^{E_a/RT}\left(\frac{p_c^z - p^z}{p_c^z}\right)^{-x}$$

$$\eta_\phi = \eta_{polymer}\exp\left(\frac{\phi_g}{1-\phi_g}\right)$$



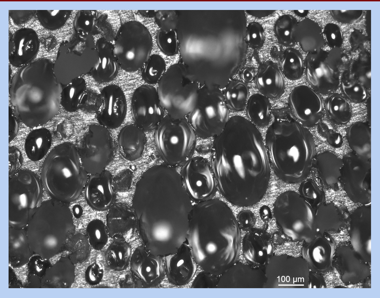
Continuous phase rheology estimated from dried (nonfoaming) material

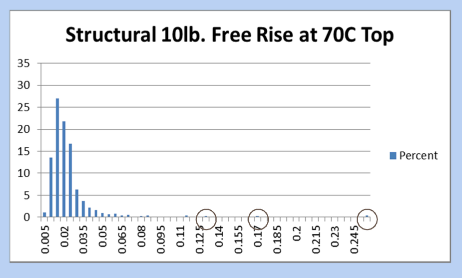


For $\varphi_g > 0.75$ estimate $\eta_{foam} = \eta_{cure} * f(\xi)$

EXPERIMENTS ON EVOLVING MICROSTRUCTURE

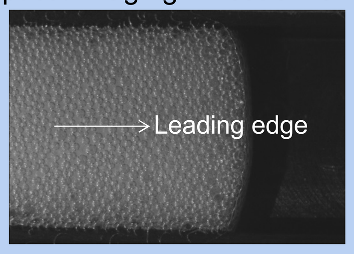
- Will allow higher fidelity models to understand the formation of density gradients, cure stresses, and the link of manufacturing processes to foam stability and aging.



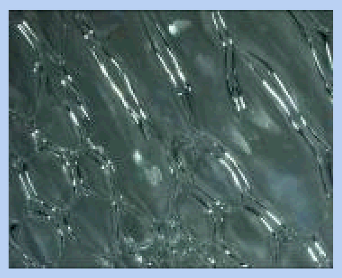


SEM **post test**: Good detail for small bubbles , can be far from walls

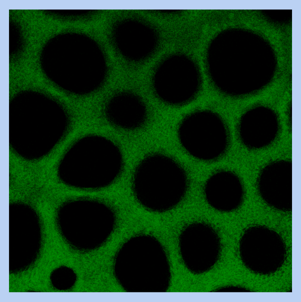
Optical imaging in **real time**



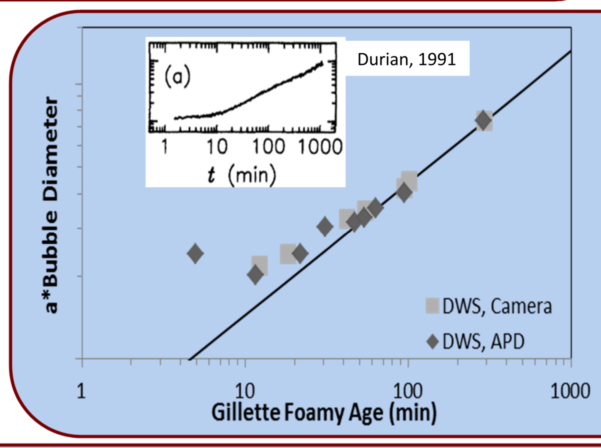
Limitation: only near a wall

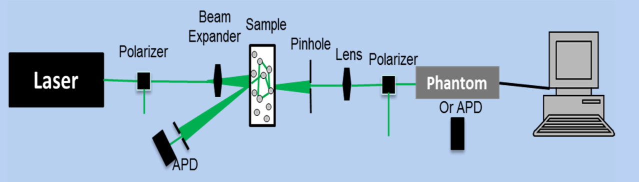


Cell elongation near a wall

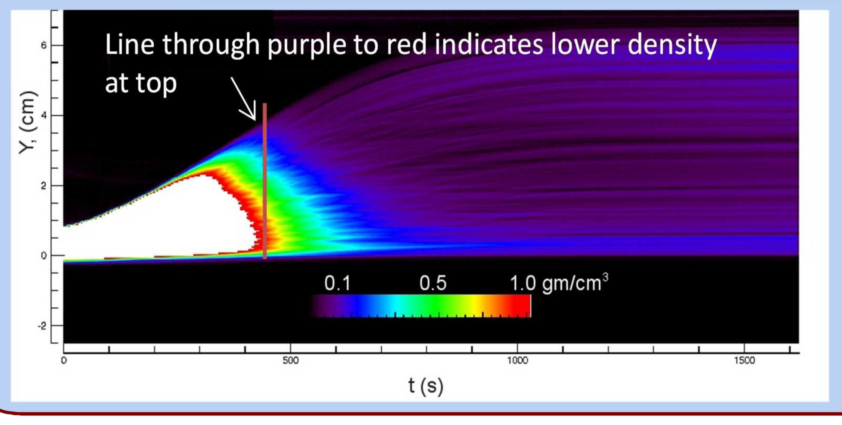


- Confocal microscopy in **real time**
  - Bubble size and shape evolution with time can be determined but only fairly near a surface
  - Better than optical imaging for the small bubble sizes in polyurethane (about 100 µm)





- Diffusing wave spectroscopy (DWS)
  - Average bubble size through a thickness in **real time**
  - DWS replicates literature values (Durian, 1991) of bubble size growth due to diffusion and coalescence as first test of technique. Confocal used to calibrate.



- 1-D NMR Imaging in **real time**
  - Foam seeded with small particles that give a signal, so signal strength proportional to density
  - Time sequence: the height of the colored zone indicates the foam height, and a vertical line at any one time with a color gradient indicates a density gradient.

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