SAND2008-1844C

PHYSICAL BLOWING OF AN EPOXY FOAM

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We describe the results of investigations of the blowing of epoxy foam with a physical blowing agent that boils as the material is heated. A series of experiments, ranging from temperature instrumented flow visualization studies to examination of single droplets, have been undertaken to understand the likely nucleation mechanisms, effects of air entrained during mixing, foam rise rates under different conditions, and the flow properties of the rising foam. With input from these experiments and microscale models, we are developing a homogenized continuum-level model based on a finite element discretization to help understand and predict the foaming process. Preliminary heat transfer models are compared to foam self-expansion experiments in geometries where exotherms from the polymerization reaction as well as heat transfer can dominate the physics. Models that also include foam expansion are described for simple two-dimensional geometries.

Introduction

Foams are ubiquitous low density materials used for a variety of applications including shock, thermal, and vibration isolation of electronic components, disposable containers, and energy production. Despite their many uses, foams are still not well understood at a fundamental level. Two major categories of foam exist: chemically blown foams and physically blown foams. Chemically blown foams expand via reactions than produce a gas phase during polymerization, e.g. polyurethanes, while physical blown foams begin with a dissolved blowing agent that boils to produce cells either by increasing the temperature or decreasing the pressure. For our applications, we are interested in a blown foam that starts off as an emulsion of Fluorinert blowing agent in epoxy monomer and curative. Once this emulsion is formed, the foam precursor is injected into the mold and inserted into an oven to boil the Fluorinert and produce foam. The complex interplay between heat transfer, polymerization, boundary conditions and nucleation of Fluorinert can make predetermination of the final foam density and amount needed to fill the mold difficult. The goal of this work is to provide a better understanding of the physical process of epoxy foam blowing and to begin to use that understanding to build engineering models.

Theory

Previous modeling of foam growth includes such work as Mao, Edwards, and Harvey [1] that assumes growth of the foam by gas diffusion into bubbles from material originally dissolved in the continuous phase. In our foams, the available gas comes from immersed droplets of the blowing agent, in this case Fluorinert (3M), which then changes from liquid to gas phase to produce gas bubbles and a foamy material. We have looked at both heat transfer limited and equilibrium limited evaporation of the inner drop into a surrounding gas layer that is in turn surrounded by the continuous phase (Figure 1).

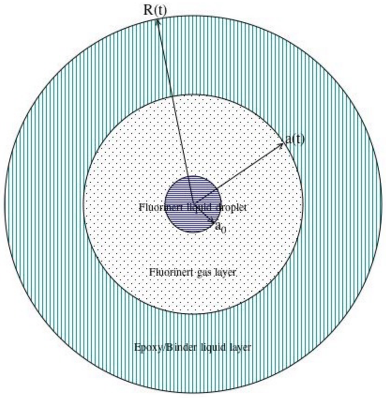

Figure 1. Single bubble model schematic

In all models, ours and Mao et al., the bubble expansion is predicted to be on the order of seconds at the longest. However, observations of our foaming process show that the growth is on the order of minutes. Therefore, we speculate that this process is actually nucleation limited and that nucleation occurs at a rate concomitant with the foam growth rate. We further speculated that one mechanism consistent with this observation is the collision between air bubbles rising and Fluorinert droplets sinking in the surrounding epoxy phase create nucleation events. (The air bubbles are introduced into the precursor foam material during mixing.)

Assuming that the bubbles and droplet are moving with their respective Stokes velocities, and knowing the sizes, densities, and viscosities of our system, we calculated that for a mean collision time on the order of one minute, the average distance between particles would be on the order of 100 μm. This is consistent with confocal images of the foam precursor emulsion (Figure 2). With our typical foams, the size of the air bubble dominates because of the dependence of the velocity on the bubble radius squared.

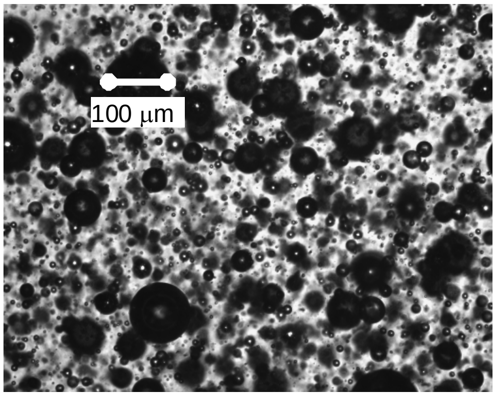

Figure 2. Microscopy of epoxy/blowing agent emulsion. Large dark circles are bubbles, small ones droplets.

Experiments

Nucleation: Single Bubble Experiments

To test this theory we examined the boiling of the epoxy/blowing agent mixture with and without the small particles normally added to be nucleating agents. We found that the particles were ineffective and that no boiling would begin until far above the oven temperature normally used, consistent with homogeneous nucleation in the absence of a nucleation site. Figure 3 shows the cell in which we study single droplet nucleation. The liquid Fluorinert is injected as a single drop above a needle that injects an air bubble. The surrounding epoxy is brought to a temperature above the boiling point of Fluorinert. Because the Fluorinert droplet is surrounded by another liquid and has no nucleation sites, it will remain indefinitely unless hit by the rising bubble (Figure 3).

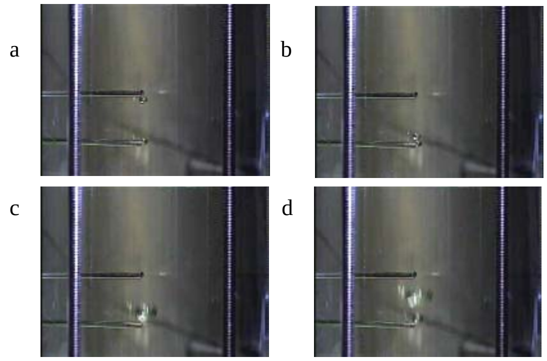

Figure 3. Fluorinert droplet held above its boiling point on the top needle drops onto an air bubble on the bottom needle and the Fluorinert vaporizes. a-d correspond to times 2.50, 2.84, 3.00, 3.04 s

Mixing studies

We also looked at the effect of mixing the two-part epoxy and how the method of air entrainment during this process affected the final product quality. Figure 4 shows the microscope images of the precursor foam for two mixing protocols. From this figure, we can also see that foam created from precursor with the highest air bubble density have the smallest, most uniform, bubbles, which is a desirable trait for our applications. This is consistent with the theory that the air provides the nucleation sites and nucleation mechanism.

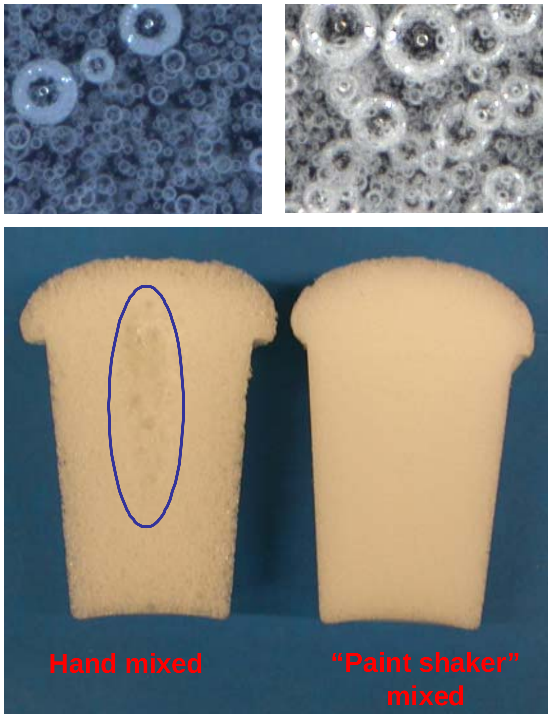

Figure 4. Hand mixing leads to fewer bubble in precursor and coarser, less uniform bubbles in the final foam, and the exotherm is also more apparent. Paint-shaker mixing gives a finer, more uniform microstructure.

Time-dependent density experiments

In order to create a preliminary engineering model of the foam rise, we decided to simply assign a rise rate to the foam based on empirical measurements using our known mixing techniques and oven temperatures. Experiments were performed in narrow slots so that the temperature would be as uniform as possible. Data on density versus time during blowing were collected, similar to that shown in Figure 5.

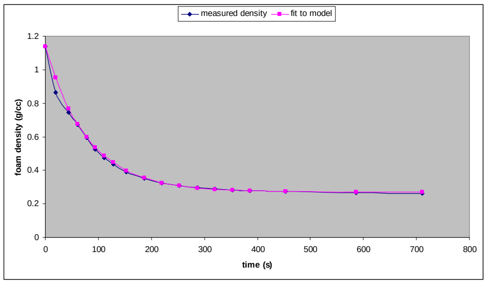

Figure 5. Density of a foam sample with time.

From Figure 5, and following Seo et al [2], we develop a simple time-dependent density model, which assumes no spatial variations.

$$\rho = \rho_f + (\rho_i - \rho_f)e^{-kt} \qquad (1)$$

For the data in figure 5, ρ_i=1.14g/cm^3, ρ_f=0.27g/cm^3 and k=1/80.

In addition, kinetic reaction data from differential scanning calorimetry and rheology data were collected. Through a formalism developed by Adolf et al. [3] we can predict the heat generation from the polymerization, as well as the viscosity evolution of a curing epoxy. What was not clear was how the generation of gas affected the viscosity of the foam. We tested the foam and showed that the Mooney Taylor relationship [4] held for our material:

$\mu = \mu_0 \exp(\frac{\phi_{gas}}{1-\phi_{gas}})$, where μ_0 is the continuous phase (epoxy) viscosity and ϕ_{gas} is the volume fraction of gas. To do this we measured the low shear rate viscosity of the foam in a conventional rheometer equipped with a parallel plate geometry, allowing the material to spill out of the rheometer as its volume increased. Using the same temperature ramp profile, we also measured the density with time as in the above experiments. Relating the two showed a good agreement with the Mooney Taylor relationship, only diverging when $\phi_{gas}>0.6$.

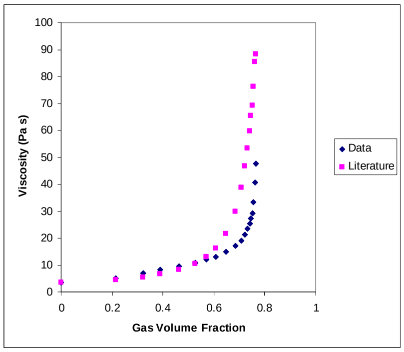

Figure 6. Foam viscosity

Finite Element Modeling and Results

We began model development by simply solving the energy equations coupled to a description of the polymerization of the epoxy based on condensation chemistry [3, 5]. Figure 7 shows a mesh representing foam in an odd-shaped mold made of two metals. The model predicts the region of highest temperature due to the exothermic polymerization (Figure 8). Figure 9 shows a photo of a cross-section of the foam, which exhibits large bubble sizes in this hot region, presumably from gas expansion before the material is fully cured.

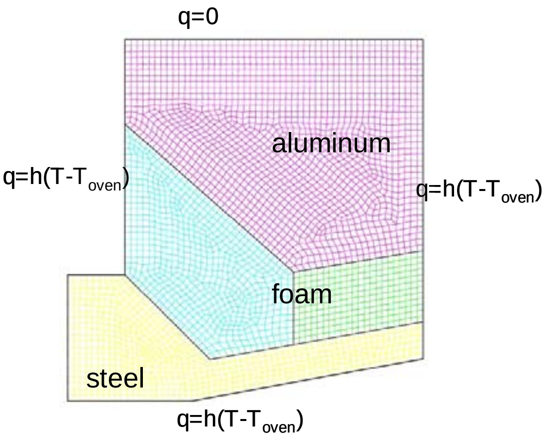

Figure 7. Axisymmetic mesh [6].

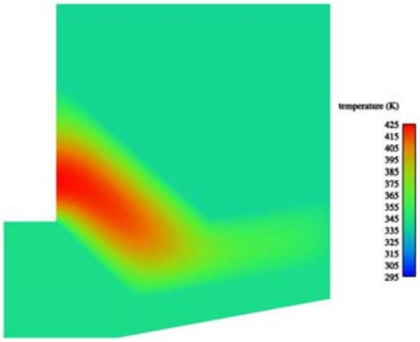

Figure 8. Model shows hot spot from curing exotherm.

Figure 9. Validation experiment [7]

Next we included the foaming process in our model by solving the momentum and continuity equations for a compressible material and adding a volume source term in the form of Equation 1. Therefore, the density is homogeneous spatially, but evolves with time. We use a level set formulation to track the advancing front [5, 8]. Figure 10 shows results of foam height and temperature evolving in a simple two-dimensional mold containing a round obstacle.

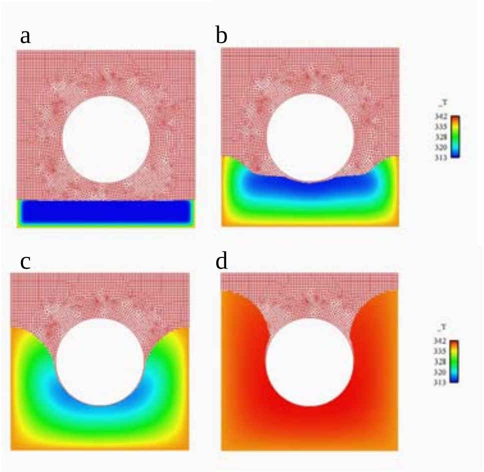

Figure 10. Foam self-expansion around an obstacle using a simple time-dependent density model with curing viscosity model: a) Unfoamed material in initial state b) Material starts to foam and heat up from the oven c) Foaming continues as does heat transfer from the oven d) Foaming is complete and material begins to exotherm creating temperatures hotter than the oven.

From this figure, we can see the precursor material at the initial time, which gives a flat interface (figure 10a). The foam precursor is preheated to a lower temperature than the oven, so no significant boiling occurs before it is placed in the oven. In the middle images (figure 10b,c), the foam begins to rise due to the heat transfer from the oven. On the final image, the foam has completed rising and has also reached the oven temperature. In addition, due to the exothermic nature of the epoxy polymerization, the material has heated up beyond the oven temperature. This reaction tends to occur at later times, making it possible to decouple the foaming and curing. The increased viscosity of the polymer keeps the foam from collapsing.

This model is simple enough that we expect to be able to use it in complex, three-dimensional geometries such as seen in figure 11.

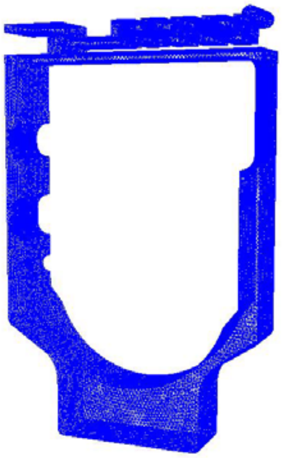

Figure 11. Complex test fixture for evaluating foams and processes

The test fixture shown in figure 11 is used to evaluate foams and test the processes used for foaming. It contains flow restrictions and sharp corners making it a good test of real materials and processes as well as numerical algorithms. We are hoping to use the methods used to produce figure 10 to foam this mold computationally.

Conclusions

We have studied a process to physically blow foam and created an empirical model to capture the changes in foam density with time, as well as the change in temperature from heat transfer and exothermic reactions. Although preliminary and with incomplete physics, this simple model can predict where hot spots, and, hence, areas of larger bubble sizes occur. It can also be used to predict fill rates and areas where the advancing front could lead to incomplete filling.

Acknowledgements

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under Contract DE-AC04-94AL85000.

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