SAND2011-1720C

Design of Chemically Blown Epoxy Foams

Lisa A. Mondy*, Mathew Celina, Jamie M. Kropka, Ed Russick, Rekha R. Rao

Sandia National Laboratories, PO Box 5800, Albuquerque, NM 87185-0346, USA

**Corresponding author: lamondy@sandia.gov*

Abstract. Polymeric foams based on epoxy or urethane systems often have limitations when complex geometries for electronic component encapsulation are being foamed. As reactive resins they may crosslink either too early resulting in flow limitations and insufficient fill, or too late resulting in drainage, beginning cell collapse and undesirable gradients in foam density and overall heterogeneity. We have developed a new epoxy foam based on an anhydride cure, which generally has slower kinetics than an amine-cured system. We use the decomposition of di-tert-butyl dicarbonate as a blowing agent. Additional gas generation and an early gelation reaction to enhance the foam stability is provided by polymeric isocyanates. We examine the cure and foaming kinetics with IR spectroscopy and volume vs. time measurements. We also use rheological measurements to correlate cell stability with relaxation and visco-elastic behavior under stress and chemical cure conversion. Finally, processing studies are used to assess the processability and quality of the final foam after filling a complex geometry.

Introduction

The typical encapsulation process we examine is to enclose an electronic part in a mold and fill the mold with pre-mixed, liquid, reactive components that then foam and cure around the part. The mold is later removed. However, foam encapsulation can be difficult to predict and control. Because the encapsulation occurs near the end of the manufacturing process, expensive components are at risk if the encapsulation is flawed.

All polymer foams have the propensity for their microstructure and density to change before it can be fixed through the polymerizing reaction. Liquid foams age by three basic processes: gravitational drainage of the continuous phase liquid, coalescence of bubbles because of rupture of the films separating them, and Ostwald ripening, which is the tendency of gas to diffuse from small bubbles to larger bubbles [1]. Our goal was to develop foams and processes that minimize these adverse behaviors of typical foams used to encapsulate electronics, specifically to: 1) Get better control of bubble formation by using a chemical blowing system for epoxy foams, 2) Minimize exothermic reactions, and 3) Make more stable foams that resisted drainage, coalescence, and ripening.

To achieve these goals we developed a “toolbox” of techniques that would not just allow development of one foam system for this project, but could be used in the future to tailor new foams for a variety of applications. In essence, we looked at the rates of foaming, curing, and destabilization processes, and we controlled these rates to develop an optimal foam for a model encapsulation application.

Chemistry

Chemical blowing for an epoxy system is not a straightforward option, perhaps the reason that cheap commercial epoxy foams are not available. Neither epoxy groups nor the commonly used amine curing agents allow for reactions that can be tweaked towards simple gas generation. The most attractive foaming principle for a chemically blown epoxy foam is either the catalytic decomposition of tert-butoxycarbonyl anhydride (BOC) [2] or the traditional isocyanate-water reaction to produce CO_2. An advantage of both CO_2 sources is that a single tert. amine catalyst (i.e. imidazole derivaties or aliphatic amines) facilitates the CO_2 generation plus the epoxy cure reaction as discussed below. Amines will instantly react with isocyanates, preventing the use of epoxy-amine systems blown with isocyanate-water. Therefore, we believe that any chemical foaming should involve epoxy systems that are amine-free. An alternative strategy was seen in the choice of acid anhydrides as cure agents; these are widely used in high-performance epoxy encapsulants. They are available as a large range of commercial phthalic acid anhydride derivatives.

Infrared (IR) cure monitoring of such systems is feasible by studying the pure resin, i.e. the pure epoxy-anhydride reaction, as well as its cure in the foam system. Key absorption bands (see Figure 1) that can be monitored are the consumption of isocyanate for foaming and parallel cure with polyol (2275cm^{-1}), consumption of the anhydride curative (1785cm^{-1}), consumption of the epoxy band (905-915cm^{-1}, but convoluted by a similar band native to the anhydride) and formation of the ester linkages from the epoxy-anhydride addition (in the range of 1733 -1700cm^{-1}).

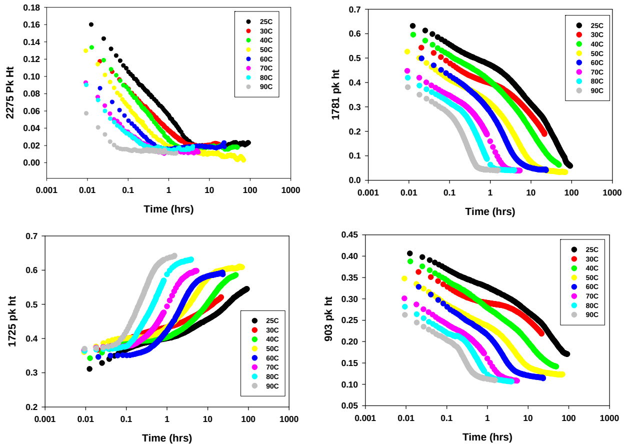


Fig. 1. The isothermal cure kinetics of a stable foam formulation in thin samples without exothermic self-acceleration. It demonstrates that the foaming and early gelation (consumption of band at 2275cm^{-1}) is considerably faster than the bulk of the resin cure (anhydride loss at 1781cm^{-1}).

The IR cure experiments demonstrate that the competition between foaming reaction and resin solidification cannot be independently resolved with spectroscopic means alone, as there is no specific signature of the CO_2 generating reaction. A better understanding of the individual foaming reaction and gas yield kinetics at different temperatures may be obtained by emphasizing the foaming reaction in an inert resin matrix. However, this approach is subject to other limitations, since the crosstalk between resin cure in parallel with the foaming process is complicated. We have observed that the epoxy anhydride cure reaction is kinetically significantly faster in parallel with the foaming reaction. We speculate that this is related to the chemical nature of the foaming reaction, most likely the contribution from the isocyanate-water addition, involving amine generation and thereby contributing additional nitrogen based nucleophilic catalysis sites. The byproducts from the foaming reaction will likely mimic the imidazole based catalysis and thereby facilitate the epoxy anhydride cure.

Regardless of the finer details of cure kinetics and their specific reactions, good quality chemically blown epoxy foams have been prepared by using a combination of epoxy resin, acid anhydride, some polyol and isocyanate, BOC, surfactant, and catalyst. While foaming is feasible at room temperature, curing is slow; therefore, elevated temperature is required to achieve suitable cure of the reactive foam system into glassy epoxy materials.

Foam stability

We can use isocyanate both as a foaming agent and as a component for an early gelation to facilitate bubble stability. Polymerization of the continuous phase will increase the viscosity of the liquid films between cells and lead to an increase in film stability and a decrease in liquid drainage rates, also slowing film thinning and lowering susceptibility to rupture. However, foam rise leads to thinner cell walls between the gas bubbles. Exactly how these competing interactions combine to define the stability of the foam as a function of time is difficult to surmise.

In order to better understand the effects of early gelation, we looked at the stability of foams blown with BOC decomposition without the anhydride curative. The viscosity of the epoxy resin was varied, as was the amount of isocyanate used for a early gelation reaction. Note that although small amounts of isocyanate were added, the polymerization reaction was limited to prevent the continuous phase from becoming rigid. Rheological measurements and images of the bubbles on a slide were then made to illuminate the effect on film stability (Figure 2).

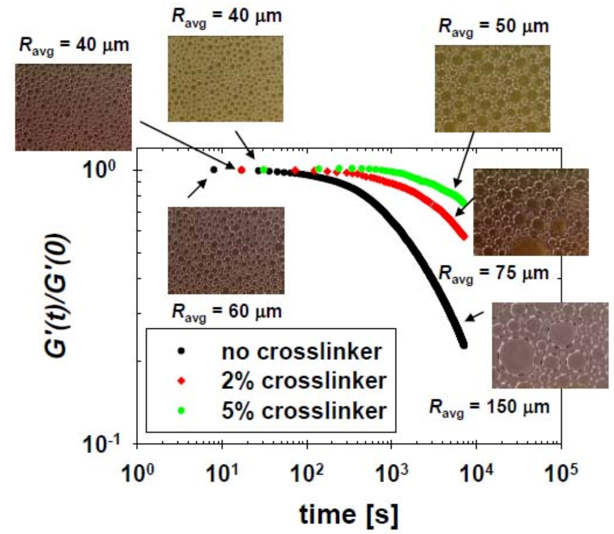


Fig. 2. Normalized elastic shear modulus versus time (foam age) for varying levels of polymerizing additive to the foam. Images of surface cells and number average cell radius are also shown at an early and late stage of the foam aging process. More crosslinking agent resulted in a later decline in the normalized elastic shear modulus and smaller bubbles at late times.

With the foams with no added polymerization, we noted that the temporal dependence of the shear modulus matches well with that of the inverse of the average cell radius, suggesting the modulus temporal evolution is a good monitor of the coarsening of the foam. Note that the foam gas fraction, which would also affect the modulus, does not change with age on the time scale of interest in these experiments.

Processing Studies

A high degree of early crosslinking will inevitably deliver quality foams but with little prospect of stability under mechanical shear (as during filling of tight places within the mold). A workable system must balance resin viscosity, early gelation, and overall cure kinetics. We also looked at the foam cell sizes and the internal structure of the resulting foams after the foams had filled a simple mold, either by self-rising around the obstacles or being pushed into the mold after reaching the ultimate gas fraction (Figure 3).

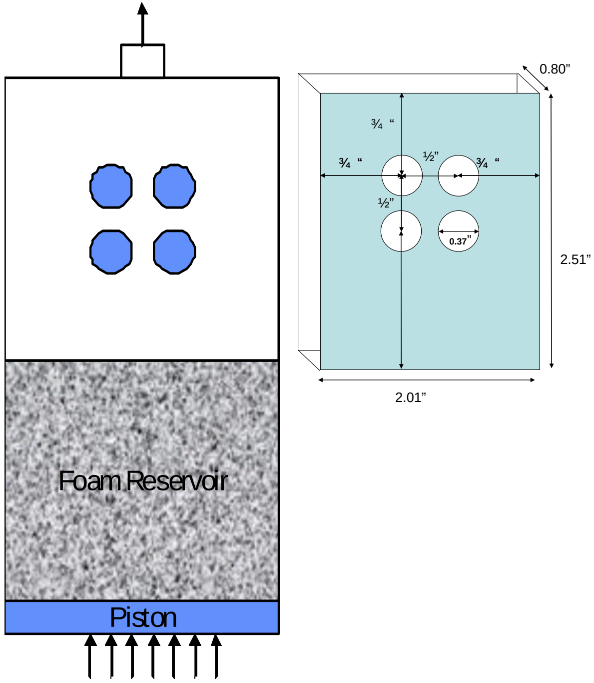
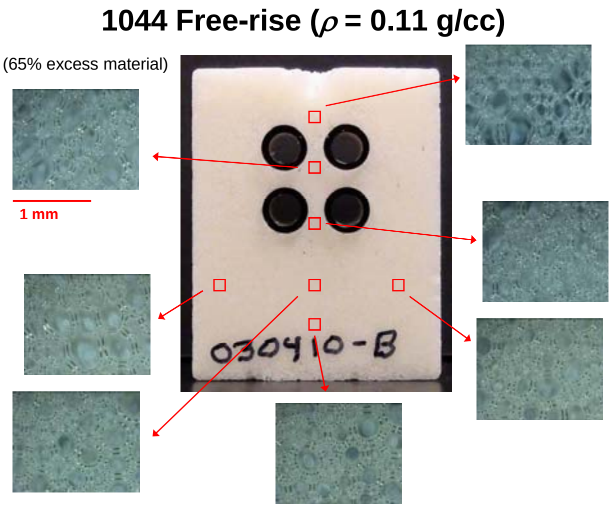


Fig. 3. Sketch of a mold (with detail of dimensions, right) where material flows around four posts, either after foaming, or if the piston starts at the top of the reservoir, during the foam rise.

Examples of results are shown in Figure 4, which compares the changes in bubble sizes for a foam, with a relatively high degree of early cross-linking, during self rising or piston-driven fill. Too much early cross-linking leads to distortion of cells near the wall when the shear rate is higher (during piston-driven flow).

Through balancing the rate of foaming and curing by varying the formulations and then testing in the apparatus of Figure 3, we chose a foam to compare to an existing physically blown foam used to encapsulate electronic parts. This physically blown foam, called REF, consists of an amine-cured epoxy mix containing a volatile liquid (Fluorinert FC-72®) that boils to act as a blowing agent when heated. The foam self-rises into the mold. We compared this foam to our new chemically blown foam (Figure 5).


1044 Free-rise ($\rho = 0.11$ g/cc)

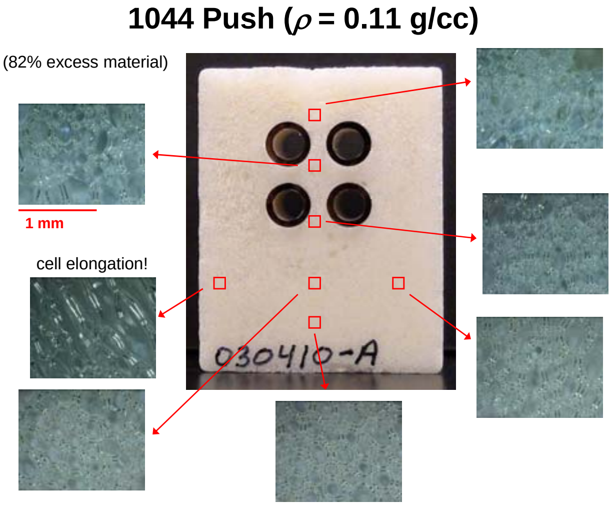

1044 Push ($\rho = 0.11$ g/cc)

Fig. 4. A test of a foam (formulation “1044”) that shows too much early cross-linking and resulting cell distortion. “Excess material” refers to the amount that flowed out the top of the mold.

Our final formulation for the new chemically blown epoxy foam also shows slightly less temperature rise during its exothermic curing reaction than the physically blown foam and much less than a polyurethane foam of similar density. This also helps the bubble size to remain more uniform.

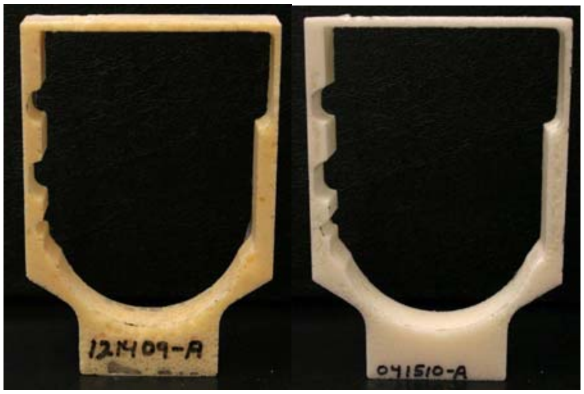


Fig. 5. Left, physically blown epoxy foam “REF”, which shows large voids near the bottom and uneven bubble sizes, compared to new chemically blown foam, right.

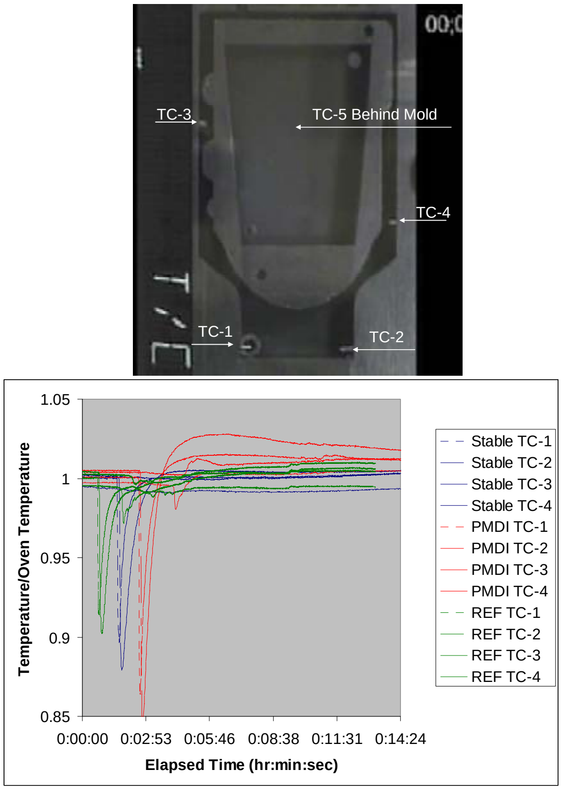


Fig. 6. Top, thermocouple locations in a mold. Bottom, normalized temperature measurements showing the effect of exothermic curing reactions of three types of foams, the new foam “Stable,” polyurethane “PMDI” and physically blown epoxy foam “REF”. All final foam products are of comparable density.

Temperature profiles in the mold used to create the pieces in Figure 5 are shown in Figure 6. The temperature goes down as the cool material enters the preheated mold. This dip is seen at different times based on the mixing protocol and speed that the foam could be injected. The times were not shifted for clarity.

Conclusions

Cheap commercial epoxy foams are not available, and we were motivated to create a new chemically blown epoxy foam in order to improve encapsulation of electronic parts. Current foam encapsulation materials are primarily either physically blown epoxy systems or chemically blown polyurethanes. The chemically blown foams have advantages of more predictable volume formation, but polyurethanes tend to cure quickly and have higher exotherms. The current epoxy systems rely on heat transfer to physically blow the foam, which can cause less predictable foam formation. Our goal was to combine the best of both classes of encapsulation materials.

Another goal was to determine techniques and a methodology to help develop new foams for many applications in the future. To this end we studied a variety of foam cell stabilization methods, one of which was discussed above and consisted of using an early gellation reaction to increase the viscosity without making the material rigid. We examined the rheology of curing foams and non-curing foams during foam aging, as well as the IR signatures of various foams and model systems during curing.

Acknowledgements

The authors would like to thank Ray Cote for helping with the flow apparatus development and experiments. This work was supported by the Laboratory Directed Research and Development program at Sandia National Laboratories. Sandia is a multiprogram laboratory operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

References

1. Weaire, D. and Hutzler, S., *The Physics of Foams*, Oxford University Press, New York, (1999).

2. M. Celina, US Pat. Appl. SD11248, Tert.-butoxycarbonyl Anhydride (BOC) as a Foaming Agent (2009).