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LOW DENSITY FOAMS FOR VACUUM INSULATION

Final Report

September 1973

Bendix Corporation
Kansas City, Missouri

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VACUUM INSULATION

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September 1973

Prepared by W. E. Richardson

An investigation to find an open cell foam polymer for vacuum insulation has shown an epoxy-modified isocyanurate foam to be superior to urea/formaldehyde foams. Though improved during the study, the urea/formaldehyde foams still had problems of being too friable, dimensionally unstable, and possessed of the odor of unreacted formaldehyde. Thermogravimetric and thermomechanical analyses showed the epoxy-modified isocyanurate foam to be more thermally and dimensionally stable than the urea/formaldehyde foams.

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SUMMARY

An open cell foam polymer is needed for insulation under vacuum. Consequently, the Bendix Polymer Laboratory investigated two kinds of open cell foam: a urea/formaldehyde, and an epoxy modified isocyanurate.

The urea/formaldehyde proved unsatisfactory. Even after basic formulation improvements were made, problems still existed with friability, dimensional instability, and an ever-present odor of unreacted formaldehyde. The final foam formulation had a density of about 1 lb/ft³ (16 kg/m³), and had an open cell content approaching 100 percent.

The epoxy-modified isocyanurate foam had a density of about 2 lb/ft³ (32 kg/m³) and an open cell content of 95 percent. Thermogravimetric and thermomechanical analyses showed the epoxy-modified isocyanurate foam thermally superior to any of the previously developed or commercially marketed urea/formaldehyde foams.

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DISCUSSION

SCOPE AND PURPOSE

A project was undertaken by the Bendix Polymer Laboratory for the evaluation of low-density open cell foams as a vacuum insulator. Chemical, physical, and thermal characterization of potential candidate materials was a prerequisite for determining the requirements necessary for developing suitable foam systems. Because present usage of urea/formaldehyde foams has been limited in technical application, the consideration of this foam system for use in vacuum insulation is state-of-the-art technology.

ACTIVITY

Urea/Formaldehyde Foams

Urea/formaldehyde foams are formulated using a resin that is the end product of a controlled condensation reaction between urea and formaldehyde to form methylol and methylene ureas and partial polymers thereof.¹ A urea/formaldehyde polymer is formed in this way:

This equation represents the formation of a methylol urea. Further propagation of this compound through a condensation reaction forms a polymeric methylol urea resin.

Another reaction between urea and formaldehyde may form methylene diurea. This compound can react further with given quantities of urea and formaldehyde to form a polymeric methylene urea resin:

The urea/formaldehyde foam technology was based on a commercially available urea/formaldehyde foam called Oasis foam. A representative sample of this commercial foam was obtained from the Filfast Corporation, Floral Development Division. The density of the foam was found to be 1.25 lb/ft³ (20 kg/m³), and the open to closed cell ratio was 98.4 percent to 1.6 percent, respectively. The decomposition temperature of this foam, as determined by thermogravimetric analysis, was approximately 464°F (240°C).

The properties of density, cell structure, and thermal behavior were found to be inherent to this family of urea/formaldehyde foams. Formulating work was initiated with consideration of these properties as tentative goals.

A literature search revealed a typical example of a urea/formaldehyde foam formulation: 100 parts by weight urea/formaldehyde resin; 50 parts by weight water; 3 parts by weight foaming agent; 5 parts by weight urea crystal; and 5 to 8 parts by weight (amount will govern rate of set) curing agent.

Two American Cyanamid resins (URAC-110, a spray-dried resin in powder form, and URAC-180, a liquid with 65 percent solids content) and a Du Pont resin (Urea Formaldehyde 25-60) were used in the initial formulating work. Typical foaming agents (similar to liquid soap in that they form nucleated bubbles upon whipping) included such compounds as the alkyl aryl sulfonates (UltraWet 40 K produced by Arco Chemical), the polyoxyethylene tridecyl ethers (Renex 31 produced by Atlas Chemical), and the alkyl aryl polyoxyethylene alcohols (Tritox X-100 produced by Rohm and Haas).

The literature recommended the supplement of urea crystals with an inorganic acid, preferably one such as 75 percent phosphoric acid, as the foam's curing agent.

Preliminary formulations attempted to blend and froth the foam premix by using a high speed air-stirrer equipped with a Conn blade. Achieving a homogeneous blend was easy, but it was difficult to obtain the desired foam froth that would produce a density of 1 to 4 lb/ft³ (16 to 64 kg/m³). Several formulations were mixed in this way, and all were between 10 and 20 lb/ft³ (160 to 320 kg/m³), required at least a 24-hour cure cycle at room temperature, were closed cell, inherited cracks and voids following cure, and retained the odor of residual formaldehyde.

Most of these foams were of inadequate quality, so it was decided to alter the frothing technique by using a Hobart mixer.⁵ This process was advantageous because only small amounts of foaming agent were needed; the mixer's wire whip action yielded highly frothed foams. These foams appeared to be of the desired density and were predominately open-cell.

The various ways to process the foam premix using the Hobart technique were examined. The most convenient and appropriate method included a two-step mixing process. The urea/formaldehyde resin, foaming agent, curing agent, and other constituents were blended to the proper degree of homogeneity; then a mixture of water and acid catalyst were added. Mixing continued until gellation began. The frothed premix was then poured into an open end container. The foam cured in this condition. The foams obtained by this method, the only one studied for processing such a foam premix, were termed free-rise billet foams.

The formulating work showed the URAC-180 urea/formaldehyde resin made by American Cyanamid to be the most suitable. URAC-180, a liquid mixture of partially reacted urea and formaldehyde, contained 65 percent solids content in water. The best foaming agent was known by the trade name Ultra Wet 40K, produced by Arco Chemical. This material, an alkyl aryl sulfonate, has the properties similar to common liquid soaps.

A major problem with this foam was the odor of formaldehyde caused by the unreacted formaldehyde in the resin mixture. Because of this, part of the formulating work examined the introduction of additional curing agents to the foam premix to react with the free formaldehyde and eliminate the formaldehyde odor problem.

Because urea was the curing agent, the effects of increasing the urea concentration were examined. Concentrations up to twenty parts per hundred parts

by weight of resin (phr) were added. Not only did the increase in urea diminish the formaldehyde odor, but foam strength and cell uniformity increased.

Although other amine compounds such as ammonium carbonate, melamine, and thiourea were evaluated, they were found to inhibit foaming action. No explanation of this phenomenon was found.

Another problem concerned the accumulation of residual water in the cured foam specimens. Although the amount of water used in the formulation premix was reduced to a minimum, small amounts were nevertheless present in the matrix of each foam specimen. The foams were cured at higher temperatures to drive off the residual water. Foams cured at 176°F (80°C) retained no excess water. However, the higher cure temperature appeared to create dimensional instability: the foams possessed various degrees of shrinkage.

The major difficulty with the formulated foams was that of friability. The urea concentration study has little effect in reducing it. No specific test was employed to determine the degree of friability; it was determined merely by how the foams responded to handling and machining.

Patent literature discloses that the addition of selective aliphatic primary diols and triols had been successful for reducing friability problems.⁷ Several foams consisting of diol and triol ingredients were prepared; the constituent most responsible for making the foam less friable was the compound, 2-hydroxymethyl-2-methyl-1,3-propanediol. Besides being less friable, the foams developed from this formulation were more dimensionally stable. The diol reacts with the urea/formaldehyde composition to create a more structurally stable foam system. Various other alterations introduced to the basic formulation did not improve the physical properties of the cured foam specimens. This is an example of the basic urea/formaldehyde foam formulation developed by the Bendix Polymer Laboratory: 100 parts by weight of URAC-180 urea/formaldehyde resin; 70 parts by weight distilled water; 5 parts by weight urea crystal; 1 part by weight Ultra Wet 40 K foaming agent; 6 parts by weight curing agent (phosphoric acid, 75 percent); and 10 parts by weight of 2-hydroxymethyl-2-methyl-1,3-propanediol.

The mixing procedure included a 30-second premix of the resin, urea, foaming agent, and diol. Then the water and phosphoric acid mixture was added and the entire premix blended for another 30 seconds using the Hobart mixer.

The dimensions of foam samples made with different formulations varied when the foams were cured at room temperature as opposed to 176°F (80°C). (A cure temperature of 80°C was recommended by the patent literature.)

Shrinkage was an inherent problem for those foams cured above ambient temperatures. Following cure, the billet diameter was often found to have shrunk by as much as 20 percent. These foams were extremely friable and only test specimens for thermal analysis were obtainable from these foam samples.

The foams cured at room temperature were more dimensionally stable: less than 3 percent shrinkage was measured for them. However, thermogravimetric analysis (TGA) showed that these same foam samples contained residual water. TGA is used for determining weight loss in the form of thermal decomposition as a function of temperature. Water formed from the condensation reaction between the urea and formaldehyde as well as from the excess water employed with the foaming agent.

The thermogram (Figure 1) indicates quite clearly the loss of water from the foam samples cured at room temperature. These foam samples lost approximately fifteen percent by weight in residual water trapped in the cell matrix; this weight loss occurred between 75 and 212°F (25 and 100°C). Those foams cured at 80°C, although more friable, lost about seven percent of their weight in the same temperature range. The remainder of the thermogram profiles for the two foams were similar, indicating the major weight loss began between 446 and 464°F (230 and 240°C), the temperature representing decomposition. The thermograms presented here represented an average TGA profile for various foam formulations cured at room temperature and at 80°C.

For comparison, the thermogram of Oasis foam is also shown in Figure 1. It exhibits only a three percent weight loss up to 100°C while the onset of thermal degradation appears to occur at approximately 508°F (265°C). These factors suggest that Oasis foam has greater thermal stability with respect to weight loss.

The open-to-closed cell void contents of the different foam samples were determined using a helium pycnometer per ASTM designation D2856-70. The closed cell contents for the Bendix-prepared urea/formaldehyde foams are clearly higher than for the Oasis foam (Table 1), a factor significant in relation to the TGA results. The higher the closed cell content of the foam, the more water it retains. The foams cured at room temperature and possessing about a ten percent closed cell content retained more water than did the Oasis foam. The predominately open cell content of the Oasis foam allowed the water to evaporate or diffuse out of the foam matrix.

Foam samples possessing entrapped water or water vapor (or both) appeared to become somewhat plasticized when heated. This phenomenon was observed during thermomechanical analysis (TMA) of the foam specimens (Figure 2).

Figure 1. Thermogravimetric Analysis Comparison of Urea/Formaldehyde Foams

TMA is a method for determining the expansion and softening transitions of a material as a function of temperature.

The thermogram for the room temperature cured foams (ten percent closed cell) indicates gradual softening of the foams from about 104°F (40°C) to the decomposition temperature of 464°F (240°C), and a similar softening profile is noted for the 176°F (80°C) cured samples. However, because less water

Table 1. Open-to-Closed Cell Void Contents for Urea/Formaldehyde Foams

	Oasis Foam	Bendix U/F Foam	
		Room Temperature Cured	Cured at 176°F (80°C)
Total Void Content (Percent)	100	100	100
Open Cell Void Content (Percent)	98.4	90.0	92.3
Closed Cell Void Content (Percent)	1.6	10.0	7.7
Bulk Density (g/cc)	0.02	0.06	0.05

was present, the foams did not soften at the same rate. The thermograms presented here represent an average TMA profile for various foam formulations cured at room temperature and at 80°C. For comparison, the Oasis foam appears to soften at a slower rate than the two foam specimens mentioned previously.

This information clearly shows that the presence of water within the foam cell matrix created a softening of the foam structure. Thermal degradation, in the form of a softening transition, occurred at very low temperatures for the urea/formaldehyde foams discussed here. Cell collapse accounted for a large portion of the softening profile for the foams examined, and was so predominate that no foam specimens could be obtained for physical testing.

Epoxy-Modified Isocyanurate Foams

The problems of formulating urea/formaldehyde foams resulted in the evaluation of epoxy-modified isocyanurate foams.⁸ The available literature sources indicated that this foam system has many of the physical and thermal properties applicable for vacuum insulation.

An isocyanate resin combined with an epoxy resin was used. The chemistry of this resin polymerization is represented by the formation of an oxazolidone linkage:

Figure 2. Thermomechanical Analysis Comparison of Urea/Formaldehyde Foams

Actual isocyanurate rings can be formed and are susceptible to reaction with the epoxy groups in much the same manner as depicted by the above reaction.

Reaction of urethane groups with the oxirane ring can lead also to the formation of oxazolidone rings:

The premix formulation included a one-shot mixture of all the foam components, after which the foam was allowed to rise unrestricted. This is a typical formulation as derived from the literature: 60 g Isonate 135 isocyanurate resin; 40 g Epon 828 epoxy resin; 15 g Freon 11 blowing agent; 1.0 g L-5340 cell stabilizer; 7.0 g DMP-30 curing agent; 30 seconds premix time; 15 seconds mix time, and 10 minutes rise time.

This is the basic formulation. Several foams used varied concentrations of the resin, blowing agent, and curing agent concentrations; however, the test results on the epoxy-modified isocyanurate foams were based primarily on the above formulation.

The cured foam samples had an average free-rise density of about 2 lb/ft³ (32 kg/m³) and an open cell void content of about 95 percent, this value being somewhat higher than for the urea/formaldehyde foams. The notable

differences between the epoxy modified isocyanurate foams and the urea/formaldehyde foams were the degrees of friability and thermal stability.

Test specimens were easily prepared from the epoxy-isocyanurate free-rise foam samples. The TMA of the epoxy-isocyanurate foam showed softening at about 346°F (175°C). The TMA of the urea/formaldehyde foams had indicated gradual but continual softening from 86°F (30°C) until final cell collapse at 482°F (250°C). TGA determined that the epoxy-modified isocyanurate foams did not start thermal degradation until 663°F (351°C), as compared to 446°F (230°C) for the urea/formaldehyde foams. These values suggest the epoxy-isocyanurate foams to be more dimensionally and thermally stable.

ACCOMPLISHMENTS

Formulation, development and testing work was limited to urea/formaldehyde and epoxy modified isocyanurate foam systems. Several properties inherent to these materials were investigated and a basic foam formulation for each system was developed. In general, the epoxy modified isocyanurate foam appeared to be a more likely candidate for vacuum insulation than the urea/formaldehyde foams.

Because of limited effort expended on this project, a low-density foam for vacuum insulation was not fully developed. The work on this project, however, was considered state-of-the-art technology for the Bendix Polymer Laboratory, and the information gained from working with such foam systems will be useful when applied to future associated foam development activities.

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