EXPERIMENTS TO DETERMINE REACTION KINETICS FOR POLYURETHANE STRUCTURAL AND ENCAPSULATION FOAM

SAND2012-1699 C
SAND2012-1699C

Lisa A. Mondy, Rekha R. Rao, Mathew C. Celina, Lindsey Gloe, Bion Shelden, Edward M. Russick, Kyle Thompson, Jaime Kropka

Sandia National Laboratories

Albuquerque, NM

James Mahoney

Honeywell Kansas City Plant

Kansas City, MO

AWE UK-US Foam Workshop 2012 under JOWOG 28
Sandia National Laboratories
Livermore, California
March 6th -7th, 2012

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000

National Nuclear Security Administration
LABORATORY DIRECTED RESEARCH & DEVELOPMENT
Sandia National Laboratories

Development of a Polyurethane Foam Processing Model

Problem Description:

- Many electronics are encapsulated with polyurethane foams
- Larger structural support parts are also made from polyurethane foam
- Foam materials critical for structural support and shock/vibration isolation
- Foaming can be unpredictable leading to unacceptable voids
- Inhomogeneities in foam material can lead to property variations & potential structural issues

Goal: Develop better process models and processes

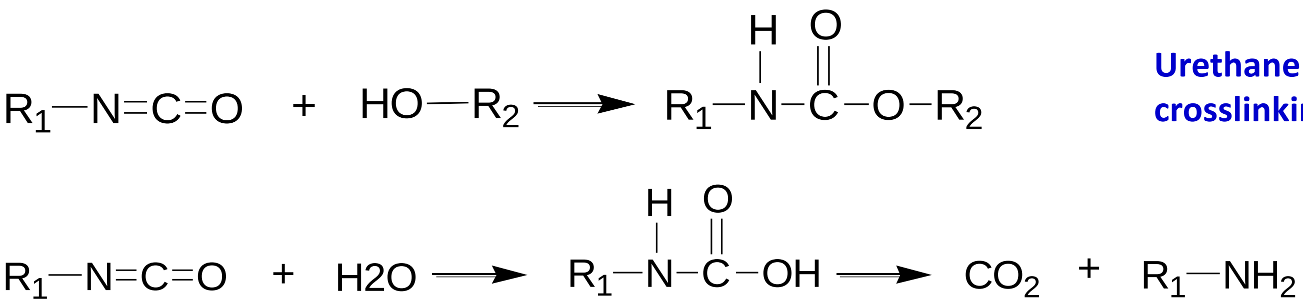
- Use to help design mold geometry, vents, gates, etc.
- Predict flow of reacting, multiphase, complex material
- Capture foaming and curing rates
- Calculate extent of fill during processing, location of knit lines, possible void locations
- Predict maximum temperatures from exothermic reactions

Focus of this talk:

Experiments to populate parameters of this model and enable validation of results

Polyurethane Resin Cure and Foaming Reactions

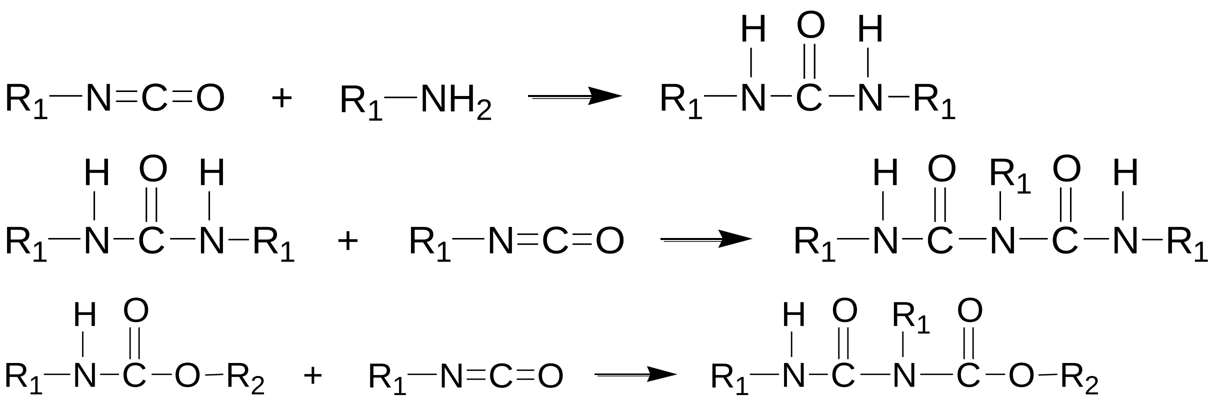
Two key reactions: **Isocyanate reaction with polyols and water**



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

Improved Kinetic Model will include CO2 Generation

$$rate_1 = k_1 e^{-\Delta E_1/RT}[isocyanate]^a[polyol]^b$$ **Polymerization**

$$rate_2 = k_2 e^{-\Delta E_2/RT}[isocyanate]^c[H_2O]^d$$ **CO_2 generation**

- Must track five species: water, polyol, polymer, carbon dioxide, and isocyanate , since we have competing primary reaction
- Use experiments to determine Arrhenius rate coefficients

$$\frac{D[CO_2]}{Dt} = +rate_2$$

$$\frac{D[H_2O]}{Dt} = -rate_2$$

$$\frac{D[isocyanate]}{Dt} = -rate_1 - rate_2$$

$$\frac{D[polyol]}{Dt} = -rate_1$$

$$\frac{D[polymer]}{Dt} = +rate_1$$

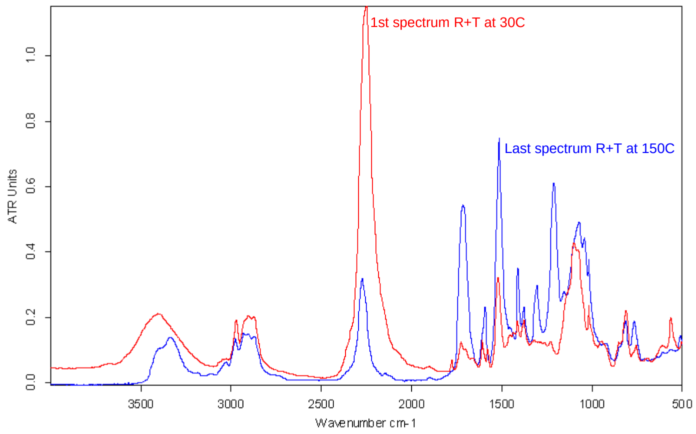
- Must provide initial conditions for all species
- Integrate rate equations as part of the simulation
- Density predicted from gas generation

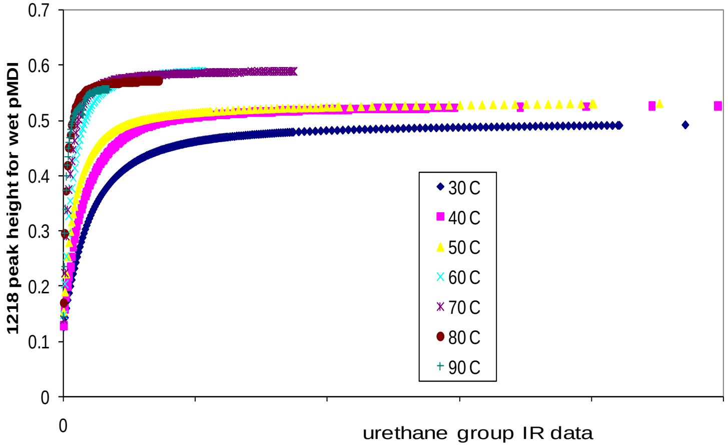
$$\phi(t) = \frac{n_{CO_2} / MW_{CO_2} \rho_{CO_2}}{n_{CO_2} / MW_{CO_2} \rho_{CO_2} + n_{liquid} / MW_{liquid} \rho_{liquid}}$$

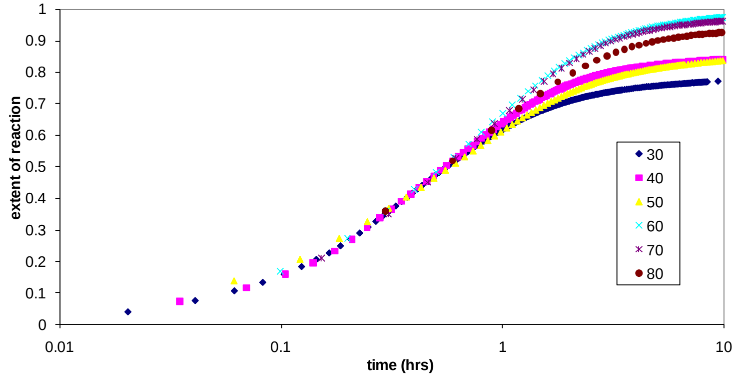
$$\rho_{foam} = (\rho_{CO_2} - \rho_{liquid})\phi(t) + \rho_{liquid}$$

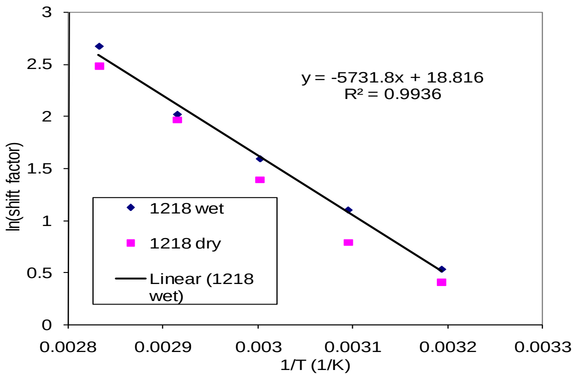
Extent of Reaction for Polymerization

- Use IR to monitor polyol-isocyanate urethane reactions in both wet and dry polyurethane
- Peak height as a function of time for the 1218 cm^{-1} peak
- Isothermal tests were carried out for various temperatures ranging from 30°C to 90°C.









- Normalize the peak height by the maximum height at the highest temperature to obtain extent of reaction
- Shifted extent of reaction for isothermal tests carried out for various temperatures
- Natural log of the shift factor versus the reciprocal temperature in Kelvin, gives the activation energy for the Arrhenius rate constant for the polymerization reaction.

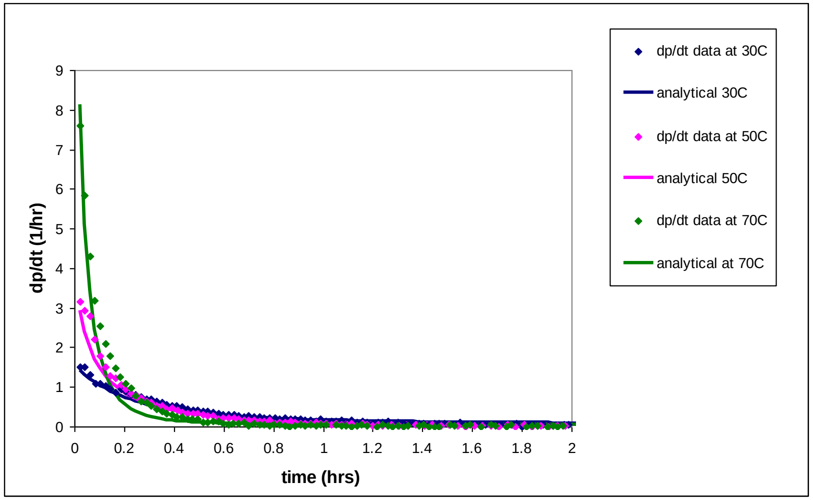
Extent of Reaction for Polymerization

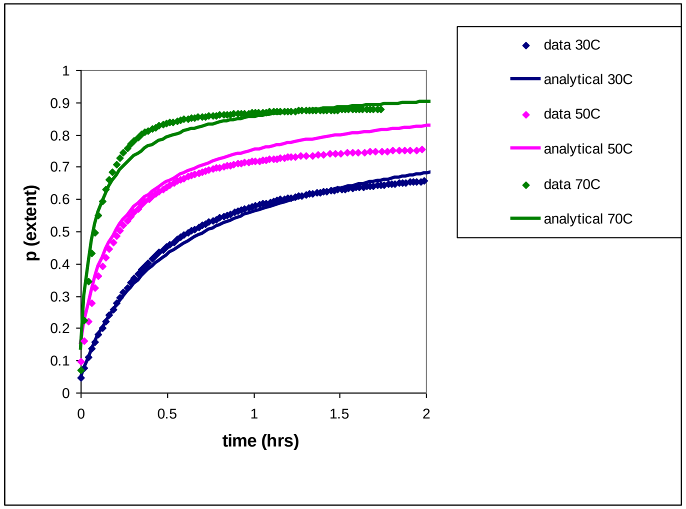
- Numerically differentiate the extent of reaction, p, to obtain the rate
- Fit the rate and the extent of reaction simultaneously to a standard equation form, where only the exponent is unknown
- Form of between 2nd and 3rd order reaction fits data

$$\frac{d\xi_{cure}}{dt} = k_0 e^{\Delta E/RT} \left(1 - \xi_{cure}\right)^{2.75}$$

k_0=2.96 x 10^8 1/hr,
ΔE/R=-5731.8 K

- "Wet" vs. "dry" slightly different rates – used full PMDI-4 (wet) formulation results



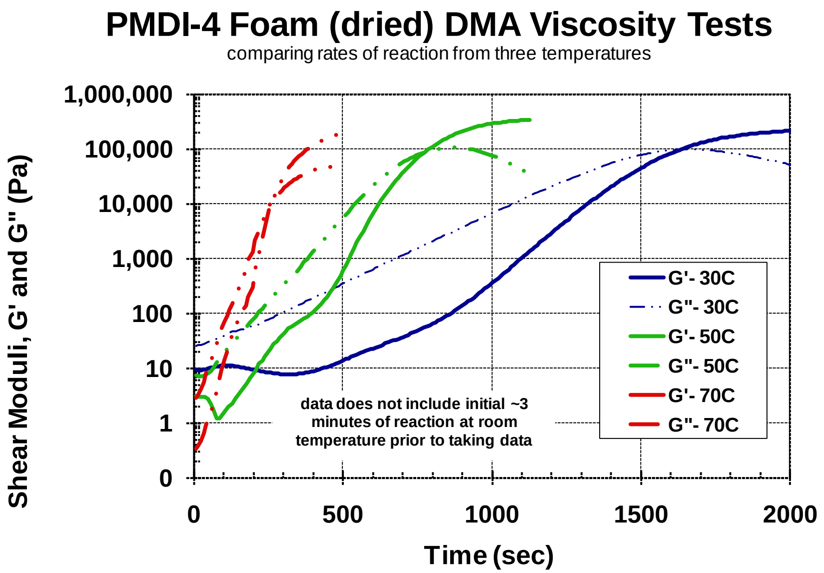


From polyol-isocyanate urethane reactions (Peak 1218 in PMDI-4 foaming)

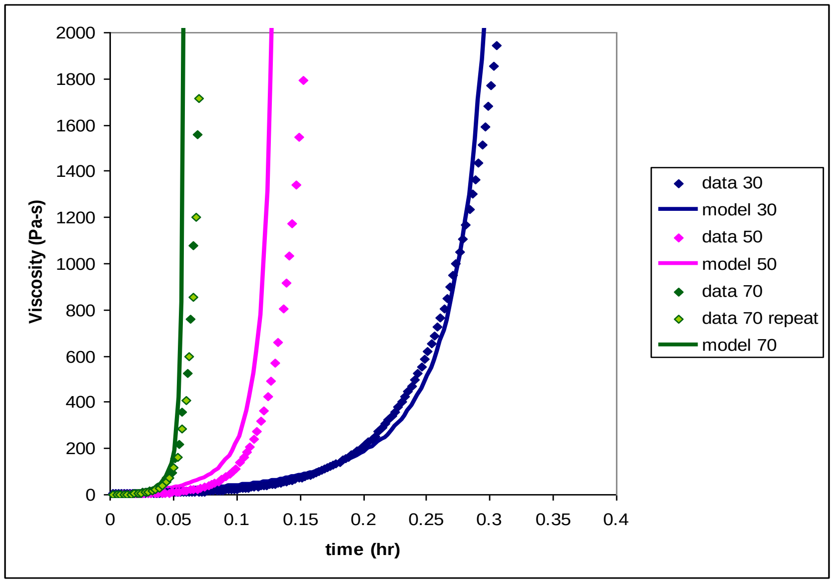
- The lumped heat of reaction was measured through differential scanning calorimetry to be 240.3 J/g for the wet (foaming) formulation

Resin Continuous Phase Viscosity

- Storage and loss modulus for dry polyurethane at 30°C, 50°C, and 70°C measure in oscillatory rheometer
- The cross over point of G' and G'' gives the gel point and gel time of the polymer (0.46).
- Viscosity is correlated to extent of reaction and compared to data



Measurements by Doug Adolf

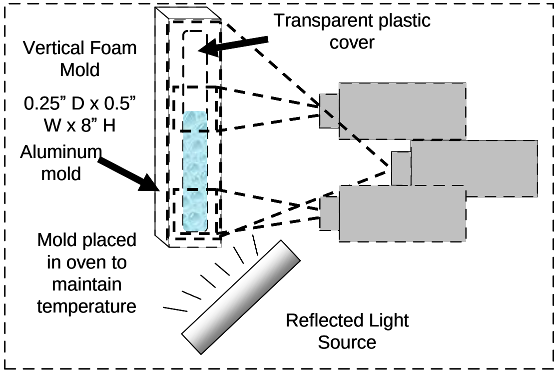


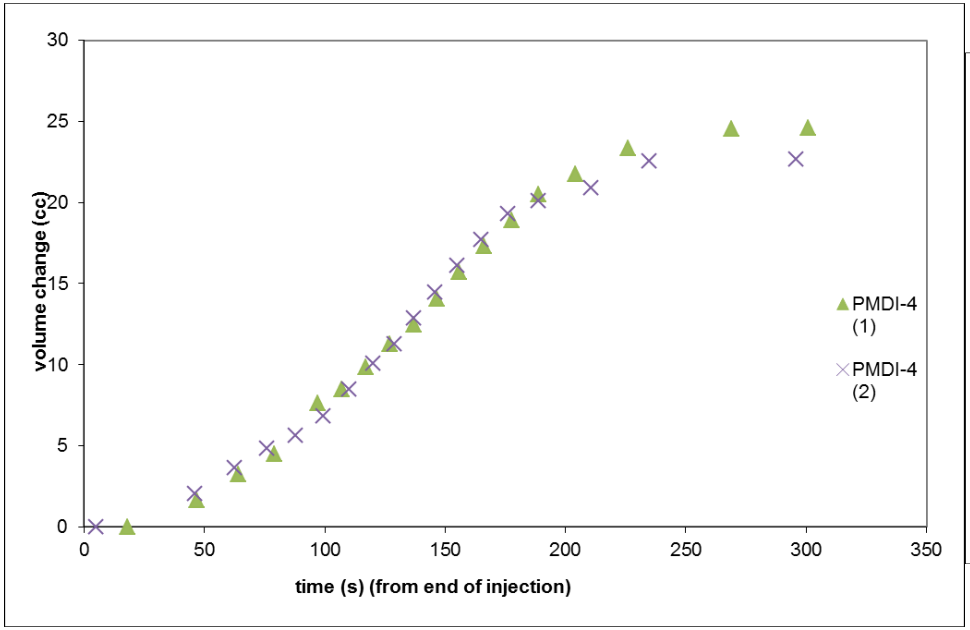
$$\eta_{cure} = \eta_0^0 \left(\frac{\xi_c - \xi}{\xi_c}\right)^{-2.0}, \xi_c = f(T)$$

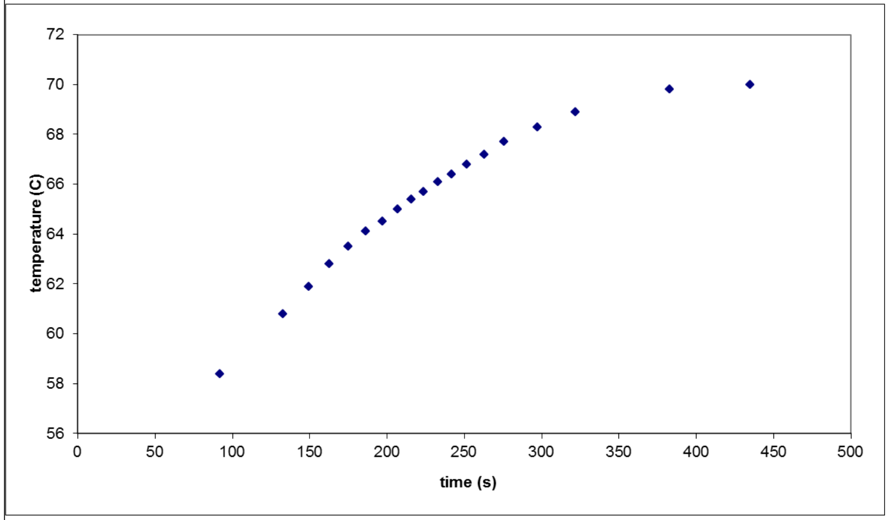
$$\eta_0^0 = 2.7x10^{-9} \exp\left(\frac{6.4kcal/(molK)}{RT}\right) Poise$$

Measure Height Change to Determine CO_2 Concentration

- Data have most uncertainty at early times because reaction is occurring during mixing and injections, but bubbles are being destroyed in these processes, too.
- We can only measure height change after these processes.
- CO_2 loss from bubble breakage at top surface? BUT bottom line: engineering model to predict volume change
- The foam cannot be preheated, so during the foam rise the temperature is not steady.

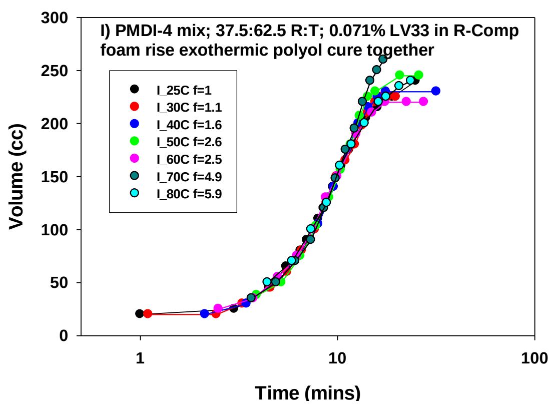


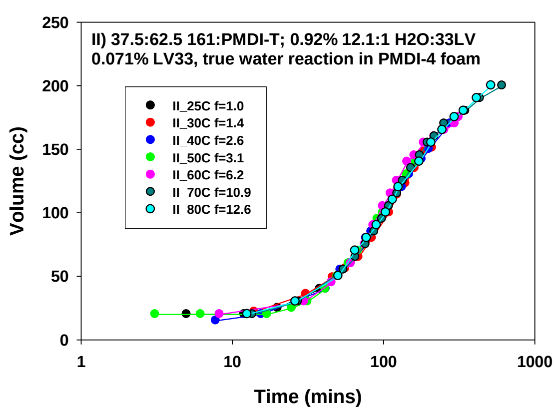




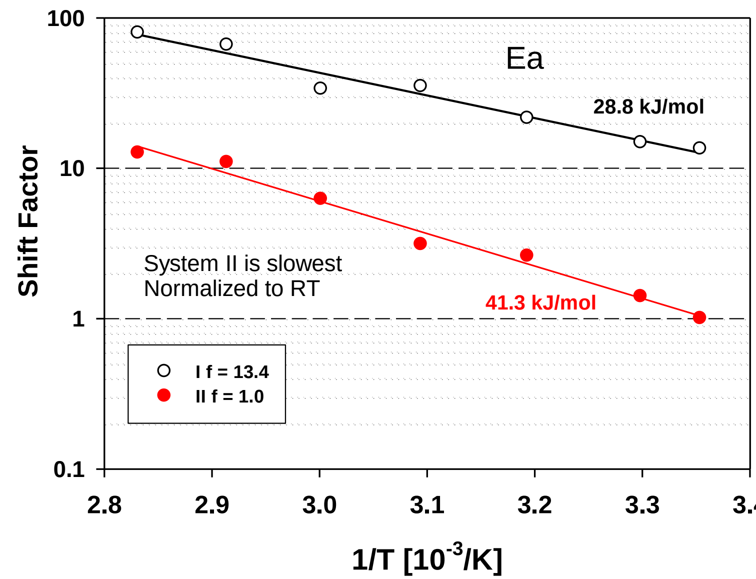
Complex Kinetics of Foaming Reaction

- CO_2 generating foaming reaction due to water-isocyanate has activation energy ΔE ~41kJ/mol
- Curing reactions due to polyol-isocyanate urethane reactions in dried PMDI-4 has roughly the same ΔE ~41kJ/mol
    - The isolated foaming reaction is relatively slow
    - The isolated curing reactions have slightly different rates than in presence of H_20
    - In the presence of polyol (as in the PMDI-4 foam system) we observe *much faster* foaming action and a different ΔE (29kJ/mol).
    - Not perfectly isothermal due to internal heat of reaction and auto-catalysis?





Superposition of volume-vs-time curves gives activation energy ΔE with and without curing



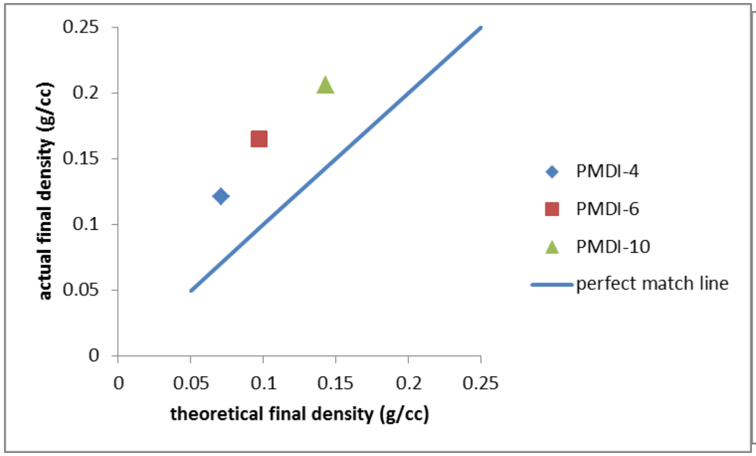
Competing reactions should slow reaction, but actually speeds up foaming while curing is unaffected

Recipe of PMDI-x

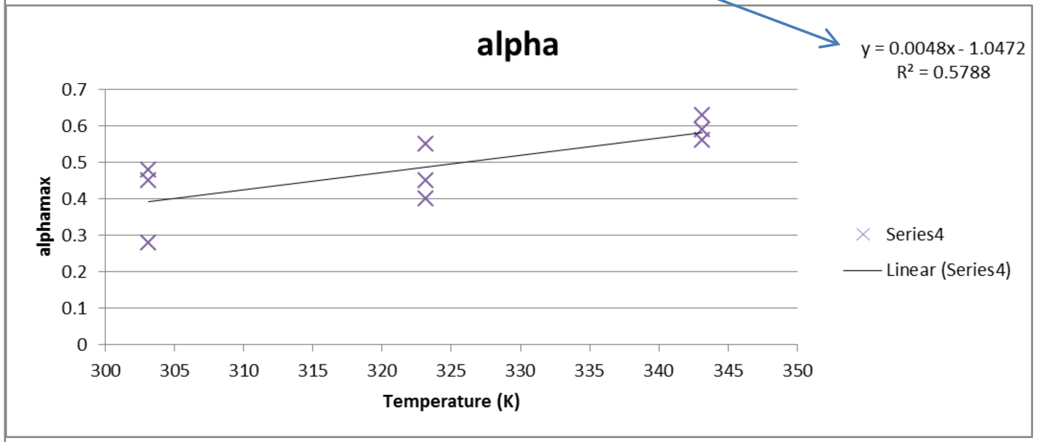
Maximum amount of CO_2 that can form is determined from the mass injected and the mass fraction of H_2O in the recipe.

PMDI type	Mass fraction H2O
PMDI-4	0.00852
PMDI-6	0.00606
PMDI-10	0.00395

But the foam actual final density is higher than the theoretical because of polymerization effectively stopping bubble expansion, bubble breakage from shear, or unreacted material, and the actual final density depends on the temperature during the reactions. Let maximum extent of CO2 generation α be an empirically fit α(T)



Measured “free rise” density at 70°C



$$\alpha_{\max} = 0.0048T - 1.0472$$

Michaelis-Menten Reaction Form for CO_2

$$\frac{d\alpha/\alpha_{\max}}{dt} = \frac{k\left(1-\frac{\alpha}{\alpha_{\max}}\right)^n}{\left(1-\frac{\alpha}{\alpha_{\max}}\right)^m + M}$$

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

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

$$\alpha_{\max} = 0.0048[1/K]T[K] - 1.0472$$

Best fits to data gives:

$$n = 2$$

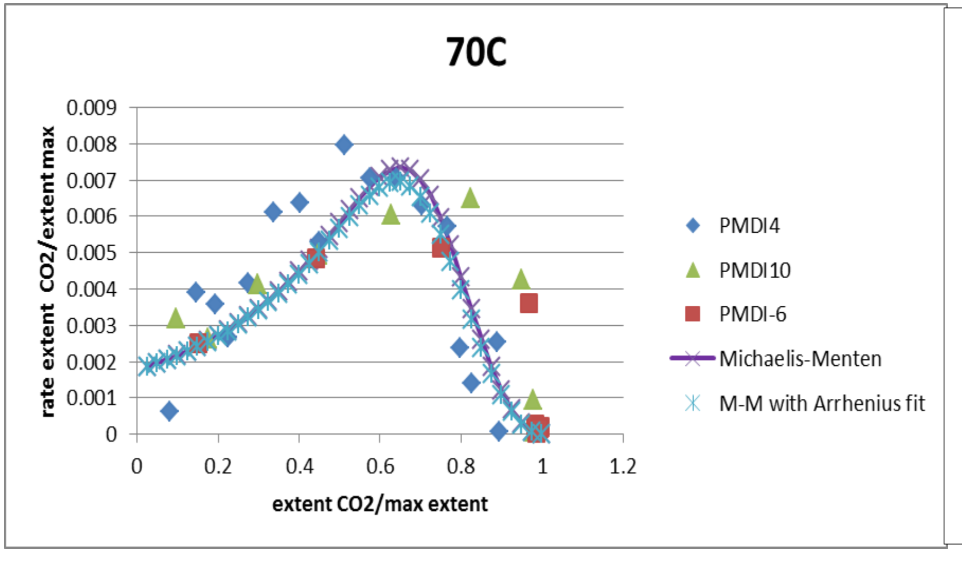
$$m = 4$$

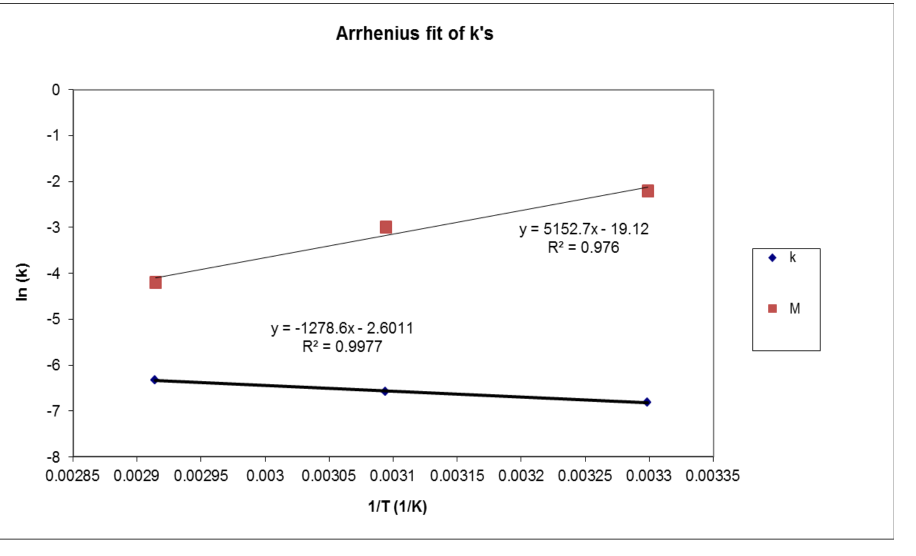
$$A_1 = 0.07419$$

$$-E_1/R = -1278.6$$

$$A_2 = 4.959\times10^{-9}$$

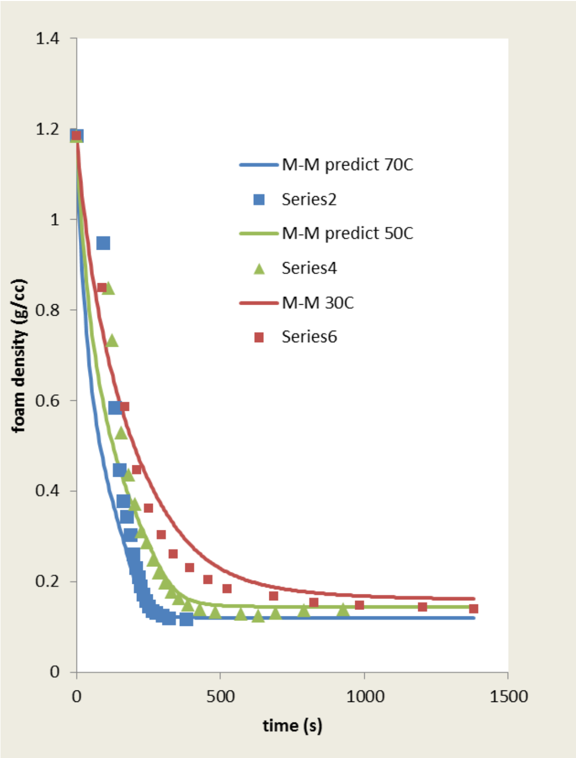
$$-E_2/R = 5152.7$$



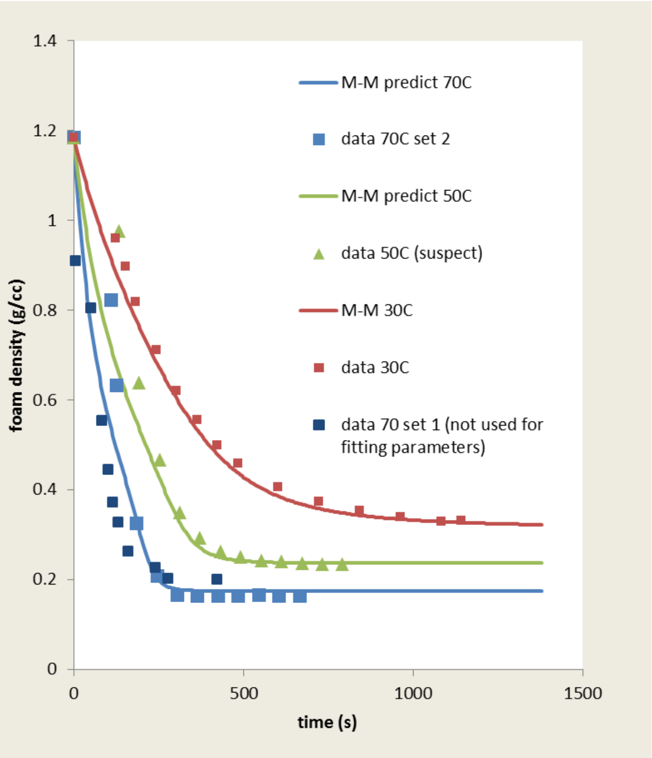


Predictions Compare Well to Data

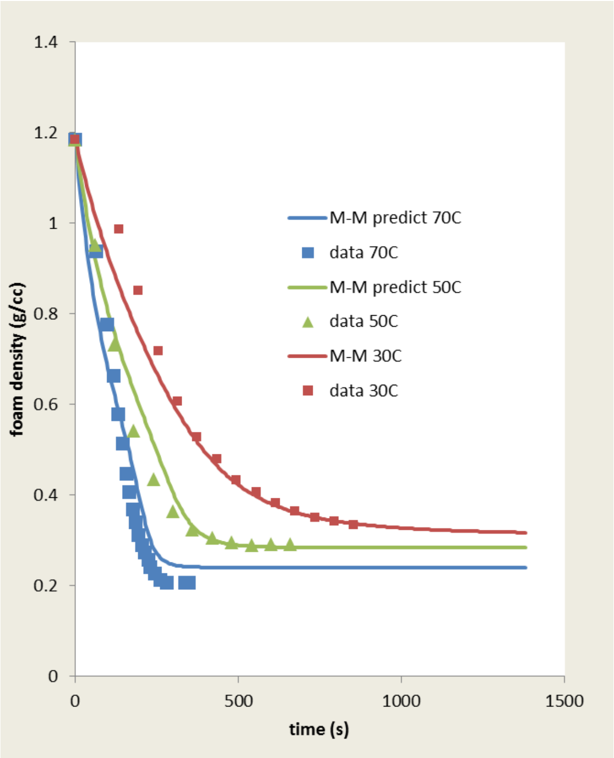
PMDI-4



PMDI-6



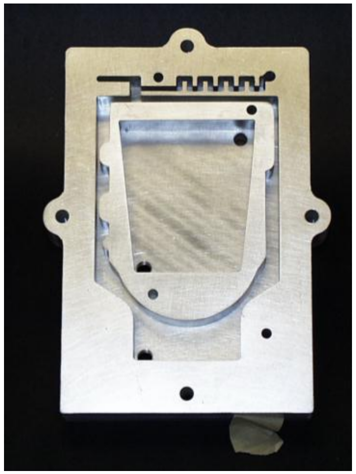
PMDI-10

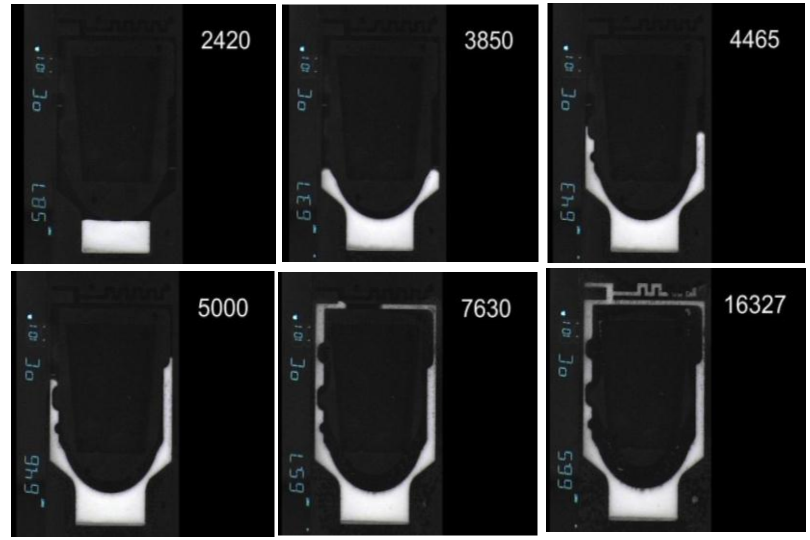


$$\phi(t) = \frac{n_{CO_2} / MW_{CO_2} \rho_{CO_2}}{n_{CO_2} / MW_{CO_2} \rho_{CO_2} + n_{liquid} / MW_{liquid} \rho_{liquid}}$$

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

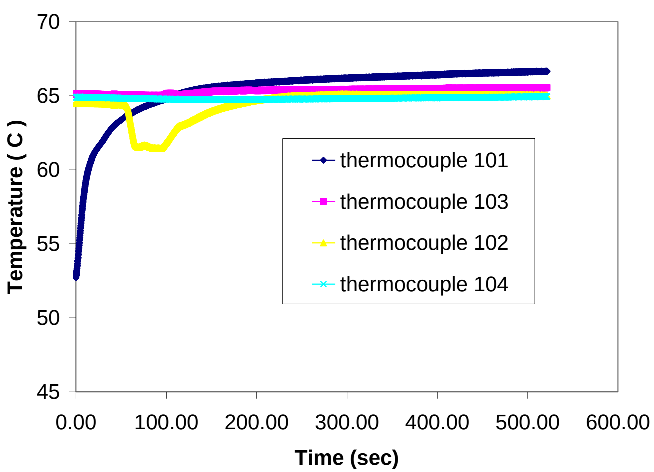
Validation Experiments in Complex Geometries





KC Mold and Temperature Monitor Layout

- **Video follows advancing front in geometry developed by KC for quality control**
- **Temperature instrumentation added**



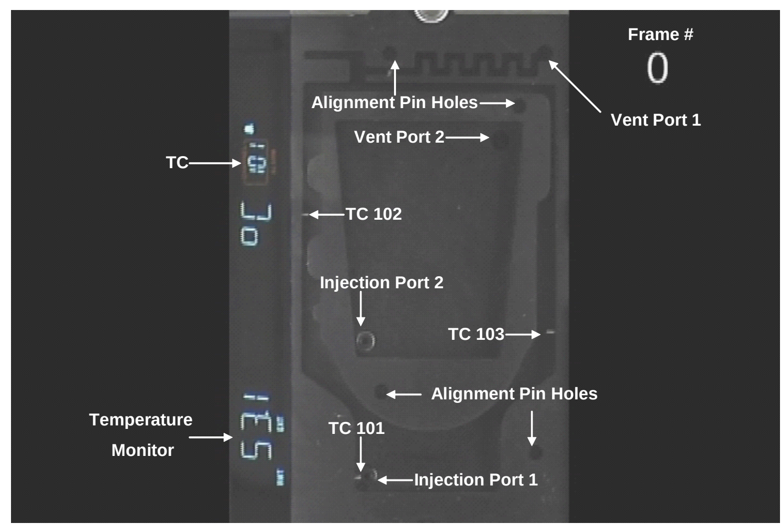
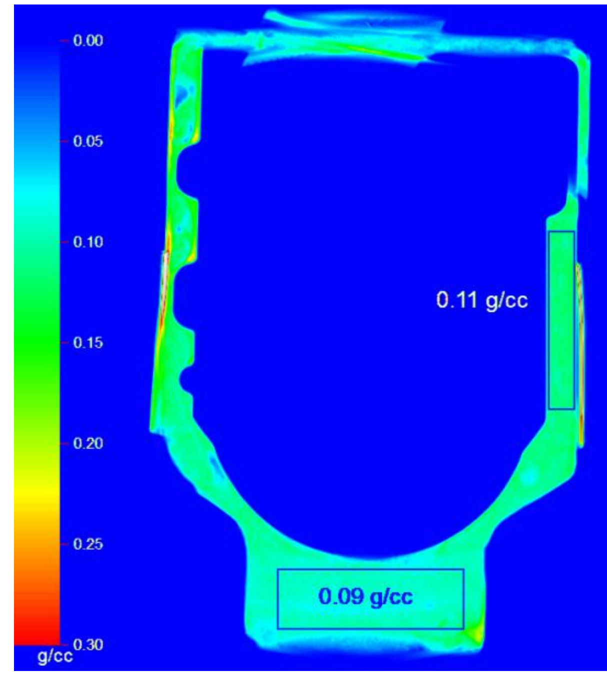


Figure 1

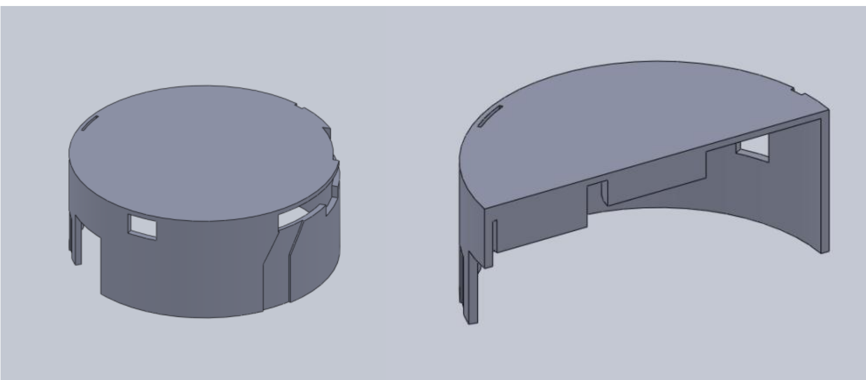
Density Gradients Occur in Polyurethane Foams

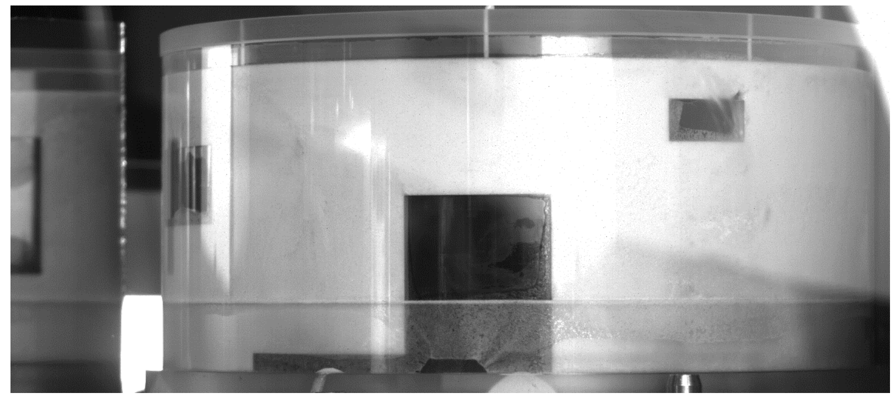
- X-ray CT of PMDI-4 part shows density gradients

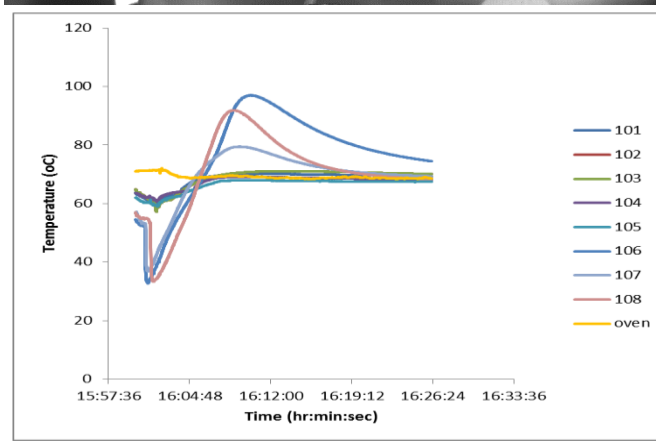


Complex Large Mold for Validation

- Mold has aspects (windows, gap sizes) that are relative to generic support parts
- Temperature instrumented with four camera views

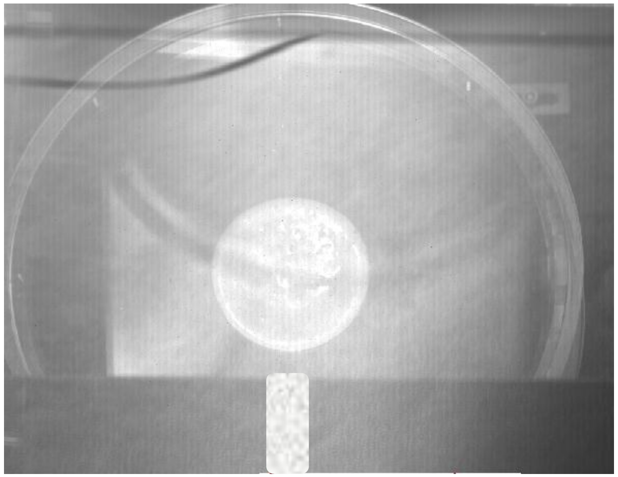




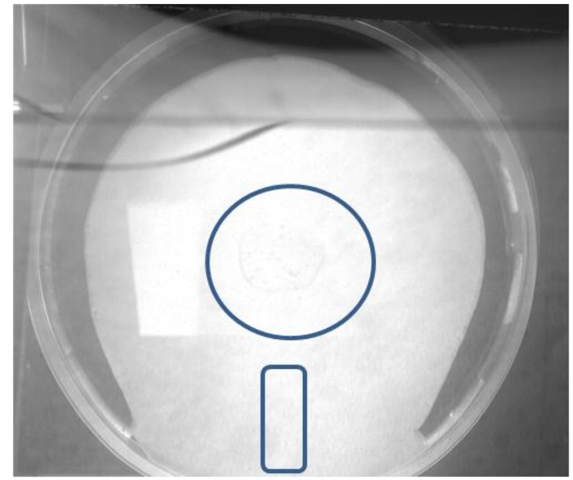


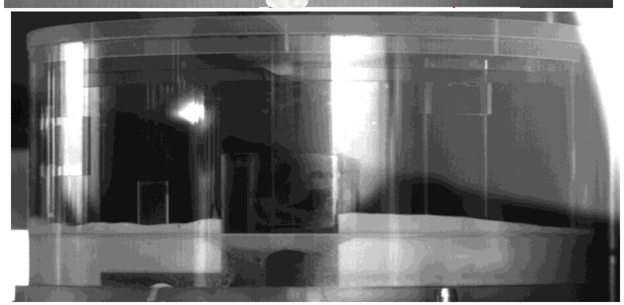
Simplified Part

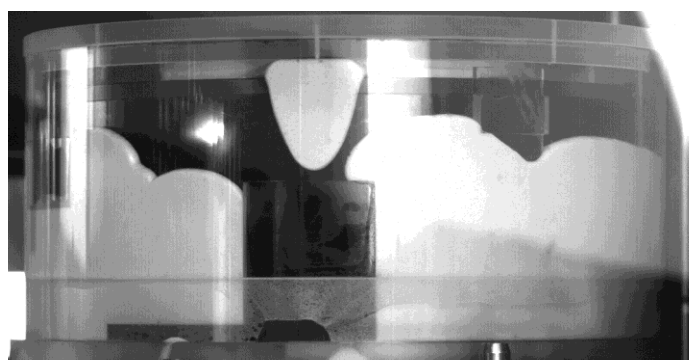
Filling Method Creates Knit Lines



Foaming material is originally placed in top rectangular and cylindrical reservoirs and in bottom rim reservoir, to simulate legacy KC filling method







Conclusions

- Advanced kinetic model almost complete
  - Rekha Rao will discuss implementation into a FE computational framework
- Polymerization kinetics obtained through IR for several types of PMDI in isothermal tests with and without H_2O to produce the foaming reaction
  - Data fit condensation chemistry model
- Gas evolution was measured by measuring foam volume evolution for several types of PMDI, at several nominal temperatures
  - Data fit Michaelis-Menten kinetic model
- Validation data have been collected in complex molds including a simplified, large, structural part
  - Front tracking (volume evolution with time)
  - Temperature at several location with time
  - Density gradients in final parts