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EPOXY FOAMS RESISTANT TO HIGH TEMPERATURES

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ABSTRACT

A new, heat resistant epoxy foam was recently reported by Chen and Nixon. It consists of Epon 828, 4,4'-diamino diphenyl sulfone (DDS) and trimethoxyboroxine (TMB). Because of its potential applications, this foam and several modifications were evaluated at Mound Laboratory. The modifications included other curing agents and a two-component resin system. The basic formulation was superior to its modifications in heat and solvent resistance. It also had a lower density and, consequently, a lower compressive strength. In flammability tests, all samples were self-extinguishing. For comparison of the basic formula with two-component systems, Epon 828 was cured separately with DDS and with TMB. These two-component systems did not foam. In qualitative determinations, the 828-DDS softened at 350-360°C; the basic formulation softened at 340°C; and the 828-TMB softened at 320°C. Chen and Nixon hypothesized that DDS and TMB react initially to form a highly cross-linked polymer, which then rapidly cures the epoxy resin. Attempts to prepare this polymer were unsuccessful. Other observations also tend to show that the hypothetical mechanism is improbable. A new mechanism is proposed in which all three components react initially to form one polymer with the evolution of methanol. This mechanism appears to fit the observed results better than that proposed by Chen and Nixon.

EPOXY FOAMS RESISTANT TO HIGH TEMPERATURES

INTRODUCTION

A new, heat resistant epoxy foam was recently reported by Chen and Nixon.^{1,2} The foam consists of epoxy resin, a primary aromatic diamine, and trimethoxyboroxine. This foam remained rigid up to 300°C and was self-extinguishing, chemically inert, and adhesive.

Because of its many potential applications, this foam system was evaluated at Mound Laboratory. The original foam was prepared and evaluated by some of the tests Chen and Nixon reported and by several additional tests. The effect of modifications to the basic formula was studied by using several different resins and curing agents in similar formulations.

As a result of this work the characteristics of the basic foam formulation were more completely defined. In addition, a curing mechanism was hypothesized which conforms more closely to the observed characteristics of the foam than the mechanism reported in the original work.

EPOXY FOAM FORMULATIONS

Description Table 1 lists the original epoxy foam formulation and three modifications which were investigated. The formulation developed by Chen and Nixon is identified as EF1.² In formulation EF2, a different curing agent was used, and in formulations EF3 and EF4 a two-component resin system was used. Epoxy resins other than those listed in the table (Epon 830, Epon 812, Epon 1002, and Oxiron 2000) were tested with various amines (p-phenylenediamine, tetraethylenepentamine, and Epon T-1); however, none of these combinations produced a foam satisfactory for comparison with the original.

To obtain a satisfactory cell structure in the modified formulations (EF2, EF3, and EF4) it was necessary to add a silicone surfactant, a nucleating agent, and acetone, an auxiliary blowing agent. None of these additives were necessary in EF1 due to its excellent cell structure and high foam rise.

Preparation Samples of the formulation of Chen and Nixon (EF1) were prepared by heating 20 grams of the epoxy resin (Epon 828) to 100°C in a 50-milliliter beaker. Six grams of 4,4'-diamino diphenyl sulfone (DDS) were slowly added while the mixture

Table 1

EPOXY FOAM FORMULATIONS (COMPONENTS IN PARTS BY WEIGHT)

Formula- ^a tion	Epon ^b 828	Oxiron ^c 2001	DDS ^d	Epon ^e U	TMB ^f	Cab- ^g o- sil	DC-113 ^h	Acetone
EF1	100	--	30	--	20	--	--	--
EF2	100	--	--	70	20	2.5	5	5
EF3	60	40	40	--	60	2.5	5	5
EF4	60	40	--	70	--	2.5	5	5

^aUnits are parts by weight; all samples were prepared using a total of 20 g resin.

^bEpoxy resin, Shell Chemical Co.

^cEpoxy resin, Food Machinery and Chemical Corp.

^d4,4'-Diamino diphenyl sulfone, curing agent.

^eModified polyamine curing agent, Shell Chemical Co.

^fTrimethoxyboroxine, Stauffer Chemical Co.

^gColloidal silica nucleating agent, Cabot Chemical Corp.

^hSilicone surfactant, Dow-Corning Corp.

was stirred with a magnetic stirrer. After the amine dissolved (approximately five minutes), the mixture was transferred to a four fluid ounce paper cup. When the mixture had cooled to room temperature, four grams of trimethoxyboroxine (TMB) were added to the mixture, which was then mixed by hand. Foaming began 55 seconds after TMB addition.

Samples of EF2, EF3, and EF4 were prepared by hand mixing all components, less TMB, in a four fluid ounce paper cup. The TMB was added last. It was found that addition of TMB to a solution of DDS in a mixture of Epon 828 and Oxiron 2001 (EF4) caused a vigorous reaction.

Sample Evaluation The foam samples prepared by the above procedures were cut into 1.2-inch cubes for density (ASTM 1622-58T) and compressive strength (ASM 1621-59T) determinations. The measured values are given in Table 2. Formulation EF1 had a significantly lower density and compressive strength than the modified formulations. Samples of EF1 were also less brittle than samples of the other formulations as shown by the values for percentage compression.

Table 2
PROPERTIES OF EPOXY FOAMS

Formula- tion	Density (lb/ft ³)	Compressive Strength (psi)	Compres- sion (%) ^a	Solvent Resistance (% wt. loss)				Heat Resistance ^b (% wt. loss)		
				Benzene	Ethanol	Acetic Acid	Dimethyl- formamide	260°C	300°C	340°C
EF1	7	33	10	5.8	12.3	0.4	1.5	6.33-R (270°C)	12.06-R	17.61-R (330°C)
EF2	21	680	5.3	0.2	10.8	8.5	12.4	18.1-SR	37.3-SR	59.2-D
EF3	13	180	5.0	6.1	49.5	39.5	47.6	14.9-R	19.8-R	28.2-R
EF4	31	597	3.0	6.2	40.0	24.9	10.9	12.2-SR	35.2-S	61.5-D

^aIndicated compression at maximum pressure.

^bThe letters in these columns refer to sample condition at the end of the test: R-Rigid; SR-Semirigid; S-Soft; D-Decomposed

The resistance of the foams to selected solvents was determined by placing a weighed sample (1/4 x 1/4 x 3/4-inch) in the solvent for seven days. After the solvents were decanted, the samples were exposed to the atmosphere for an additional seven days. The last traces of solvent were removed by placing the samples in a vacuum oven for 24 hours at room temperature. The percentage weight loss, based on initial sample weight, was then determined (Table 2). The solvent resistance of EF1 was generally superior to the other formulations. The only solvent in which EF1 swelled was dimethylformamide. Formulation EF2 surpassed EF1 only in resistance to benzene and ethanol.

The effect of short-term exposure to high temperatures was determined by placing a weighed sample in an oven at the test temperature for one hour (see Table 2, Heat Resistance). Before removal from the oven, the sample was examined for rigidity. After the foam cooled, the percentage weight loss was determined. The superior heat resistance of EF1 as compared with the other formulations is shown in Figure 1.

Figure 1

EFFECT OF SHORT-TERM EXPOSURE TO HIGH TEMPERATURES
ON EPOXY FOAMS

Flammability was determined simply igniting the foam samples. All samples were self-extinguishing. This property is attributable to the formation of B_2O_3 upon initial burning.

These physical tests indicated that formulation EF1 is superior to the other formulations in all aspects except compressive strength. That EF1 has a lower compressive strength is to be expected due to the low density of the foam.

Preparation and Comparative Evaluation of Two-component Systems

Samples of Epon 828 were also cured with DDS (828-DDS or TMB (828-TMB) to compare the thermal stability of these two-component systems with the three-component foam system.

The sample of 828-DDS was prepared by slowly dissolving six grams of the amine in 20 grams of heated (100°C) Epon 828. The mixture was transferred to a cardboard mold ($3 \times 1\frac{3}{4} \times \frac{3}{4}$ -inch) and cured for one hour at 120°C ; then the sample was post-cured at 200°C for an additional two hours. The sample of 828-TMB was prepared in a similar manner. All the samples including EF1, were post-cured under similar conditions. The two-component systems did not foam.

Thermogravimetric analyses of EF1, 828-DDS, and 828-TMB were performed on an Aminco Thermogravimetric unit in air at a nominal temperature rise of 6°C per minute. The weight loss was determined at 10°C intervals. The weight loss curves obtained from thermogravimetric analyses of these materials are shown in Figure 2.

The softening point of EF1, 828-DDS and 828-TMB was determined by placing the samples in a muffle furnace at 200°C and heating at an arbitrary rate of 2.6°C per minute. The samples were examined for rigidity at approximately 10°C intervals until they had softened. The 828-DDS sample remained rigid at 350°C , decomposing between 350° and 360°C . EF1 softened at 340°C , while 828-TMB softened at 320°C .

CURING MECHANISM

In proposing a mechanism for the cure of their epoxy foam system, Chen and Nixon hypothesized that the primary aromatic diamine and the trimethoxyboroxine react initially to yield a highly

Figure 2

WEIGHT LOSS AS A FUNCTION OF TEMPERATURE FOR AN EPOXY FOAM (EF1), AN AMINE-CURED RESIN, AND A BOROXINE-CURED RESIN

cross-linked polymer containing B-N bonds and the methanol blowing agent. The equation is as follows:

The polymer then reacts to give a rapid cure of the epoxy resin according to the following equation:

The polymerization is terminated by the scission of boron-nitrogen or boron-oxygen bonds. This mechanism was based essentially on the fact that

- (a) the foam resulting from EF1 was rigid above 300°C while a foam prepared from Epon 828 and TMB softened at 158°C; and
- (b) a rapid, highly exothermic room temperature cure was obtained in the foam system but not in 828-DDS or 828-TMB.

The hypothetical mechanism was tested in the following experiment. Sixteen grams of DDS and 12 grams of TMB were added to a 500-milliliter, round-bottom flask fitted for distillation. The flask was heated in an oil bath maintained at 150°C. The DDS-TMB mixture was a clear amber liquid at 150°C; a vapor was evolved from the mixture. The portion of vapor distilling at 40-50°C (vapor temperature) was collected. Upon cooling, the residue in the flask solidified. Recrystallization of this solid from ethanol gave crystals which melted at 173°C; the melting point was undepressed upon admixture of pure DDS. The distillate was collected and treated with water; the resultant precipitate was recrystallized from water (d. 173-175°C). It is reasonable to assume that the original distillate was trimethyl borate, which is known to decompose in water to boric acid and methanol.³ The formation of a polymeric substance was not observed.

Since the attempts to prepare a polymer from TMB and DDS were unsuccessful, the question arose as to validity of the hypothesized mechanism in which the two were reported to have formed a highly cross-linked polymer. Also, results showed that the 828-DDS system remained rigid at a temperature slightly higher (approximately 10°C) than the epoxy foam. This fact diminishes the validity of postulate (a) above. The same type of mechanism as postulated by Chen and Nixon could operate regardless of prior polymerization of DDS and TMB. This mechanism is shown in the following equation:

Since the amine has three reaction sites remaining, and the boroxine two, a highly cross-linked structure would be expected. The rapid exothermic reaction observed during foaming may be explained by the possibility that a mixture of TMB and DDS could have a synergistic effect in Epon 828. The reaction in Equation (3) would proceed until gelation of the resin rendered the unreacted ends of the polymer chains immobile and unable to approach any remaining reaction sites. If such is the case, there would be a polymer structure similar to the following:

Comparison of the weight loss curves (obtained by thermogravimetric analysis) of an EF1 sample which was not post-cured with one which was post-cured (Figure 3) shows a weight loss in the non-post-cured sample at a temperature much lower than the initial weight loss in the post-cured sample. This otherwise unexplainable weight loss is probably due to decomposition of the unreacted boroxine groups shown above. The mechanism shown in Equation (3) does not require the beaking of B-N or B-O bonds as the means of terminating the polymerization. Such a method of termination seems rather anomalous, for these bonds (B-N and B-O) must themselves be stable if the postulated initial TMB-DDS polymer is to contribute to the thermal stability of the foam.

CONCLUSIONS

The epoxy foam system of Chen and Nixon is superior to any of the modified systems tested. Although this material has relatively low compressive strength and contains material which volatilizes below 200°C, it has excellent heat and solvent resistance. The

Figure 3

EFFECT OF POST-CURING AT 200°C ON THE VOLATILES
CONTENT OF EPOXY FOAM, SAMPLE EF1

superior thermal stability of the formulation is attributable to two factors, a highly cross-linked structure and the fact that each of the components imparts thermal stability to Epon 828.

While the curing mechanism proposed as a result of these tests is not entirely proved, it fits the observed results better than the mechanism proposed by Chen and Nixon.

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