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PHYSICAL BEHAVIOR AND DECOMPOSITION CHEMISTRY OF POLYMER FOAMS EXPOSED TO FIRE ENVIRONMENTS[*]

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ABSTRACT

The physical behavior of epoxy and polyurethane foams during thermal decomposition in oxygen-deficient environments was examined experimentally. Experiments were done with foam samples in a variety of configurations that imposed different thermal and physical boundary conditions. Depending on the polymer and the physical boundary conditions, samples liquefied and flowed due to gravity, formed a two-phase (vapor-liquid) material that flowed due to a pressure gradient, or formed a large volume of relatively stable char. In closed containers, erosive channeling by hot fluids also produced complicated three-dimensional foam decomposition zones.

INTRODUCTION

Organic polymer foams are used frequently in structures and transportation systems. Foams often provide mechanical or thermal isolation. Modeling the response of such structures and systems in fire environments has important applications in safety and vulnerability analyses. Polymer foams may provide fuel for a fire or be damaged catastrophically by an incident heat flux. Thermal damage can be important to analyses involving foams in oxygen-rich environments, such as air, or oxygen-deficient environments, such as closed containers. In oxygen-deficient environments, predicting heat transfer through thermally degrading foam materials can depend strongly on the physical behavior of the foam during degradation. Physical behavior depends on thermal and physical boundary conditions, initial polymer structure, and chemical mechanisms and kinetics controlling polymer decomposition. This paper discusses the physical behavior of epoxy and polyurethane foams during decomposition in oxygen-deficient environments. Experiments were done with foam samples of varying size. The largest samples were typically cylinders that were 8.8 cm in diameter and 5 to 15 cm in length. Several experiment configurations were used to impose different thermal and physical boundary conditions and gain insight into physical behavior of polymer foams in fire environments.

Depending on the polymer and the physical boundary conditions, samples liquefied and flowed due to gravity, formed a two-phase (vapor-liquid) material that flowed due to a pressure gradient, or formed a large-volume of relatively stable char. In closed containers, erosive channeling by hot fluids also produced complicated three-dimensional foam decomposition zones. Additionally, internal pressures reached 25 to 75 atmospheres, which usually caused violent failure of the container and an accompanying fireball. Pressure growth was reasonably reproducible; container failure was not.

EXPERIMENT

Results from two types of experiments are discussed in this paper: (1) tube-furnace experiments and (2) foam-in-can experiments. The tube furnace experiments were relatively simple

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and were used for initial investigations. Samples were normally rectangular in cross-section, about 2 cm on a side, and were about 3 to 4 cm long. The foam-in-can experiments were used for more detailed investigations, including examining heat transfer to foam encapsulated objects. Foam samples were typically cylinders about 8.8 cm in diameter and 5 to 15 cm in length.

The apparatus for the tube furnace experiments is shown in Figure 1. The foam sample was placed in a 25-mm O. D. quartz tube (~43 cm long). Flexible silicone purge and vent lines were connected to the quartz tube using 1-inch, 316 SS, ultra-torr™ (Swagelok) fittings with Viton® o-rings. UHP N_2 was used as purge gas. Flow was left to right, facing the figure. A tee was used on the purge outlet side to allow a K-type thermocouple to be placed in the center of the foam sample. The sample was periodically monitored by opening the furnace lid by a few centimeters and viewing the sample.

The apparatus for the foam-in-can experiments is shown in Figure 2. The basic features of the experiments are shown schematically in Figure 3a. Variations among experiments involved length and diameter of the foam sample, sample orientations, which are illustrated in Figure 3b-d, venting and pressurization, the maximum temperature of the heated plate, and the bulk density of the foam.

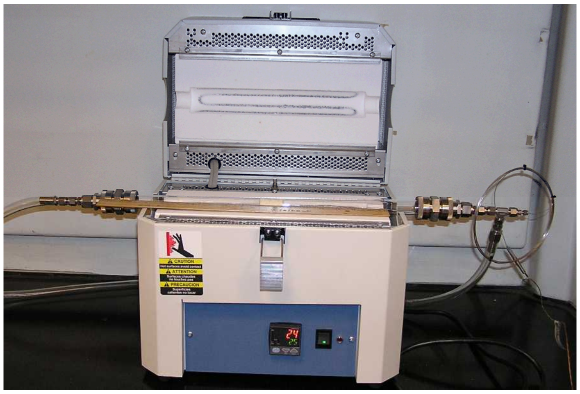

Figure 1. Tube furnace apparatus.

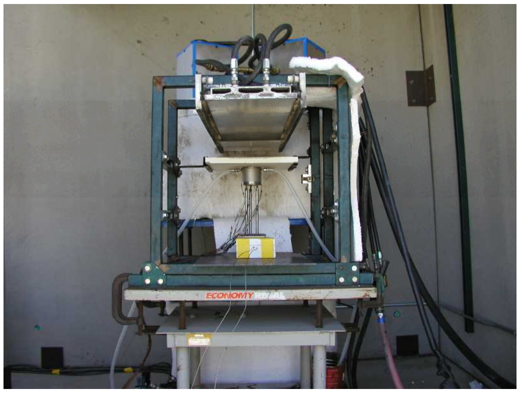

Figure 2. Foam-in-can apparatus.

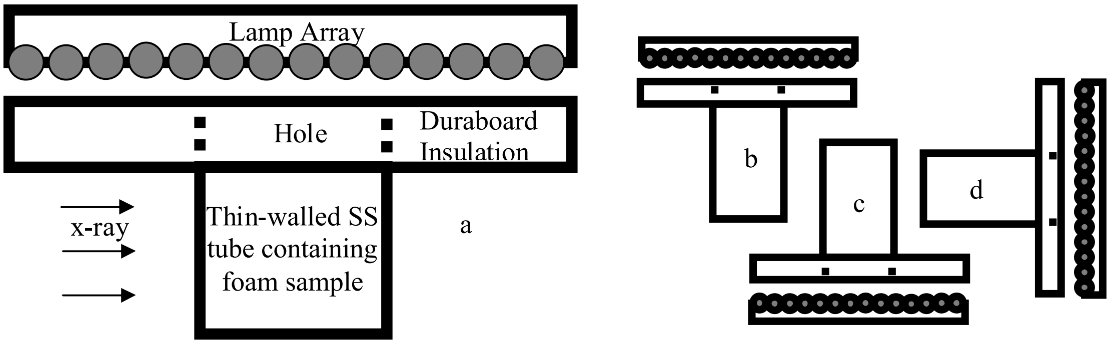

Figure 3. Foam-in-can experiments. (a) Schematic diagram of configuration. Sample orientations: (b) upright, (c) inverted, and (d) prone.

The foam-in-can experiments were done as follows. A foam cylinder was inserted into a metal sleeve, which was then sealed at each end. The end plate that was exposed to the heat lamp array (Figure 3a) was electron-beam welded to the sleeve. The opposite end was either sealed with another plate (electron-beam weld) or with epoxy. Variations in the design included (1) the number and size of vent/pressure-transducer ports near the heated plate of the container, (2) the sample and container length, (3) the thickness of the heated plate, and (4) the number and locations of thermocouples used for heating control and monitoring thermal boundary conditions. In each design, the sleeve was 321 SS tubing, with 8.89-cm (3.5-in.) outside diameter and 0.508-mm (0.020-in.) wall thickness. Metal end plates were made from 304 SS bar stock. The heated plate of each container was painted on both sides (interior and exterior) with Pyromark^{TM} 2500 series flat black paint to ensure consistent, uniform radiative properties. Usually, the foam was cast oversized and machined to a snug fit in the sleeve. Some experiments were done with foam samples having a diameter much smaller than the sleeve.

Seventeen quartz lamps were used to heat the samples. Each lamp was 9.53 mm (0.375 in.) in diameter and 25 cm (10 in.) in length. Each lamp had a maximum power rating of 6 kW. The 17 lamps were spaced 1.8 cm (0.72 in.) apart to form an array that was approximately 30 cm (11.8 in.) square. The lamps were mounted in a water-cooled aluminum holder with a polished surface behind the lamps. A maximum of 480 volts was supplied to the lamps through phase-angle fired Silicon Controlled Rectifiers, which had a maximum capacity of 1000 Amperes. A board of rigid insulation, 2.54 cm (1 in.) thick, was placed 3.8 cm (1.5 in.) from the lamps. An 8.9-cm (3.5-in.) diameter hole was located in the center of the board. The sample container's heated plate was located 5.7 cm (2.25 in.) from the lamps, under the insulation board, and aligned with the hole in the board. The plate was heated at a constant rate of 200 K/min to hold temperatures that were varied from 773 to 1273 K, after which the temperature of the plate was held constant for about 30 minutes.

Depending on the experiment, between 6 and 30 thermocouples were used for temperature control, recording temperatures over the container's surface, and in some cases recording temperatures inside the sample container. Temperatures were monitored with ungrounded, 0.81-mm (0.032-in.) diameter Inconel™-sheathed K-type thermocouples. Pressure data were usually acquired using Setra model 206 transducers. Temperature and pressure data were recorded at nominally 0.5 Hz using a LabView™-based data acquisition system.

Experiments were done outdoors in a three-sided concrete bunker (with concrete roof and concrete floor). The sample container and test fixture were monitored continuously with video cameras. The foam inside the sample container was imaged using a one- or two-X-ray camera system. The X-ray units were Philips 225 systems operated at 140kV and 15mA. The X-ray image frame rate was 0.2 Hz. In the two-camera case, the angle between the camera views was nominally 60 degrees.

RESULTS

Results from the tube furnace and foam-in-can experiments indicated similar types of physical behavior. Depending on the polymer and the physical boundary conditions, samples liquefied and flowed due to gravity, formed a two-phase (vapor-liquid) material that flowed due to a pressure gradient, or formed a large-volume of relatively stable char. In closed containers, erosive channeling by hot fluids produced complicated three-dimensional foam decomposition zones. Examples from tube furnace and foam-in-can experiments are given below.

Tube Furnace Experiments

Liquefaction and fluid flow due to gravity occurred with the TDI-polyether-polyol based flexible polyurethane foam TF-5070 (General Plastics Manufacturing Company). Figure 4a shows the initial sample and Figure 4b shows the sample following liquefaction and flow at a furnace temperature of about 543 K. Similar behavior was observed with a solid epoxy based on EPON 828 epoxy resin and polyamide curing agent.

Different behavior was observed with the MDI-polyether-polyol based rigid polyurethane foam FR-3712 (General Plastics Manufacturing Company), which liquefied and formed a two-phase (vapor-liquid) material that flowed due to a pressure gradient and subsequently formed char. Figure 5a shows the initial sample and Figure 5b shows the sample following liquefaction and two-phase flow at a furnace temperature of about 573 K. The resulting char had a highly non-uniform pore structure.

Experiments with Ablefoam (based on a novalac epoxy resin and Ancamine® Z curing agent) produced char and vapor[1]. Figure 6a shows the initial sample, and Figure 6b shows the char remaining after heating at 873 K for 4 hours. The sample retained its original shape but underwent a substantial reduction in volume during decomposition. (Liquid may accumulate in un-vented containers.)

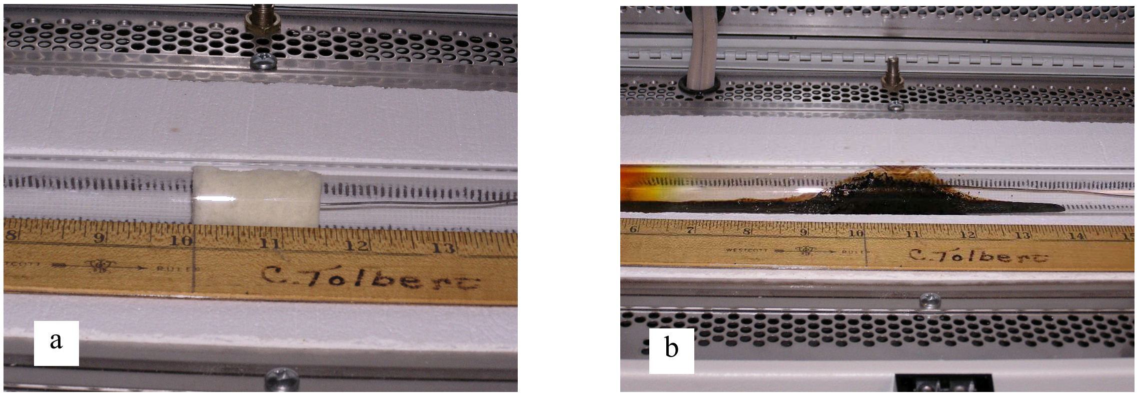

Figure 4. Results from a tube furnace experiment with TF 5070 flexible polyurethane foam: (a) initial sample and (b) liquefied sample.

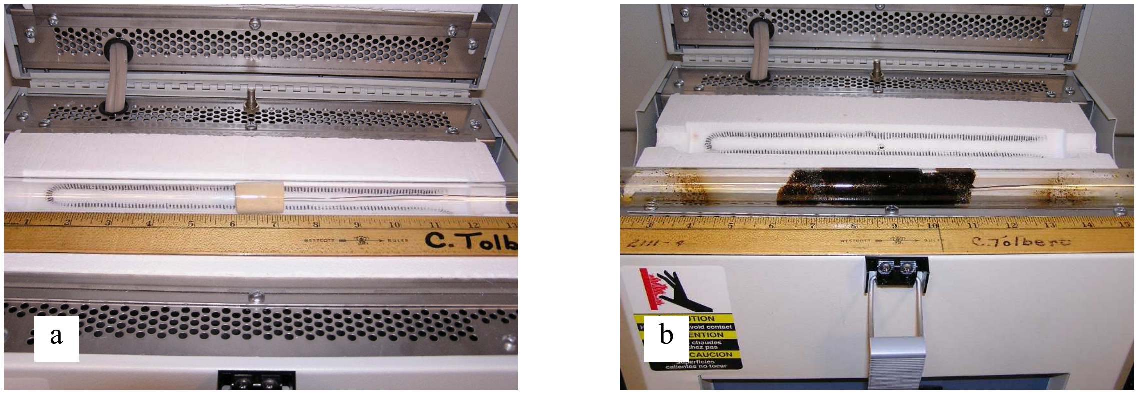

Figure 5. Results from tube a furnace experiment with FR3710 rigid polyurethane foam: (a) initial sample and (b) char residue after liquefaction and expansion due to internal gas generation.

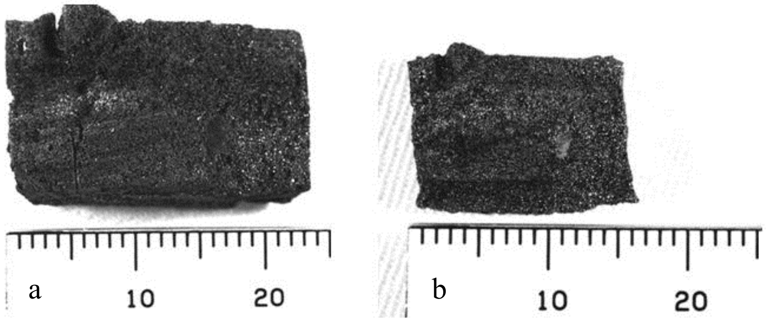

Figure 6. Results from a tube furnace experiment with Ablefoam: (a) initial sample and (b) char.

Foam-in-Can Experiments

Liquefaction and flow due to gravity were observed in vented foam-in-can experiments with a removable epoxy foam[2] (REF) developed at Sandia National Laboratories. Figure 7 shows results from a sample in the prone orientation[3] (see Figure 3d). The heated plate was heated at 200 K/min to a hold temperature of 1023 K. Figure 7a is an X-ray image of the initial sample, and Figure 7b is an X-ray image obtained midway through the experiment and shows a curved solid-fluid interface resulting from liquefaction and flow due to gravity.

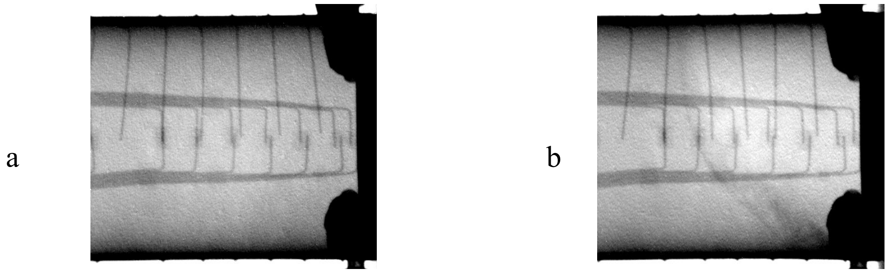

Figure 7. X-ray images from vented foam-in-can experiment with REF in prone orientation: (a) initial sample (b) midway through experiment.

Much different results were obtained during un-vented foam-in-can experiments with REF, which were done in upright, inverted, and prone positions. The heated plate was heated at 200 K/min to a hold temperature of 1193 K. Results from all configurations were similar. Initial liquefaction followed by erosive channeling by hot fluids produced complicated three-dimensional foam decomposition zones. Internal pressures reached 25 to 75 atmospheres that caused violent failure of the container and an accompanying fireball. Figure 8a shows an x-ray image of the initial sample, which had a bulk density of about 310 kg/m^3 (20 lb/ft^3). The x-ray image in Figure 8b shows the erosive channeling that occurred at about 2 minutes after heating began. Figure 8c shows an x-ray image of the deformed container at about 4.5 minutes after heating began and immediately prior to violent failure.

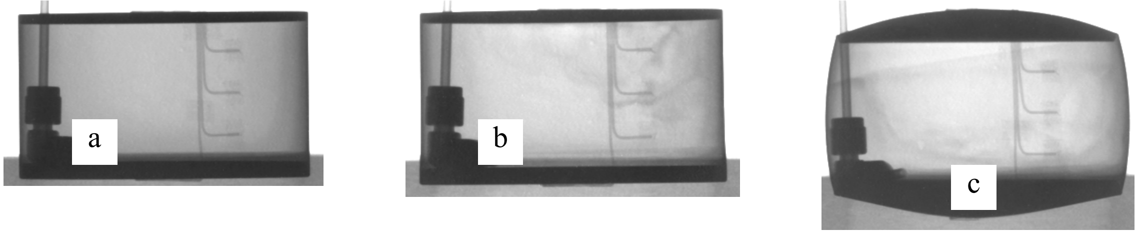

Figure 8. X-ray images from un-vented foam-in-can experiment with REF in inverted orientation: (a) initial sample (b) about 2 minutes after heating began, and (c) about 4.5 minutes after heating began.

Figure 9 shows results from a vented foam-in-can experiment with a removable syntactic epoxy foam (RSF) that contains 20 percent by weight (50 percent by volume) glass micro-balloons[2].

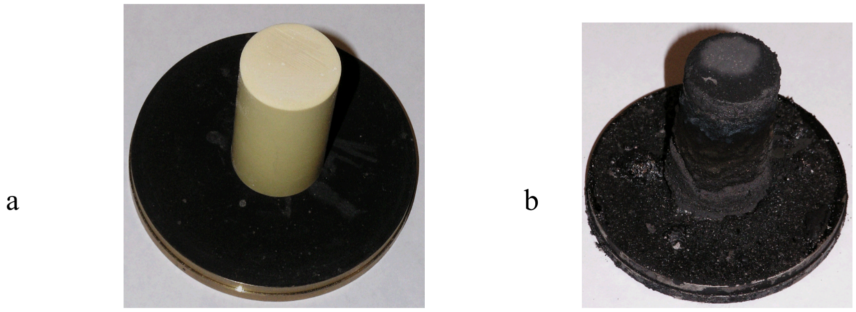

Figure 9. Results from vented foam-in-can experiment with a RSF: (a) initial sample prior to inserting in container and (b) sample after removing container following experiment.

The vented sample evolved decomposition gases and formed a char that retained the shape and volume of the original sample. The results from un-vented experiments were similar, except that some liquid accumulated in the bottom of the container.

SUMMARY AND CONCLUSIONS

The results described above show that polymer decomposition can, to varying degrees, involve the following types of physical behavior:

(1) Low-molecular weight inorganic gases and organic vapors will evolve, will exert pressure under confinement, and can cause bulk motion of the decomposing condensed phase. The decomposition of FR-3712 in a tube furnace experiment (Figure 5) illustrates two-phase flow due to internal gas generation and a pressure gradient in a vented system. The un-vented foam-in-can experiments with REF (Figure 8) illustrated erosive channeling by hot fluids that produced complicated three-dimensional decomposition zones. Furthermore, the container failed violently as pressure increased.

(2) The decomposing condensed phase will (a) form a liquid or fluid-like phase that flows due to gravity, which was illustrated by the tube furnace experiment with TF-5070 (Figure 4) and the vented foam-in-can experiment with REF (Figure 7); (b) form gases, vapors, and a solid char that may retain the shape and volume of the original sample, which was illustrated by results from the tube furnace experiments with Ablefoam (Figure 6) and by the results from the vented foam-in-can experiment with RSF (Figure 9); or (c) form both fluid-like phase and solid char, as well as gases and vapors.

The physical behavior discussed above depends on the thermal and physical boundary conditions during decomposition and the chemical mechanisms controlling decomposition. Decomposition mechanisms have been studied previously[4,5]. However, a discussion of physical behavior in terms of decomposition mechanisms is beyond the scope of this paper and is deferred to a later publication.

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