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Experiments to Estimate Polyurethane Foam Reaction Kinetics

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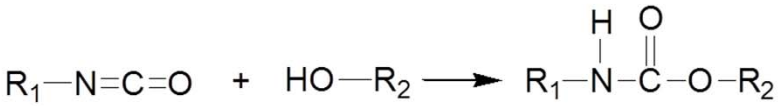
Polyurethane (PMDI): Model Development

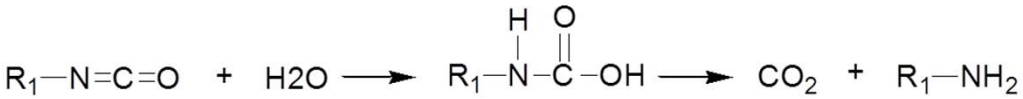
- PMDI is used as an encapsulant for electronic components, to mitigate against shock and vibration
- We would like to develop a computational model to help us understand foam expansion for manufacturing applications.
- Exothermic reactions lead to competing physics: heat decreases viscosity initially but expands bubbles and increases reaction rates leading to higher viscosity.

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

Two key reactions: Isocyanate reaction with polyols and water

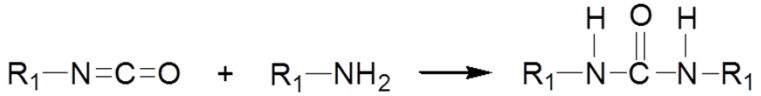


Urethane formation, crosslinking

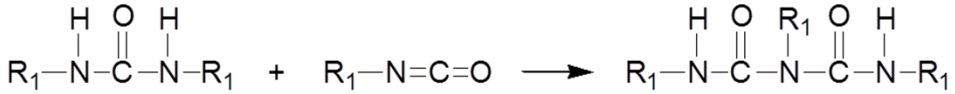


Foaming reaction yields CO_2 and amine

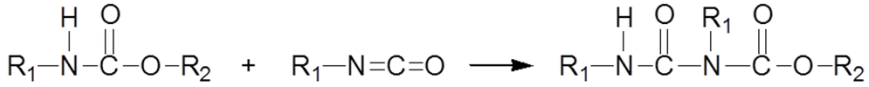
Various follow up reactions: Isocyanate reaction with amine, urea and urethane



Urea formation



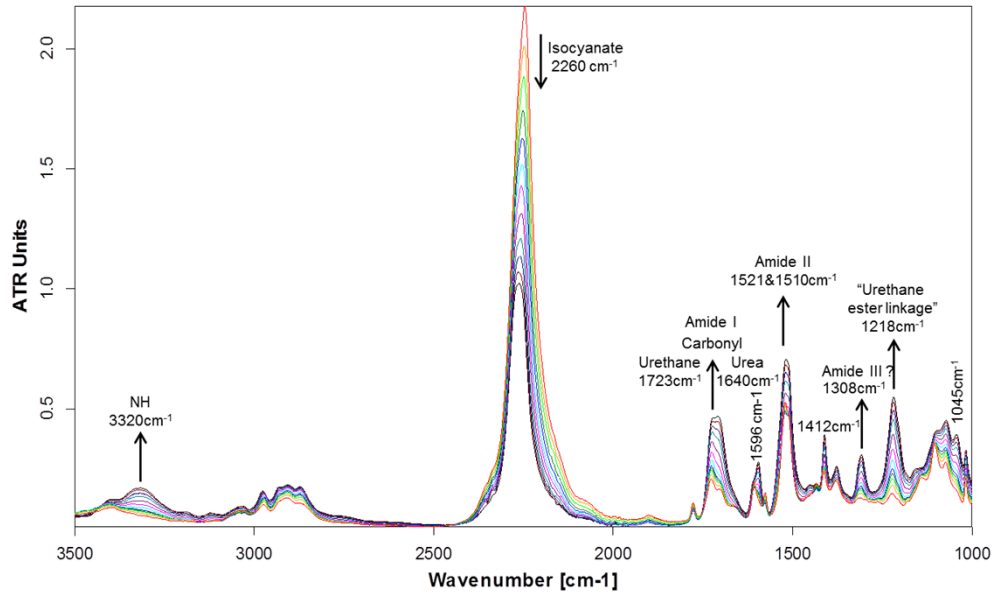
Biuret formation



Allophanate formation

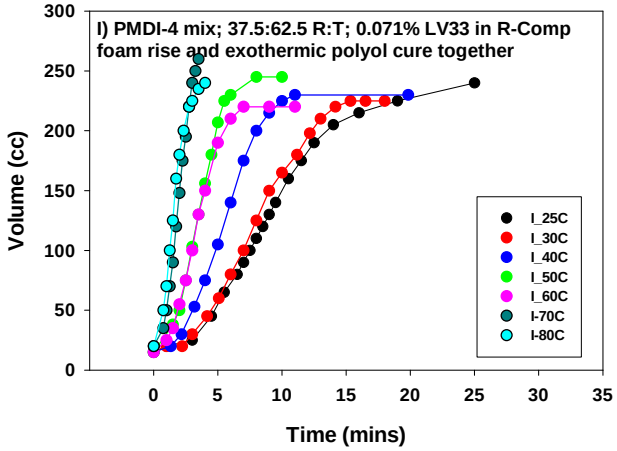
Can We Separate the Effects of Curing and Foaming?

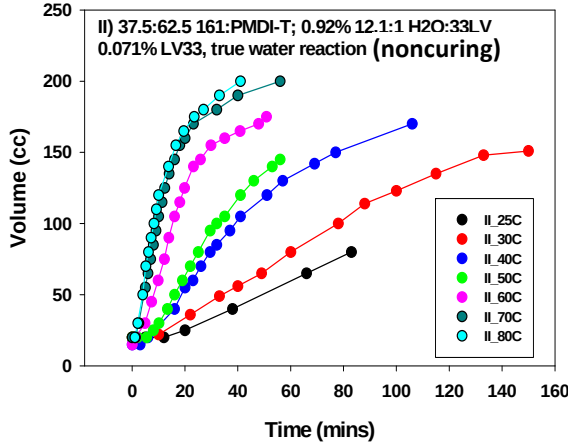
- Use IR to monitor polyol-isocyanate urethane reactions in both wet and dry polyurethane
  - "Wet" vs. "dry" slightly different rates of cure



- Micro-attenuated total reflection (ATR) infrared spectroscopy (IR) measurements
- Urethane ester linkage (1218cm^{-1}) and carbonyl (1700 cm^{-1} range) are great indicators of cure kinetics.

- No IR peak indicates foaming reaction, so measure the volume generated
  - Compare curing pMDI-4 foam with noncuring model foam system (epoxy carrier with similar viscosity)
  - Curing system foams faster: extra heat (reaction synergism)

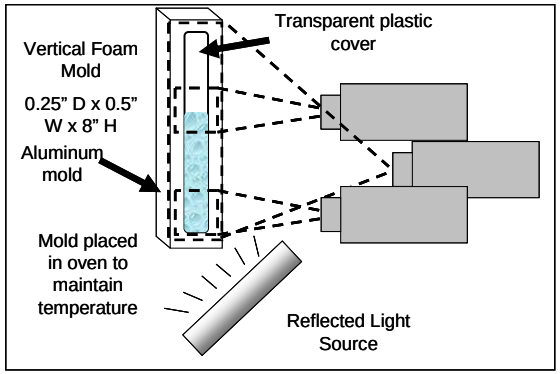


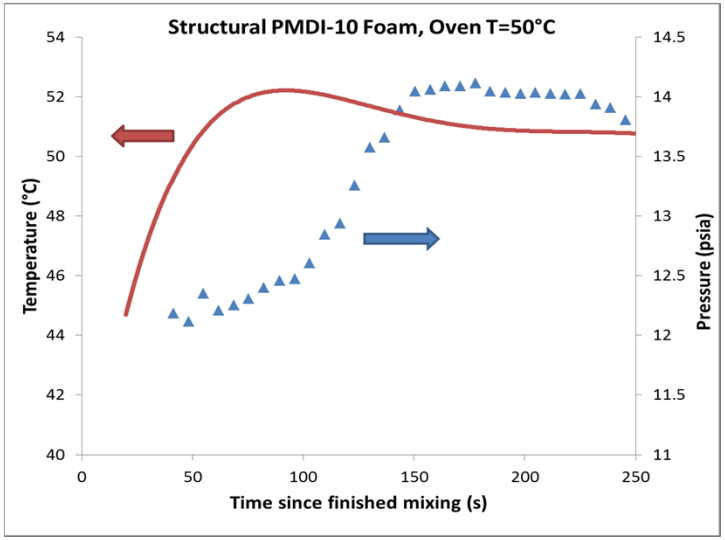


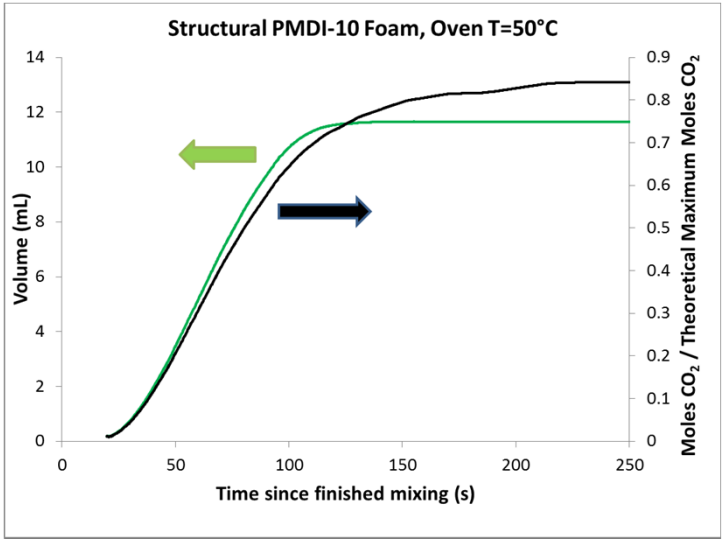
- Foaming slows in curing system at about 15 min (30C)
- Foaming slows in noncuring system at about 140 min (30C)

Measure P, V, T in Simple Geometry to Quantify Foaming Reaction in Curing System

- We can only measure after injection, but reaction is occurring during mixing and injection, but bubbles are being destroyed in these processes, too.
- Pressure continues to rise after foam has stopped expanding.
- Implies CO_2 reaction progressing after foam viscosity restricts expansion.
- The foam cannot be preheated, so during the foam rise the temperature is not steady.
- CO_2 loss from bubble breakage at top surface?

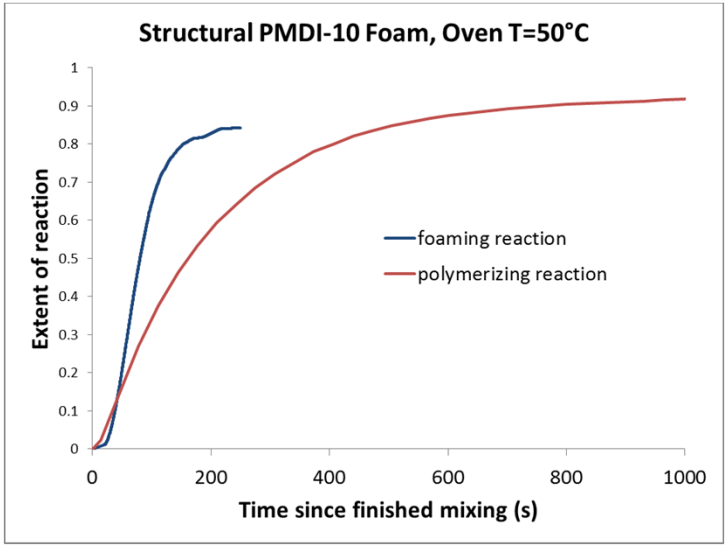






Polymerization Continues After Foaming Complete

- Comparing to IR, we see that polymerizing reaction is slower than foaming reaction
- Model by decoupling reactions assuming isocyanate is in excess during foaming
- Track two extent of reactions with time
- Assume heat of reaction primarily from polymerization
- Extent of foaming reaction gives foam density with time



ξ is the extent of polymerization reaction

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

$$S_{rxn} = \Delta H_{rxn}\rho\frac{d\xi}{dt}$$

α is the extent of reaction generating CO_2

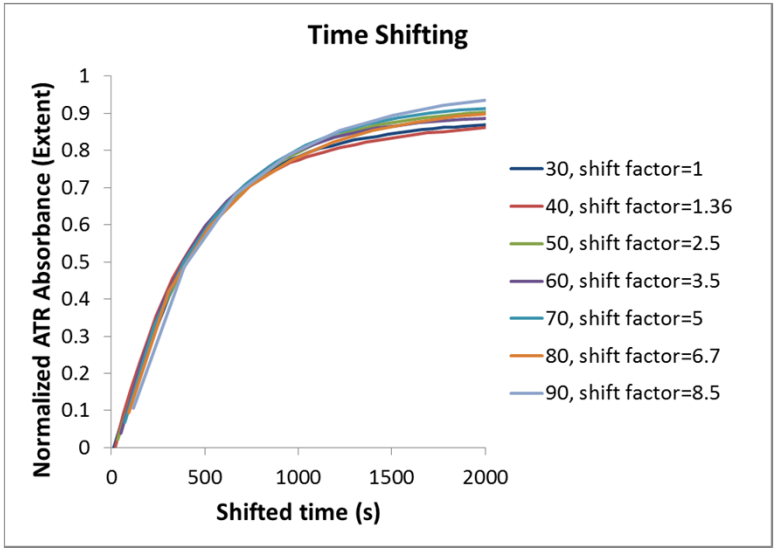
$$\frac{d\alpha}{dt} = \frac{k(1-\alpha)^n}{(1-\alpha)^m + M} \quad \text{where} \quad k = A_1 \exp(-E_1/RT), \quad M = A_2 \exp(-E_2/RT)$$

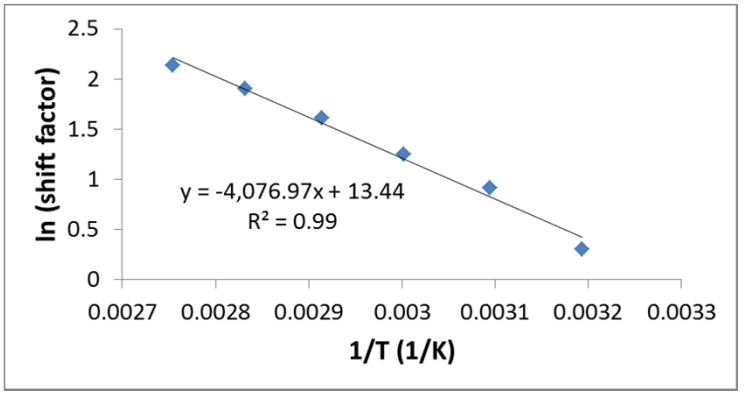
$$n_{CO_2}(t) = n_{CO_2}^{init} + \alpha(t) n_{CO_2}^{\max}$$

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

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

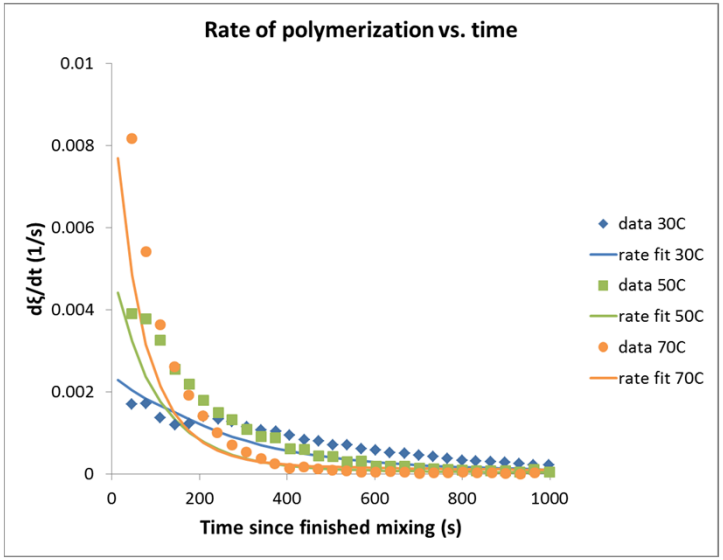
Fit IR Data to Get Polymerization Reaction Rate

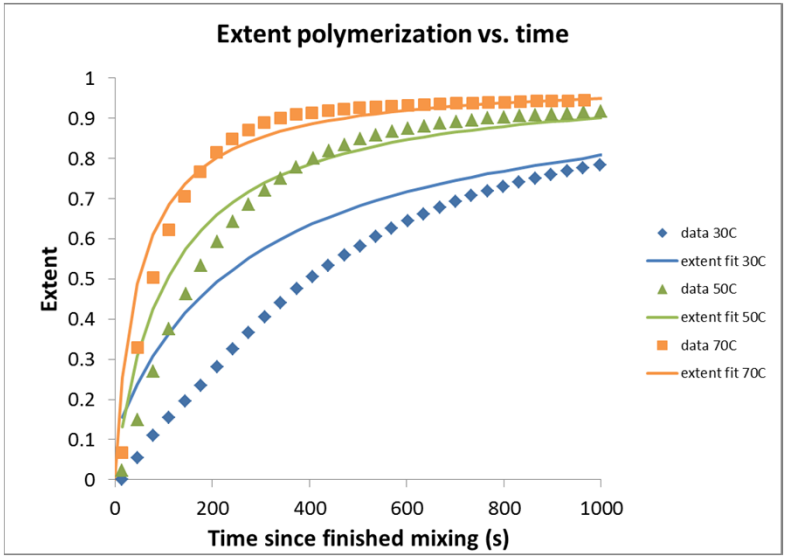




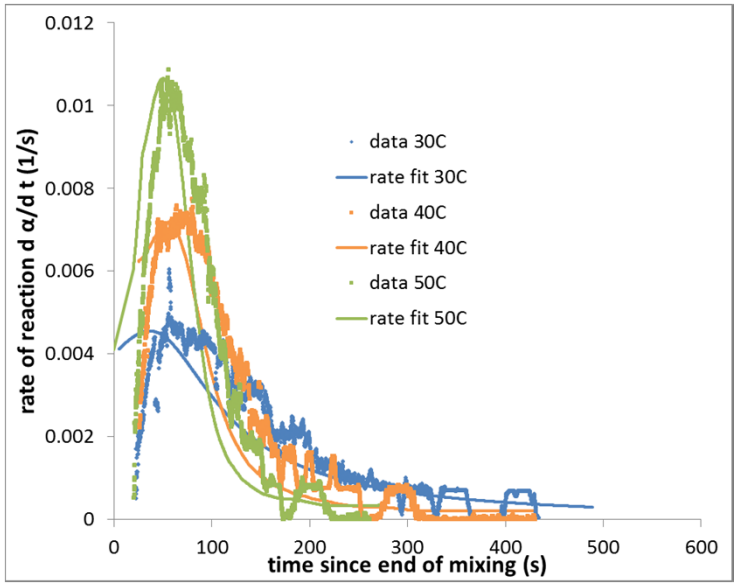
Time-temperature shift gives ΔE

$$\frac{d\xi}{dt} = k_0 e^{\Delta E / RT}(1-\xi)^q \qquad k_0 = 2772 \qquad q = 2$$

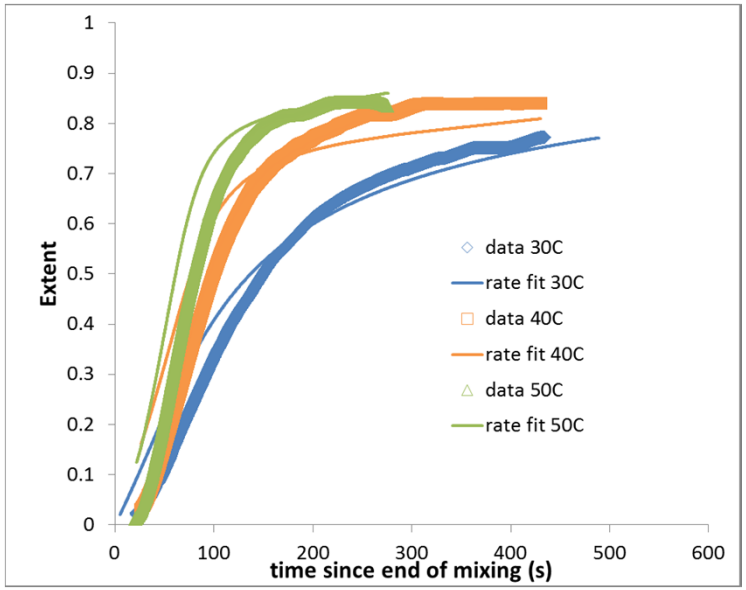




Fit Foam Rise Data to Get Gas Generation Reaction Rate

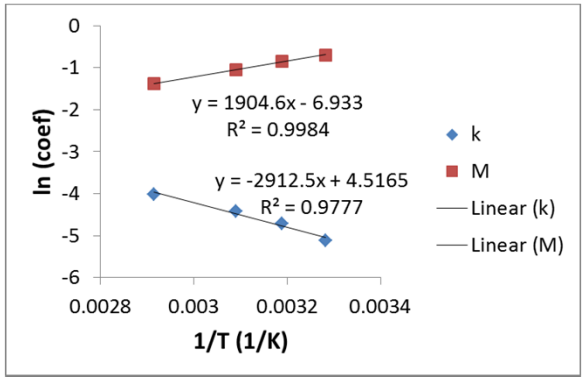


$$\frac{d\alpha}{dt} = \frac{k(1-\alpha)^n}{(1-\alpha)^m + M}$$



Fit numerically integrated to compare to nonisothermal data

$$k = A_1 \exp(-E_1 / RT)$$
$$M = A_2 \exp(-E_2 / RT)$$



Model Requires Foam Properties

Process model requires solving balance equations for momentum, energy, mass

From foaming kinetics

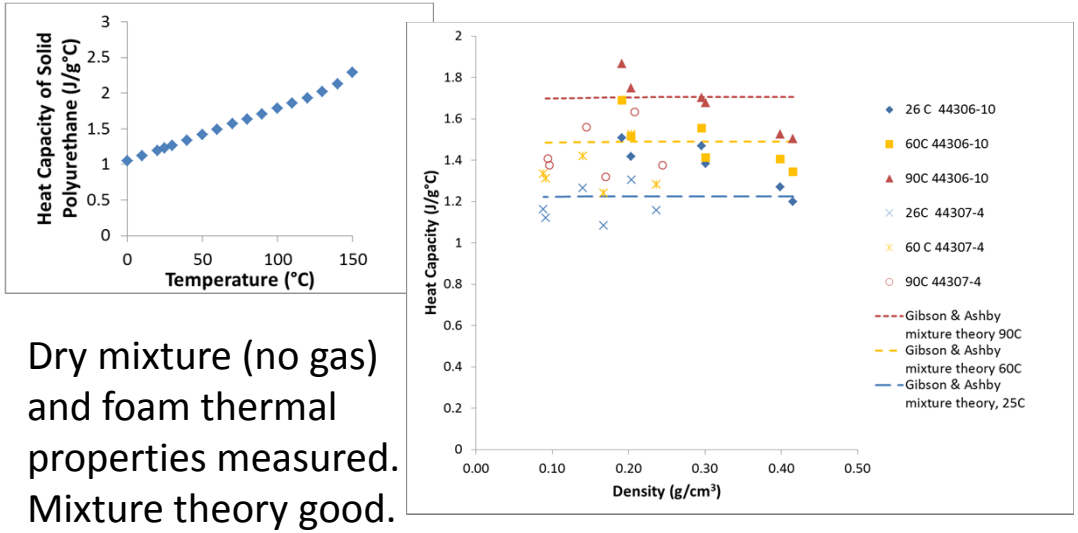
$$\rho\frac{\partial \mathbf{v}}{\partial t} = -\rho\mathbf{v}\bullet\nabla\mathbf{v} - \nabla p + \nabla\bullet(\eta_f(\nabla\mathbf{v} + \nabla\mathbf{v}^t)) - \nabla\bullet\lambda(\nabla\bullet\mathbf{v})I + \rho\mathbf{g}$$

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

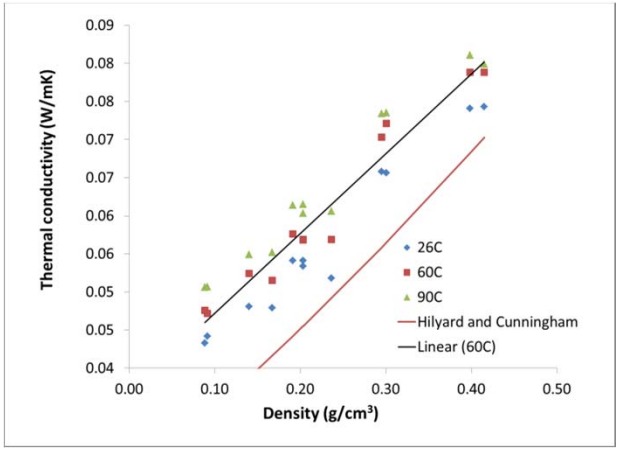
Polymerization kinetics

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

- Differential scanning calorimetry (DSC) gives lumped heat of reaction
- Thermal properties are functions of the temperature and the gas fraction (extent of foaming reaction)



Dry mixture (no gas) and foam thermal properties measured. Mixture theory good.



Mixture theory only gives a bound. But behavior linear.

Viscosity of Foam is Complex

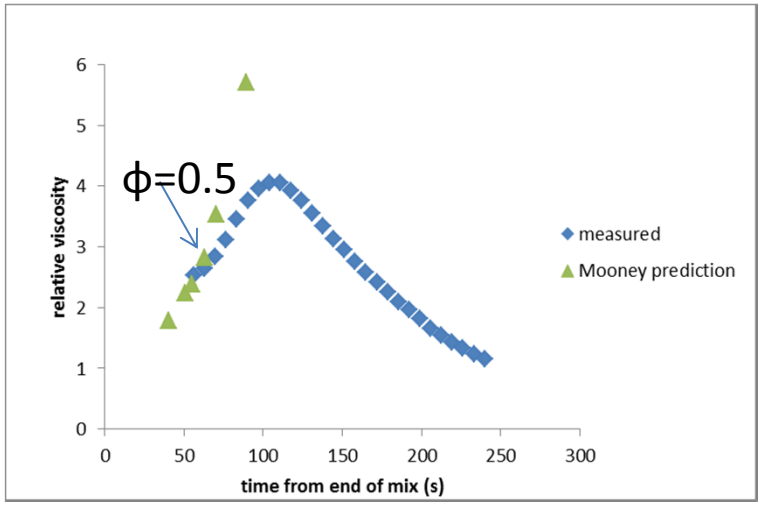
- Foam rheology evolves as gas fraction and polymerization increase
- Dry formulation gives an approximation of the curing continuous phase rheology

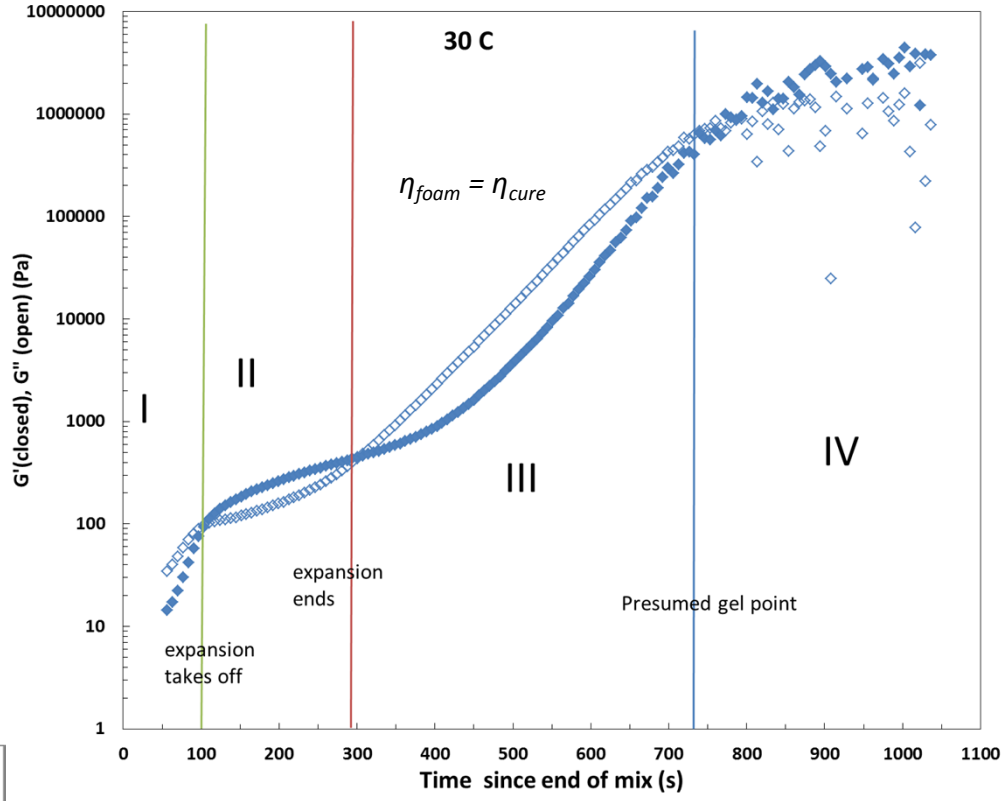
$$\eta_{cure} = \eta_0^0 \left(\frac{\xi_c - \xi}{\xi_c} \right)^{-2.0}$$

- Knowing density evolution from separate foam rise experiments we relate the gas fraction and the foam viscosity
- Mooney prediction (for $\phi_{gas} < 0.5$)

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

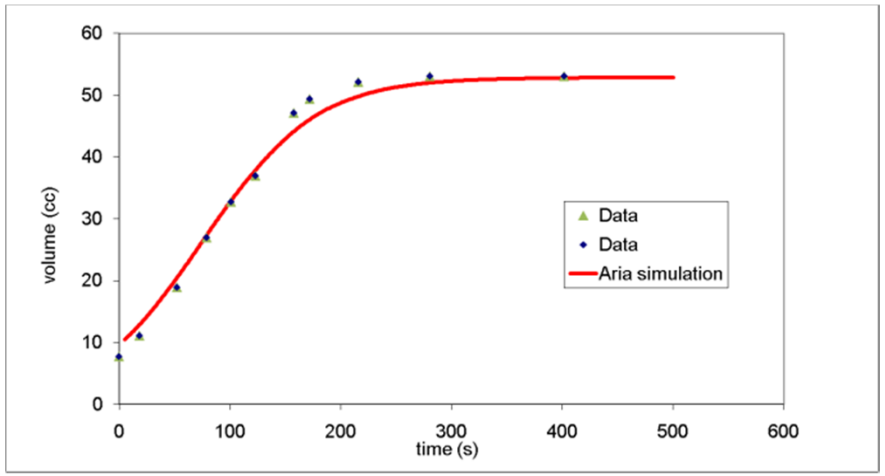
- For $\phi_{gas} > 0.7$ estimate $\eta_{foam} = \eta_{cure}$

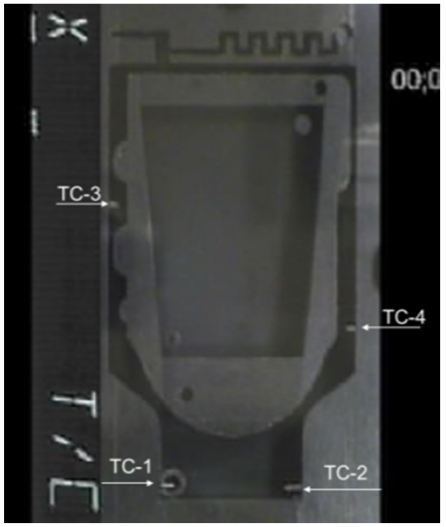


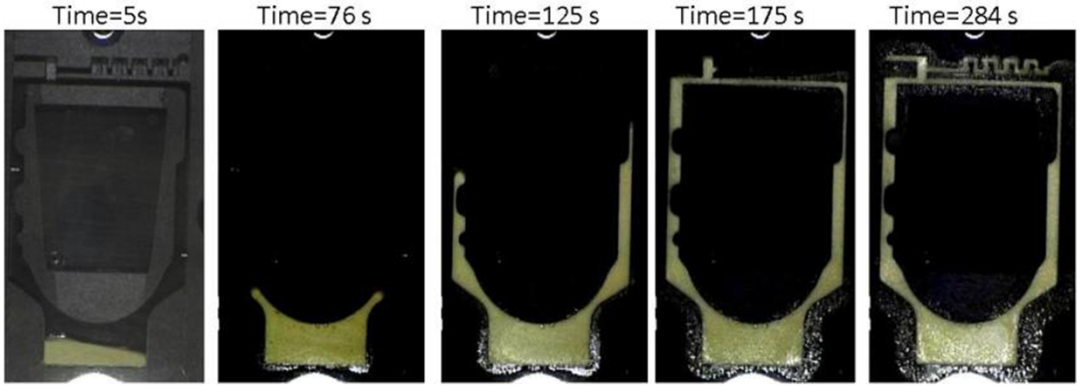


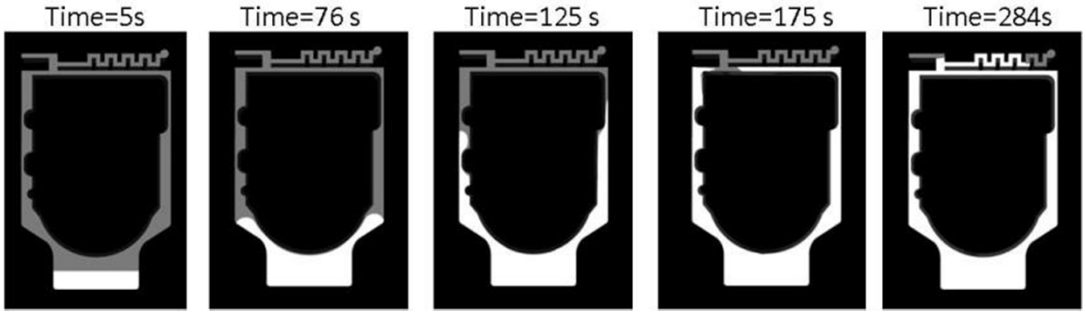
After Bouayad et al. Int J. Mater Form (2009), plot foam rheology as function of distinct phenomenological characteristic times.

Free Surface Validation Study





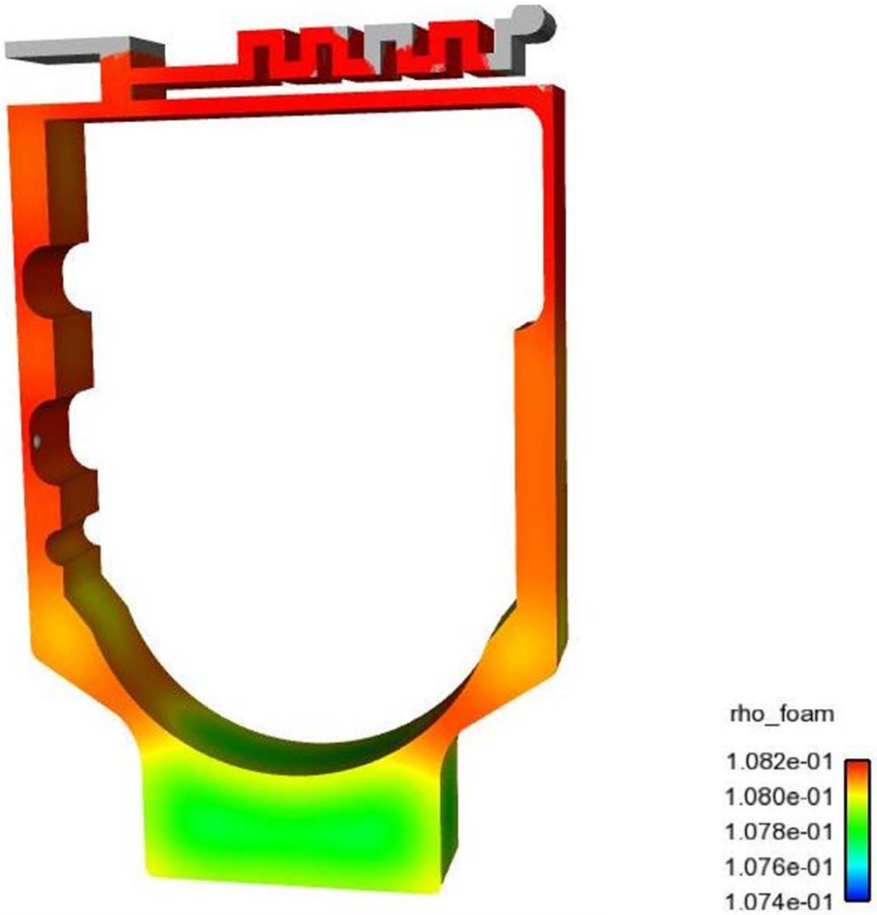




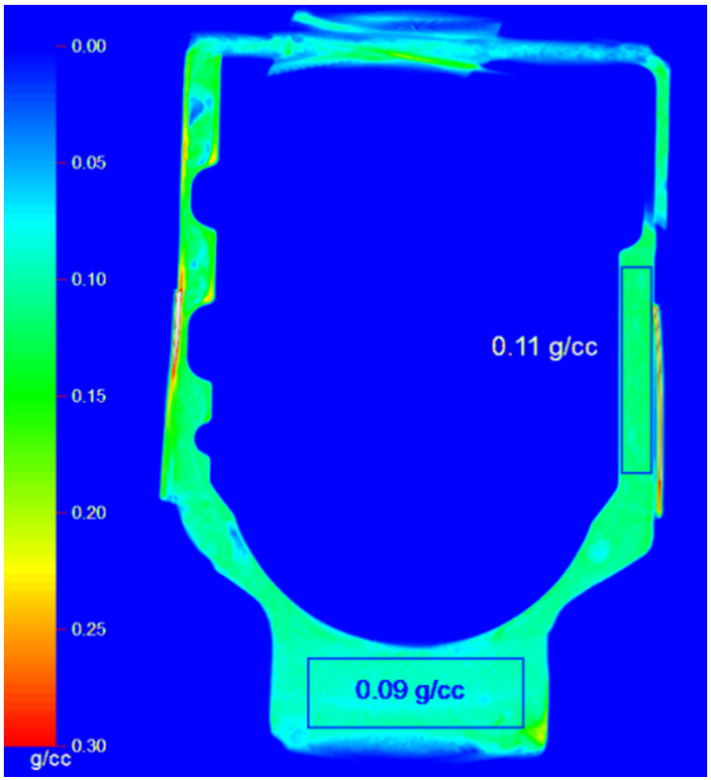
- Model tracks density change for foaming in full system
- But validation data show that model foams too fast and then too slow with this simplification
- Current work:
  - Improve density model
  - Add a function to tie volume change generation to gelation

Density Gradients Occur in Polyurethane Foams

- X-ray CT of PMDI-4 part shows density gradients



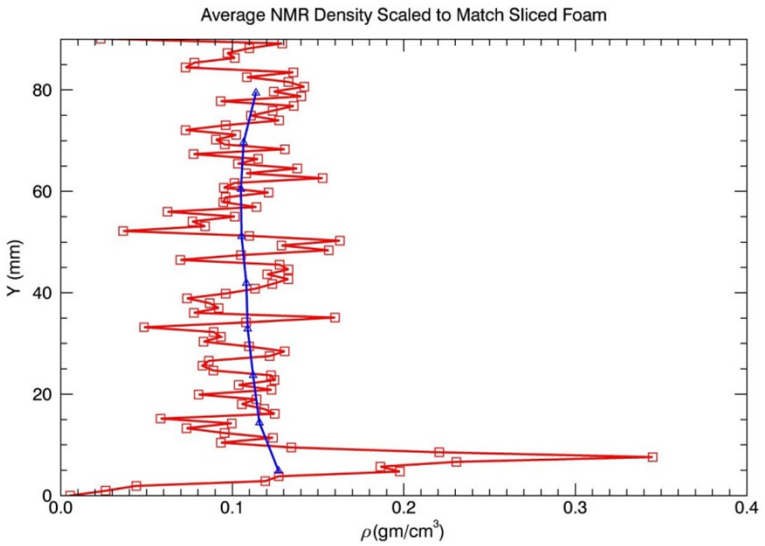
Modeling extent of reaction for CO_2 generation can give trends to help understand foam density variations



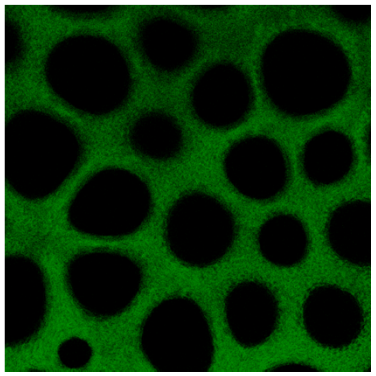
Experimental CT gives density gradients in artifact mold (CT courtesy of Kyle Thompson, SNL)

Experiments on Evolving Density and Microstructure

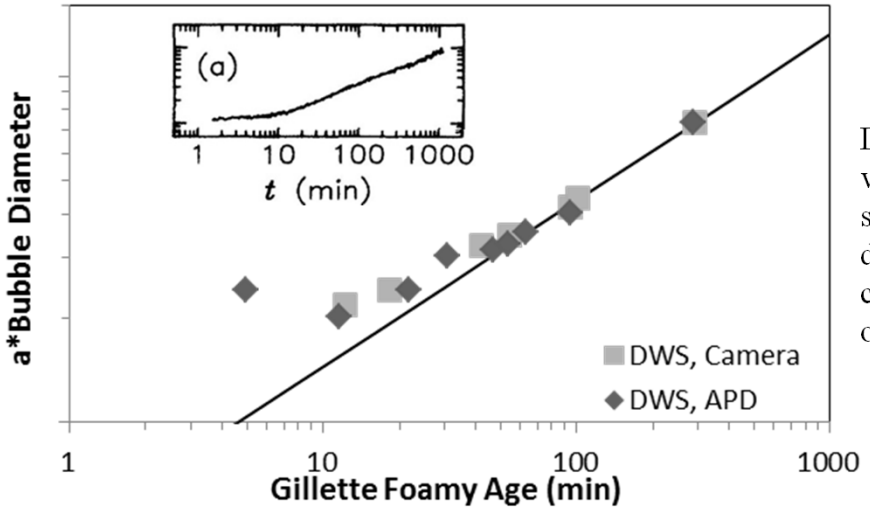
- Nuclear Magnetic Resonance (NMR) imaging
  - NMR signal includes density and isocyanate content, both of which decrease with time
  - We separate effects by using tracer particles that indicate density
- Confocal microscopy
  - Bubble size and shape evolution with time can be determined but only fairly near a surface
  - Better than optical imaging for the small bubble sizes ir polyurethane (about 100 µm)
- Diffusing wave spectroscopy (DWS)
  - Average bubble size through a thickness can be determined



NMR signal (red) from tracers corresponds well to averaged density of surrounding block determined from weighing post test. NMR can be used during the foam rise, unlike post test destructive analysis.



Fluorescent confocal image of foam doped with Nile Red. Multiple optical "slices" give 3D information with good time resolution.



DWS replicates literature values (inset) of bubble size growth with time due to diffusion and coalescence as first test of technique.

Conclusions

- Current model is adequate for production calculations
  - Determining metering, initial placement, voids, gate, and vent location
  - Investigate encapsulation of new geometries of interest
- Advanced foam kinetic model complete
  - Polymerization and rheokinetics are accurate
  - New foam kinetic model implemented (Rekha Rao's talk on Tuesday)
  - New results – comparison to experiment underway
- Current work:
  - Improve density model with knowledge of microstructure
  - Add a function to tie volume change generation to gelation