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Improving Engineering Models of Molding Polyurethane Foams

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Abstract

- **Objective:** To provide and interpret empirical data to improve an engineering model of foam expansion and reaction for manufacturing purposes.
- **What was done:** Data collection and analysis focused on three areas:
  - Kinetics of major reactions
  - Compressibility of the foam
  - Evolution of the bubble microstructure
- **Major Findings:** Equation forms and parameters that describe the chemical kinetics as well as the compressibility of the foam during the process were determined.
- **Major Conclusions:** Mathematical descriptions of important physical characteristics that will make the engineering model descriptions of evolving foaming materials more accurate and robust were determined.

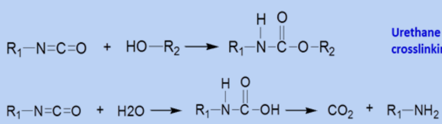
Introduction

Polyurethane foams are chemically blown foams that are formed by mixing two component solutions. The industrial applications of these foams are to provide lightweight structural support and to protect sensitive electronics from shock and vibrations. A number of different polyurethane foams are being studied, while their exact formulations vary the two component solutions always contain the same types of chemicals:

- Resin component- polyol, water, surfactant, and catalyst
- Curative component- polyisocyanate

While many competing reactions occur during the foaming process, for an engineering model it is sufficient to focus on the two dominant reactions: the polymerization reaction and the gas generation reaction.

Two key reactions: Isocyanate reaction with polyols and water



For the model to be sufficiently accurate it was necessary to determine the kinetic rate laws that both of these reactions most closely followed. The polymerization reaction is best described by a condensation chemistry form, the gas reaction is best described by the Michaelis-Menten reaction form, both are shown below. While the general equations were known, the values of the equation parameters were not; experiments were required to determine their exact values.

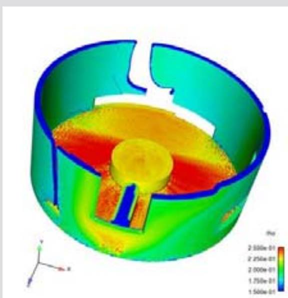
Polymerization Kinetics

$$\frac{d\xi}{dt} = k_0 e^{-\frac{E_a}{RT}}(1-\xi)^n(A+\xi^m)$$

Gas Generation Kinetics

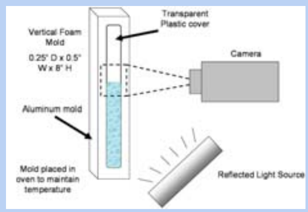
$$\frac{d\alpha}{dt} = \frac{Nk(1-\alpha)^n}{(1-\alpha)^m + M}$$

The current engineering model for polyurethane foams used at Sandia is based on solving equations of motion and kinetic equations. On the right is an image of a simulation of structural foam filling a mold with a complex geometry. The color scale indicates varying density throughout the foam. More information on the reaction kinetics, the foam's compressive properties, and the foam microstructure will allow for more robust simulations and better predictions of density as well as other physical properties.

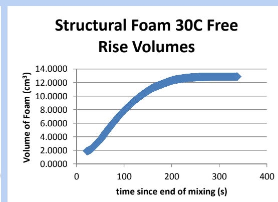


Methods

- **Foam Rise Experiments**
  - The foam was allowed to react and rise in a column
  - Pressure and temperature readings were taken in the column.
  - Images were taken with a 10 fps cameras of the rising foam.
  - Image processing software was used to determine the foam volume from images.
  - The amount of CO_2 present in the foam at any given time was calculated according to the ideal gas law with the pressure, temperature and volume data.
  - The foam was also analyzed by IR (Infrared spectroscopy), data was provided and analyzed to determine the degree of polymerization at a number of time points.
- **Pulsed Pressure (Compressibility) Experiments**
  - Small pulses of pressure were applied to the foam during expansion.
  - Pressures ranged from 0.25 psi to 1 psi.
  - Column with double sided glass and backlight was used to ensure accurate volume measurements.

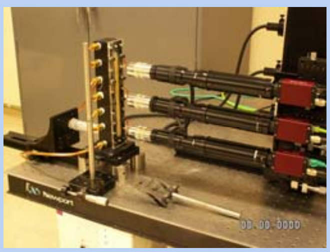


A diagram of the foam rise apparatus used for free rise and overpacked experiments.

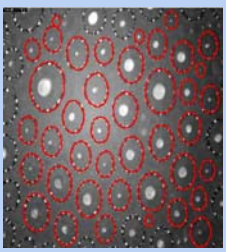


The volume data for a structural foam run at 30 C plotted against time.

- **Bubble Sizing Experiments**
  - A column of expanding foam was monitored by three close-up cameras (bottom, middle, top).
  - The resulting images allowed determination of the bubble size distribution at varying locations within the foam at the wall.
  - Multiple formulations and packings of foam were tested to observe the bubble size distribution of multiple formulations and the effects of overpacking on foam microstructure.
  - SEM images were taken after the foam had expanded to establish a relation between the foam on the inside of the column and the outer layer.
  - Image processing was performed on both image types. The majority of the wall images were analyzed using a Matlab image processing program (written by Grant Soehnel). The SEM images as well as the wall images that were particularly unusual were analyzed manually.



The bubble size testing apparatus. Water flows through the tubes to maintain the column at a reasonably constant temperature.



Example image from the bubble sizing experiments after Matlab image analysis.

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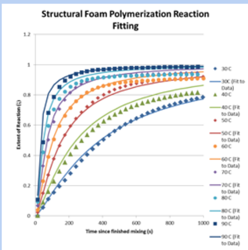
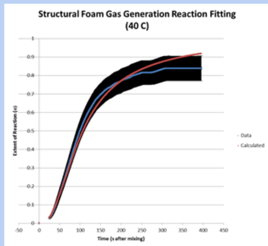
Results

- Kinetics Models
  - IR data as well as pressure, temperature and volume data was used to determine the extents of reaction at multiple time points.
  - Both rate laws were found to accurately predict the extent of reaction at early times.

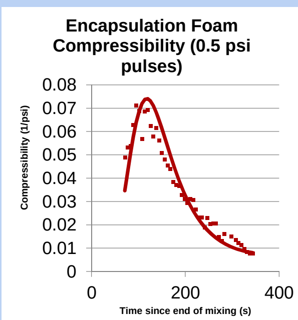


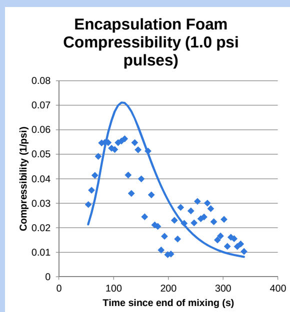


The fit of the polymerization reaction at temperatures ranging from 30 C to 90C.

The fit of the gas generation reaction at 40 C (the black bands are error bars of 8%).

- Compressibility
  - The volume data from the pulsed pressure experiments was used to calculate the compressibility of the foam at a number of time points.
  - A general equation form was developed by considering the physical transitions the foam undergoes (liquid to liquid/gas to gelled polymer/gas)

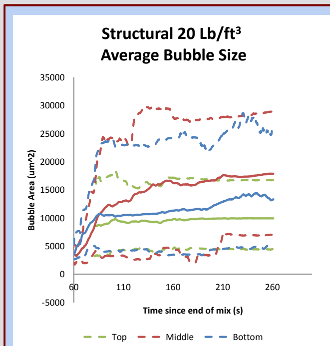


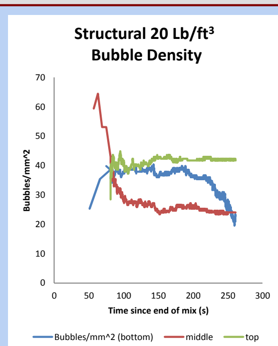


The compressibility equation fit against the compressibility data for encapsulation foam for both 0.5 psig and 1.0 psig. Note that the 1.0 psi data fits very poorly.

$$\beta_{Foam} = \beta_{Ideal}\alpha[k_1(\xi_{Max} - \xi)^n + k_2(\alpha_{Max} - \alpha)^m]$$

- Bubble Sizing
  - Bubble density, average bubble size, and bubble size distribution were determined using Matlab codes.



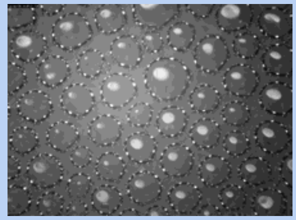


The average bubble size plotted against time, note that the dotted lines are the average bubble areas of the largest and smallest 10% of bubbles in each frame.

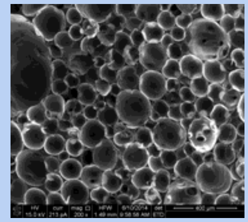
The bubble density for overpacked structural foam plotted against time for each camera.

Results (continued)

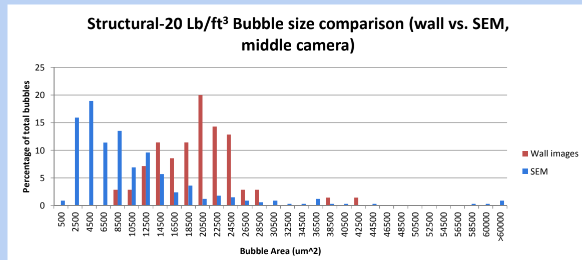
- Bubble size distributions at the side of the column and in the middle are very different, a relation between the two would allow a predictive model of bubble size at different locations during the foaming reaction.



Wall image of the foam after it has stopped expanding.



SEM image of the cured foam.



A comparison between the bubble size distribution of the outer wall of the foam and the inner portion of the foam.

Conclusions

- Kinetic Models
  - Both parameterized rate laws fit the data well at early times. The reaction forms and the parameters should be useful in improving the accuracy of the foam expansion model.
- Compressibility
  - The compressibility data confirms that the foam transitions from an incompressible liquid, to a slightly compressible gas-liquid mixture, to a slightly compressible gelled polymer-gas mixture during the reaction. The forms and parameters that define compressibility should also be useful in defining how the foam responds to pressure in the engineering model.
- Bubble Sizing
  - There is a significant difference between the bubble size distributions of the outer wall of the foam and the inner portion of the foam. The size distribution is also shown to vary significantly with height in the column.

Future Work

- Kinetic Models
  - While both rate laws fit the data well at early times and low temperatures, a better fit might be needed at higher times and temperatures. This would involve using an equation that switches smoothly from one behavior to another at a certain temperature or time.
- Compressibility
  - The 1 psi experiments did not match up well with the other experiments or the expected compressibility values. These deviations may be due to bubbles popping or uneven compression of the foam (leading to inaccurate volume measurements.) Further experiments may provide more details.
- Bubble Sizing
  - A mathematical definition of bubble size distribution as a function of position and time is still required.

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