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Curing of Epoxy Resin with Phosphorylated Diamine

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ABSTRACT

The diglycidyl ether of Bisphenol-A (DGEBA), suitable for the manufacture of epoxy-glass fiber laminates, has been cured with bis(m-aminophenyl)methylphosphine oxide (BAPO), and the results have been compared with a commercially available 4,4'-diaminodiphenyl sulfone (DDS). DSC studies indicated that an increase in the concentration of diamine resulted in an increase in the extent of the curing reaction even above the optimum level of diamine. Cured resins were stable up to 300°C and started losing weight above this temperature. Glass fabric-reinforced laminates based on DGEBA:BAPO exhibited a higher limiting oxygen index (LOI), as well as higher shear and flexural strength than those based on the DGEBA:DDS system. Thermal aging at 185°C for 100 h did not affect the mechanical properties of laminates. However, a significant decrease was observed in interlaminar shear strength by boiling in water for 100 and 200 h.

INTRODUCTION

Application of composites—defined as a combination of organic matrix resins and fiber reinforcement—has grown considerably in the aerospace industry and in load-bearing structural applications. Epoxy polymers have emerged as the most important matrix material in such advanced fiber-reinforced composites. The major motivation for such growth has been the reduced weight, which leads to a decrease in fuel consumption by the aerospace and automobile industries. It is, however, desirable to have flame-resistant resins in fiber-reinforced composites.

A variety of epoxy resins which retain their properties at high temperatures have been developed [1-5]. The chemical structure, functionality, composition, and extent of reaction can influence the properties of these resins. In the present work an attempt has been made to improve the flame resistance of epoxy resin by curing with phosphorylated diamine. The system based on diglycidyl ether of Bisphenol-A (DGEBA) and bis(m-aminophenyl)methylphosphine oxide (BAPO) was selected. The effect of composition was investigated by varying the ratio of diamine to DGEBA. Glass fiber-reinforced composites were fabricated, and their mechanical properties and aging behavior were also investigated. A literature survey has revealed that no systematic work on curing of DGEBA with BAPO has been carried out.

EXPERIMENTAL

Starting Materials

The diglycidyl ether of Bisphenol A (DGEBA) (Hindustan Ciba-Geigy) was used. The epoxy equivalent (176.8) and the percent oxirane oxygen of the epoxy resin were determined by an acidimetric method [6]. Synthesis of bis(3-aminophenyl)methylphosphine oxide (mp 146-149°) was carried out starting from triphenylphosphine (SISCO), the details of which have been described elsewhere [7]. 4,4'-Diaminodiphenyl sulfone (Fluka AG) was used as received.

Curing of Epoxy Resin

Curing studies of epoxy resin were done by varying the amounts of diamine (BAPO) (10, 20, 30, 35, 40, and 50 phr). 4,4'-Diaminodiphenyl sulfone (DDS) was also used for curing (10, 20, 30, 37, 40, and 50 phr). About 2 g of epoxy resin was slightly heated and mixed with the known amount of diamine, then ~5% methyl ethyl ketone was added as a diluent. The solution was thoroughly mixed before placing it in shallow aluminum dishes. These dishes were then kept in an air oven for 2 h at $175 \pm 5^\circ\text{C}$

for BAPO and $185 \pm 5^\circ\text{C}$ for DDS. After curing, the dishes were cooled to room temperature in a desiccator.

The extent of crosslinking was determined from the quantity of the insoluble fraction remaining after extraction with DMF. Percentage solubility of these resins in DMF was calculated by weighing the resins before and after extraction:

$$\% \text{ solubility} = \frac{W_0 - W_1}{W_0} \times 100,$$

where W_0 = initial weight of polymer and W_1 = weight of insoluble material.

Characterization

The curing behavior of DGEBA with BAPO was monitored by differential scanning calorimetry (DSC) in the temperature range $40\text{--}320^\circ\text{C}$, by using a Du Pont 1090 Thermal Analyzer with a DSC module (Du Pont Model 910). For this purpose, 10–15 mg samples of epoxy resin containing different concentrations of diamine (phr) were placed in aluminum crucibles which were then crimped. A heating rate of $10^\circ\text{C}/\text{min}$ was used.

The thermal stability of cured epoxy resin was determined by use of a Du Pont 1090 Thermal Analyzer with a 951 TG module. The measurements were carried out in a nitrogen atmosphere (flow rate 100 mL/min) at a heating rate of $10^\circ\text{C}/\text{min}$. The glass-transition temperature of composites in an N_2 atmosphere was determined with a Du Pont 982 Dynamic Mechanical Analyzer (DMA). A heating rate of $5^\circ\text{C}/\text{min}$ was used. IR spectra of the cured resin samples were also recorded on a Sp-1200 PYE Unicam IR Spectrophotometer.

Composite Fabrication

Test laminates were prepared by using epoxy-compatible glass fabric (RP-6, Fiberglass, Pilkington, weighing $200 \text{ g}/\text{m}^2$). Eight pieces of $5'' \times 5''$ glass fabric were coated with DGEBA having 35 phr BAPO and diluted with 30% (w/w) methyl ethyl ketone. These "prepregs" were dried in air at room temperature for 15 min and then kept at 100°C for 30 min in a circulating-air oven. The dried prepregs were stacked together and pressed between steel sheets coated with silicone mold-release agent. The resulting laminate was then cured in a flat platen press (Carver Laboratory Press) at 100°C for 1 h at a pressure of $10 \text{ kg}/\text{cm}^2$ and then at 140°C for another 4 h at $20 \text{ kg}/\text{cm}^2$. Postcuring was done at 180°C for 4 h.

The resin content of the laminates was determined by pyrolysis in a furnace. A known quantity of laminate (~ 0.3 g) was heated in a furnace at 500°C in a silica crucible for 4 h, and the residual fibers were weighed. There is a possibility of formation of phosphorus oxides during pyrolysis which may be chemically incorporated into the glass, leading to a slight overestimate of the residual fiber weight. The void content was determined according to the ASTM Standard D2734-37.

The limiting oxygen index (LOI) of test laminates was determined by using a Stanton Redcroft FTA flammability unit (ASTM D2863-70). LOI, which is the quantity of oxygen (by volume) in a mixture of oxygen and nitrogen which supports burning, was evaluated as follows:

$$\text{LOI} = \text{O}_2 / (\text{O}_2 + \text{N}_2).$$

Interlaminar shear strength (S_H) was determined according to ASTM D 2344-76 using an Instron (Model No. 1122). A span-to-depth ratio of 5:1, a crosshead speed of 1 mm/min, and a sample width of 0.5 in. were used.

$$S_H = (0.75 \times P) / bd,$$

where P = breaking load (kg), b = width of the specimen (m), and d = thickness of the specimen (m).

The flexural properties of the laminates were determined according to ASTM D790-71. A span-to-depth ratio of 32:1, a width of 0.5 in., and a crosshead speed of 10 mm/min were employed.

$$\text{Flexural strength} = 3PL / 2bd^2,$$

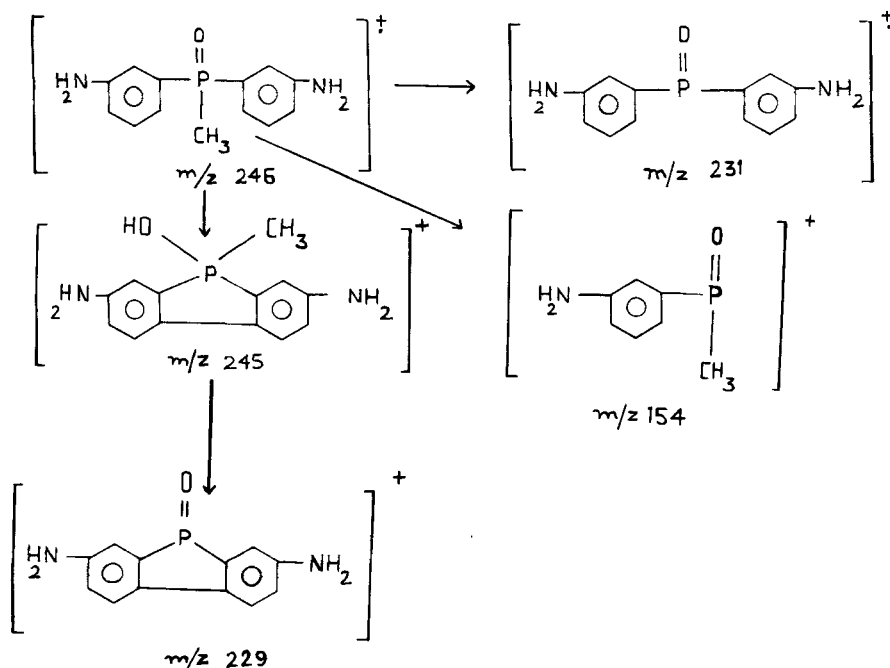
where P = load at the moment of break (kg), L = support span (m), b = width of specimen (m), and d = specimen thickness (m).

The effect of heating on laminates was also evaluated. The composites were cut into suitable pieces, weighed, and subjected to heat treatment at $185 \pm 5^{\circ}\text{C}$ in an air oven for 100 h. The samples were preserved in desiccator. The change in weight of samples as a result of heating was determined. The mechanical properties of heat-aged laminates were also evaluated.

The effect of boiling water on the shear strength of laminates was evaluated by boiling the samples in water for 100 and 200 h. The change in weight of the samples, which is indicative of moisture regain, was determined as was the shear strength.

RESULTS AND DISCUSSIONS

Bis(m-aminophenyl)methylphosphine oxide (BAPO) was characterized by IR, $^1\text{H-NMR}$, and mass spectroscopy. Characteristics absorption bands due to the amino group were observed at 3370 and 3220 cm^{-1} . Other absorption bands were observed at 1620 cm^{-1} (N-H bending vibrations), 1440 cm^{-1} (P-C stretch), 1280 and 1320 cm^{-1} (C-N stretch), and 1600 and 1480 cm^{-1} (aromatic groups, skeletal vibrations). In the mass spectrum of BAPO, the molecular ion peak (m/z 246) was also the base peak. The m-1 fragment ion, which arises by the loss of a proton and formation of a bridged phosphafluorenyl ion, was also very prominent in the spectrum. The M+1 peak which arises due to proton acceptance by an amino group and isotopic contribution of ^{13}C was also observed in the spectrum. The fragment ions M-15/M-16 could be explained by loss of CH_3 groups as indicated in Scheme 1. Other prominent fragment ions were observed at m/z 229, 214, 182, 167, 154, 139, 106, 93, 92, and 65.



SCHEME 1.

The optimum BAPO content for curing of DGEBA could be calculated on the basis of epoxy equivalent and ranged from 34-35 phr. In the present work, DGEBA was cured by systematically varying the concentration of diamine. DSC curves obtained for various epoxy amine systems are given in Figs. 1-3. A broad exothermic peak in the temperature range of 120-240°C was observed in the DGEBA-BAPO system, while in DGEBA-DDS the exothermic transition was observed at higher temperature (above 170-310°C). The exothermic transition occurs in two steps. The position of the exotherm is highly dependent on the nucleophilicity of the diamine. Aliphatic amines, which are stronger nucleophiles than aromatic amines, initiate curing at a much lower temperature. The lower exothermic transition in BAPO, compared to DDS, indicates a more nucleophilic character of the former diamine. The sulfone group is a strong electron-withdrawing group both by induction (-I) and resonance (-R). Since the amino group is in the para-position in DDS, the nucleophilic character of this diamine is considerably reduced. Phosphine oxide also has -I and -R effects, but since the amino group is in the meta-position, the nucleophilicity of this diamine is higher than that of DDS.

From DSC exotherms, the onset of the curing reaction, T_0 (obtained by extrapolating the initial steep portion of the exotherm), the peak temperature, T_{max} , and the final temperature of curing, T_f , were determined and are given in Table 1. The heat of polymerization, ΔH , which could be obtained from the area under the exothermic peak, was also determined (Table 1). These studies indicate a significant effect of the BAPO concentration on the curing behavior of DGEBA. T_{max} values decrease by $\sim 25^\circ\text{C}$ on increasing the BAPO concentration from 10 to 50 phr. Similarly, the ΔH values increased regularly on increasing the amine concentration. The extent of residual cure at any given diamine level can be calculated by assuming that almost complete cure has taken place at 50 phr. The ΔH value at this level can be taken as the heat of complete polymerization, H_0 , and the ratio of H (heat of polymerization at any given level of diamine) to H_0 can give an idea regarding the extent of curing. The quantity $1 - H/H_0$ will then indicate the extent of residual cure. A linear relationship was observed between the extent of residual cure and concentration of the diamine (Fig. 4). It has been reported elsewhere [8] for the DDS:epoxy system that, due to steric and diffusional limitations during the cure, a higher concentration of DDS leads to a higher degree of cure. The present observations with BAPO-DGEBA can be explained on similar grounds. The extent of crosslinking was also evaluated by solubility of these cured resins in DMF. The soluble fraction of the cured resins having 10 and 20 phr of diamine was 97 and 21%, respectively. Only DMF-insoluble products were obtained above 30 phr amine, indicating that a highly crosslinked structure was obtained.

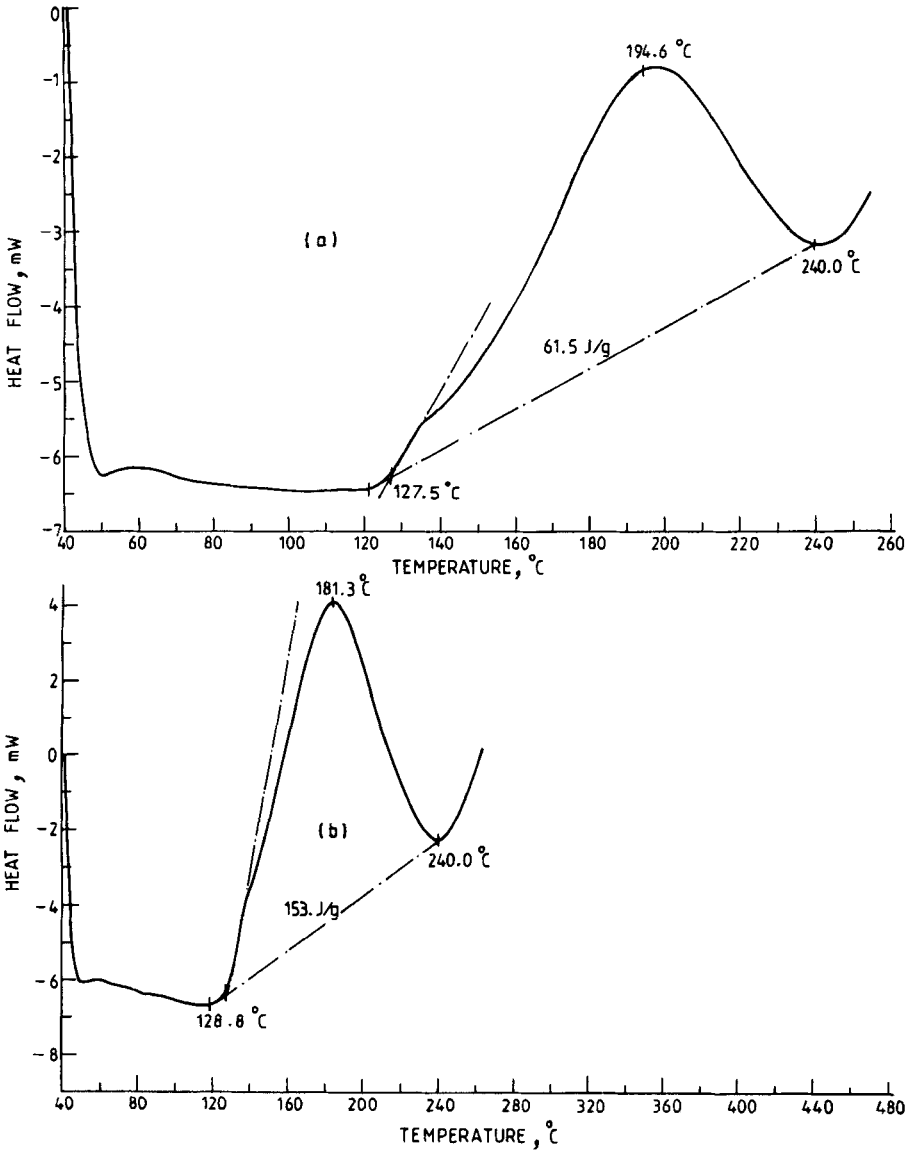


FIG. 1. DSC traces of epoxy-BAPO resins; (a) 10 phr, (b) 20 phr.

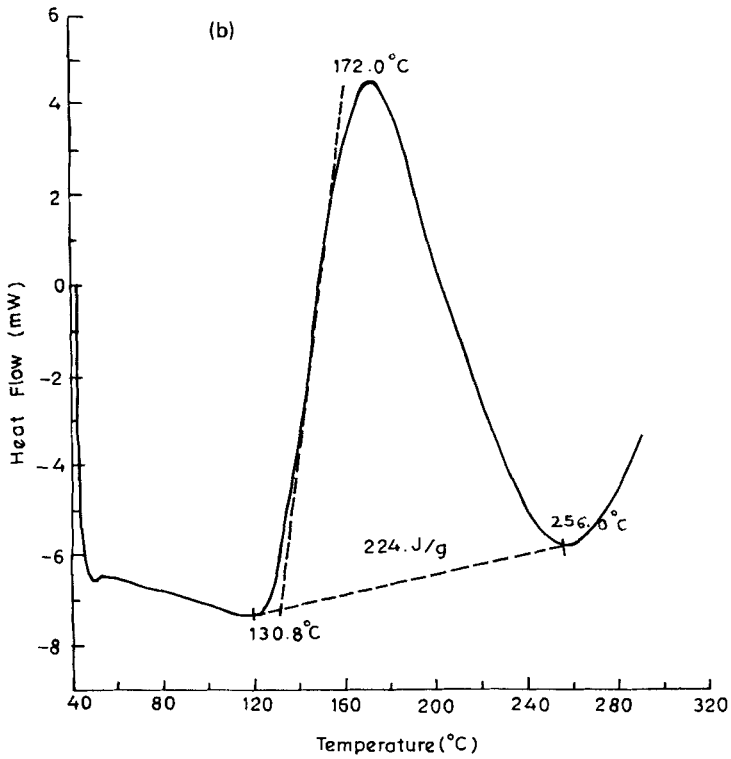
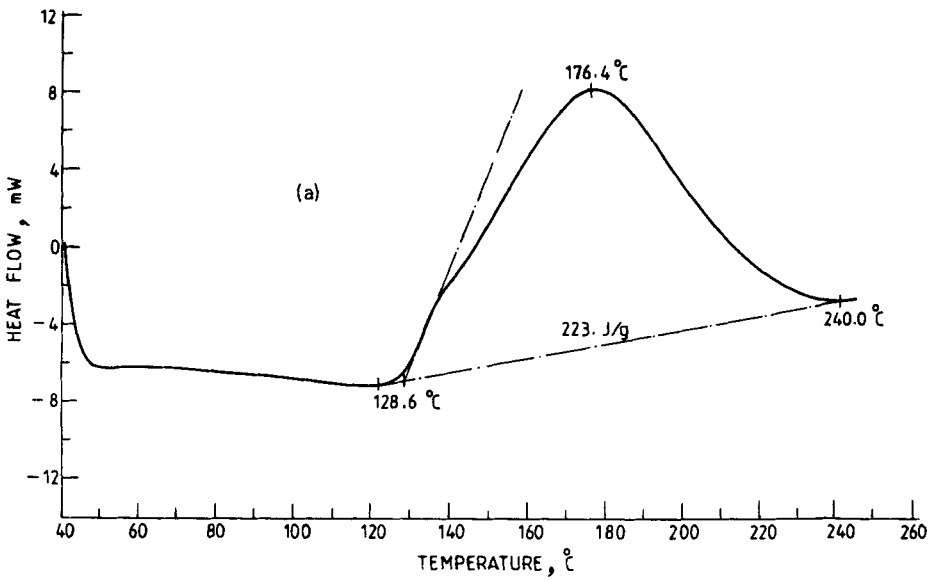


FIG. 2. DSC traces of epoxy-BAPO resins: (a) 30 phr, (b) 35 phr.

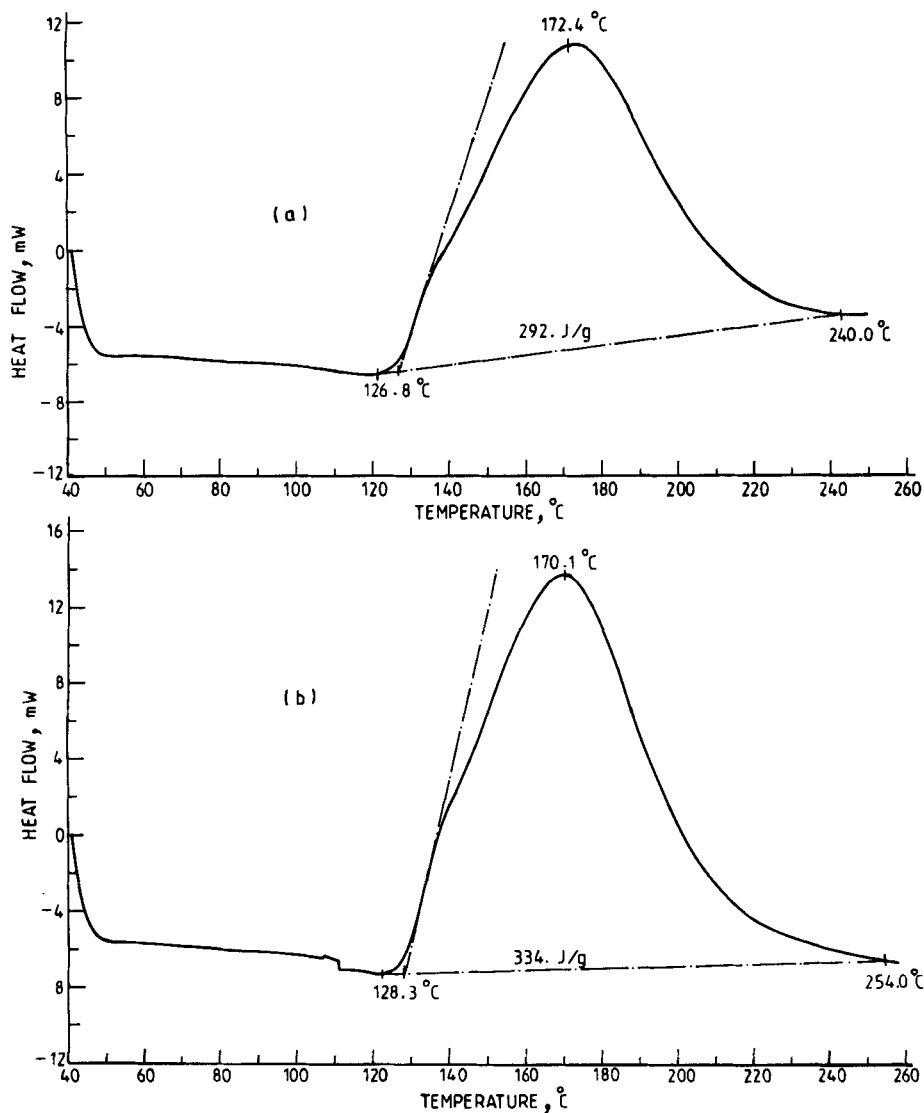


FIG. 3. DSC traces of epoxy-BAPO resins: (a) 40 phr, (b) 50 phr.

TABLE 1. DSC Data for Epoxy/BAPO Resin (heating rate 10°C/min, static air atmosphere)

Amounts of amine (phr)	T_o , °C	T_{max} , °C	T_f , °C	ΔH , J/g
10	127.5	194.6	240.0	61.5
20	128.8	181.3	240.0	153.0
30	128.6	176.4	240.0	223.0
35	130.8	172.0	256.0	224.0
40	126.8	172.4	240.0	292.0
50	128.3	170.1	254.0	334.0

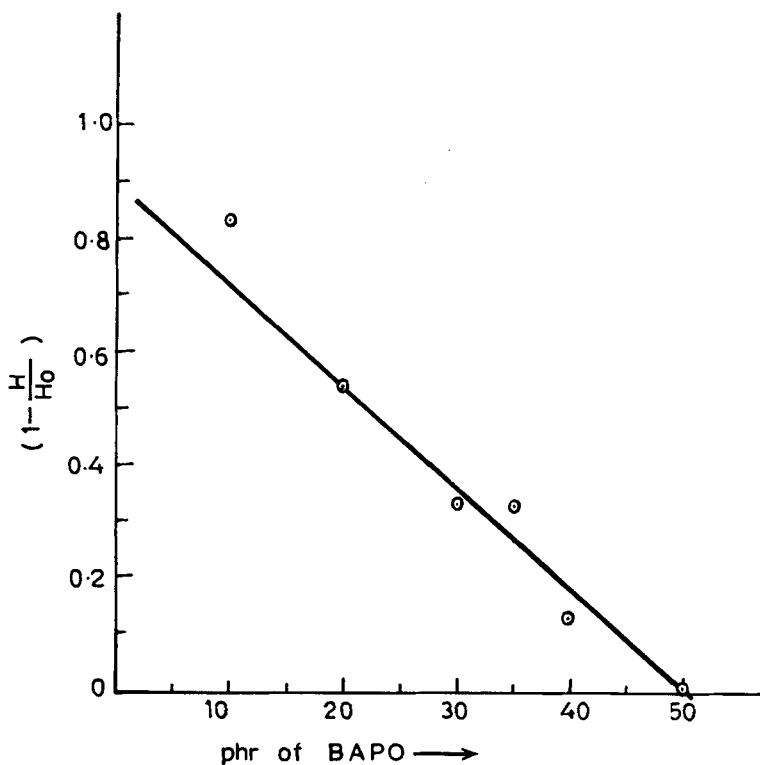


FIG. 4. Relationship between residual cure and concentration (phr) of BAPO.

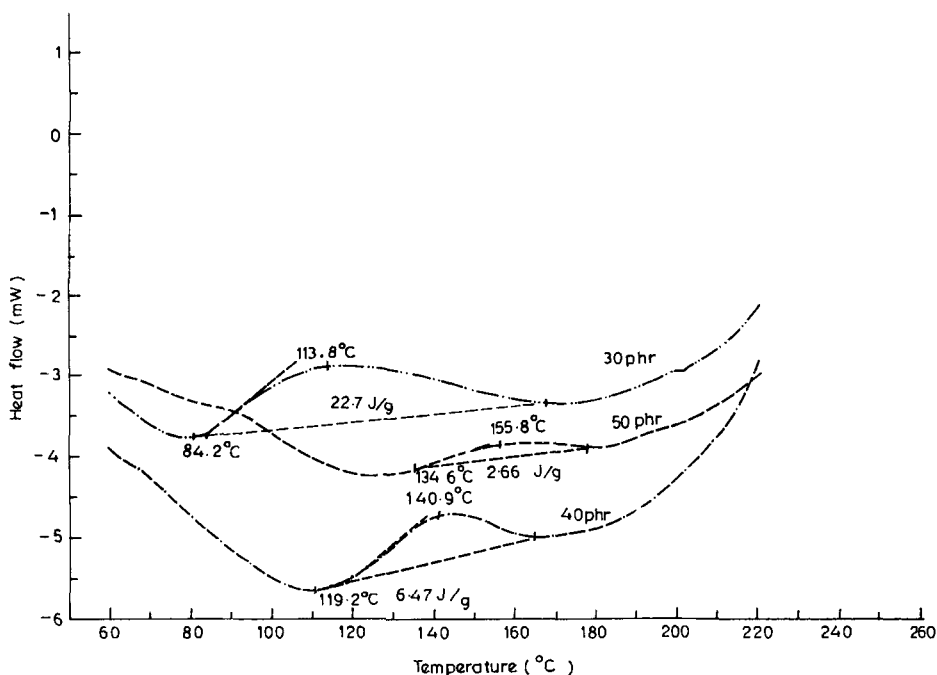


FIG. 5. DSC traces of cured epoxy-BAPO resins of 30, 40, and 50 phr.

The IR spectra of cured epoxy resins showed that characteristic absorption bands due to epoxy groups (at 1260, 916, 865, and 785 cm^{-1}) disappeared upon curing, and bands indicative of hydroxyl groups formation appeared at $\sim 1200 \text{ cm}^{-1}$ (O-H bending vibration), 1410-1310 cm^{-1} (C-O stretching vibrations), and 3680 cm^{-1} (O-H stretching vibrations).

DSC scans of epoxy/BAPO resins cured in air at $175 \pm 5^\circ\text{C}$ for 2 h were recorded in the temperature range of 50-250 $^\circ\text{C}$ in static air atmosphere (Fig. 5). In some of these resins, a broad exothermic peak indicating residual cure was observed. At 10 phr, no exotherm was obtained, which showed that the amine was completely consumed in the curing reaction, and further curing could not take place. As the amine concentration was increased from 10 to 50 phr, an exotherm was observed, showing that these systems had residual amino and epoxy groups and that, therefore, further curing was possible.

The thermal stability of cured resin was evaluated by thermogravimetric analysis. The results of the analysis carried out in a N_2 atmosphere are shown in Figs. 6 and 7. From the TG traces, the initial decomposition temperature (IDT), temperature of maximum rate of weight

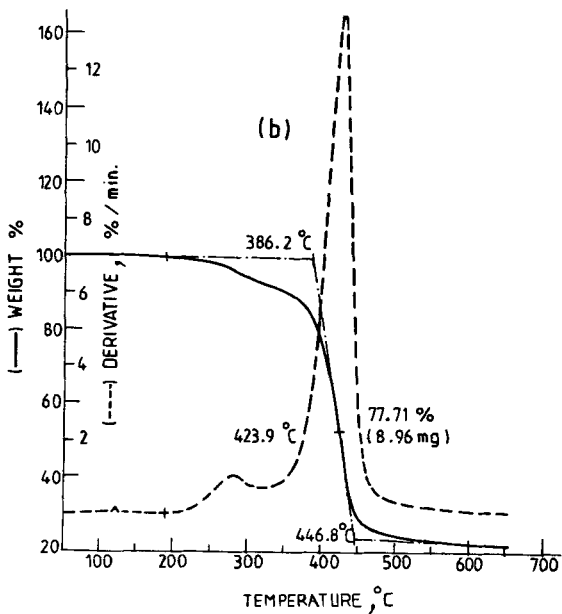
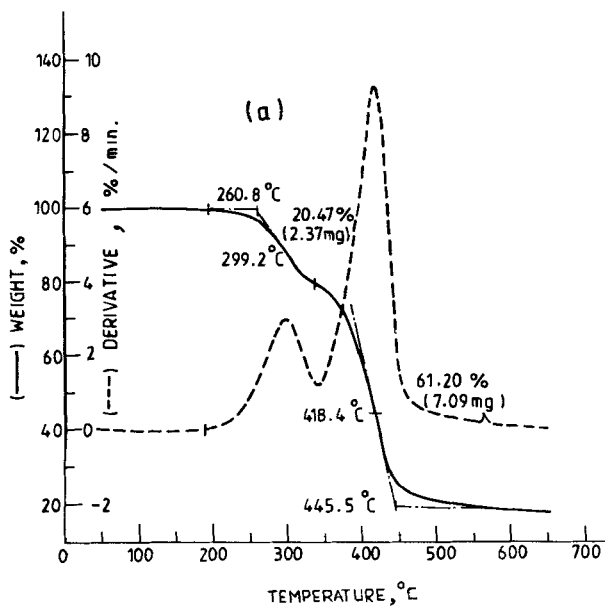


FIG. 6. TGA traces of cured epoxy-BAPO resins in N_2 atmosphere: (a) 10 phr, (b) 20 phr, (c) 30 phr, (d) 35 phr.

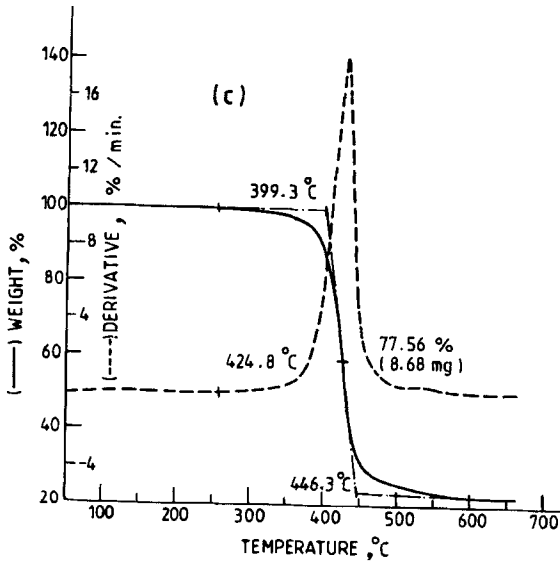


FIG. 6c.

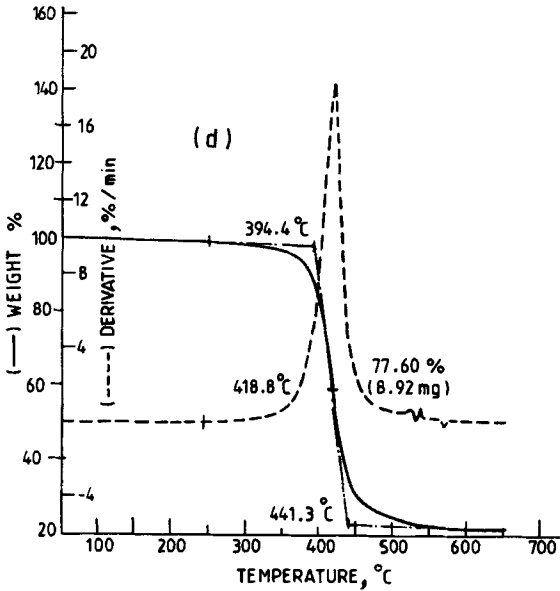


FIG. 6d.

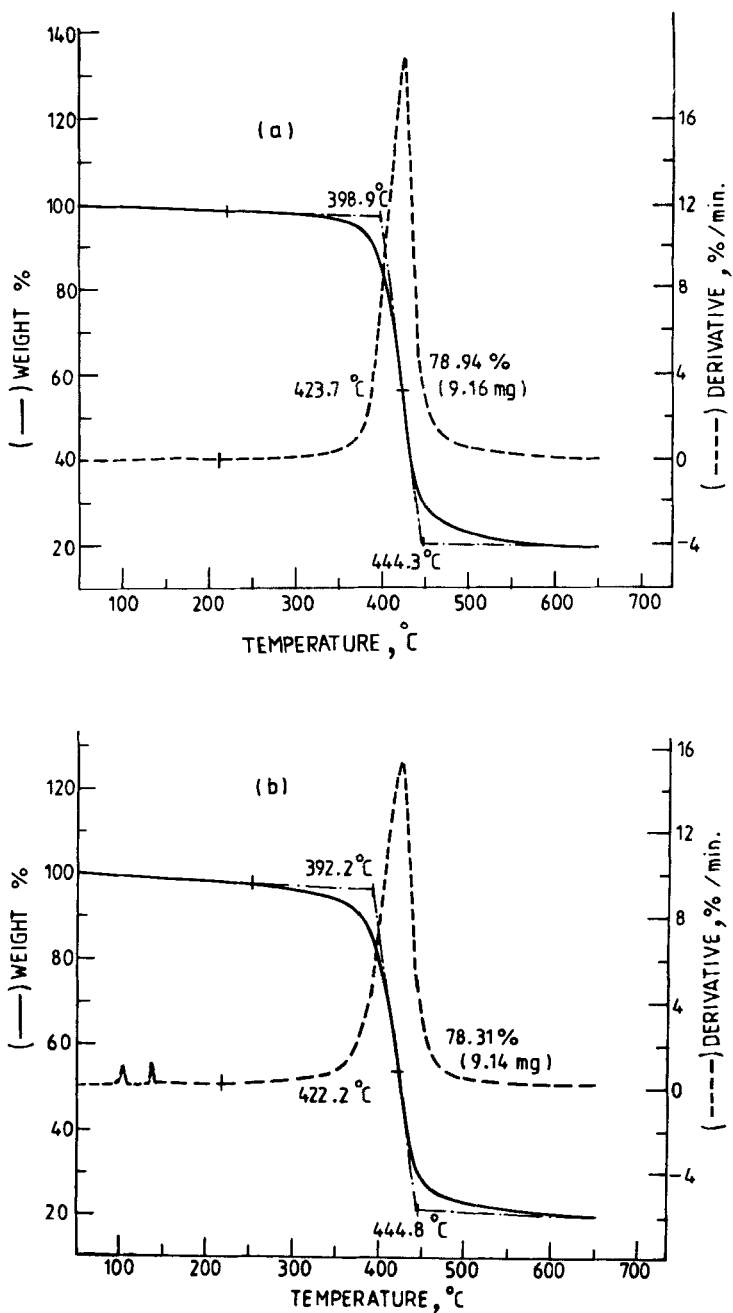


FIG. 7. TGA traces of cured epoxy-BAPO resins in N_2 atmosphere: (a) 40 phr, (b) 50 phr.

TABLE 2. Results of Thermogravimetric Analysis of Epoxy Resin Cured with BAPO in N₂ Atmosphere at a Heating Rate 10°C/min

Amounts of amine (phr)	IDT, °C	T _{max} , °C	IPDT, °C	Char yield, wt %
10	261	300 420	411	51
20	386	285 425	414	31
30	399	425	420	51
35	394	415	423	51
40	399	430	435	40
50	392	425	439	51

loss (T_{max}), integral procedural decomposition temperature (IPDT) [9], and char yield (residual weight %) at 650°C were determined (Table 2). It was observed that epoxy/amine composition plays an important role in determining degradation processes. With 10 and 20 phr BAPO, the thermal degradation occurs in two steps, while with higher amine concentration a one-step process was noticed. This is due to the fact that, at the lower BAPO levels, the crosslinking is very low and the residual epoxy groups degrade at comparatively earlier stage, while with the higher amine levels, the crosslinking is complete, which makes the system thermally stable. High char yields could be obtained due to increased condensed-phase reactions in the presence of phosphorus compounds.

The glass fiber-reinforced epoxy laminates were fabricated using 35 phr of BAPO and 37 phr of DDS, and their mechanical properties were evaluated (Table 3). It is observed that glass fiber-reinforced epoxy/BAPO composites had higher flexural strength (38.6%) and shear strength (25.9%) than composites made with DDS, indicating that the BAPO system is more resistant to bending stresses. The BAPO-cured epoxy resin had improved flame resistance over DDS, showing it to be a thermally more stable system.

Dynamic mechanical analysis of a four-ply laminate of DGEBA-BAPO glass fabric was done in a nitrogen atmosphere. The glass-transition temperature of the laminate was determined by an extrapolation method (Fig. 8) and was found to be 142°C. This indicates that, in structural applications, these composites can be used only up to ~120°C. Durability studies of the laminates were done by accelerated aging at 185 ± 5°C for 100 h and by boiling in water for 100 and 200 h. The results of the thermal aging and boiling-water treatment on the

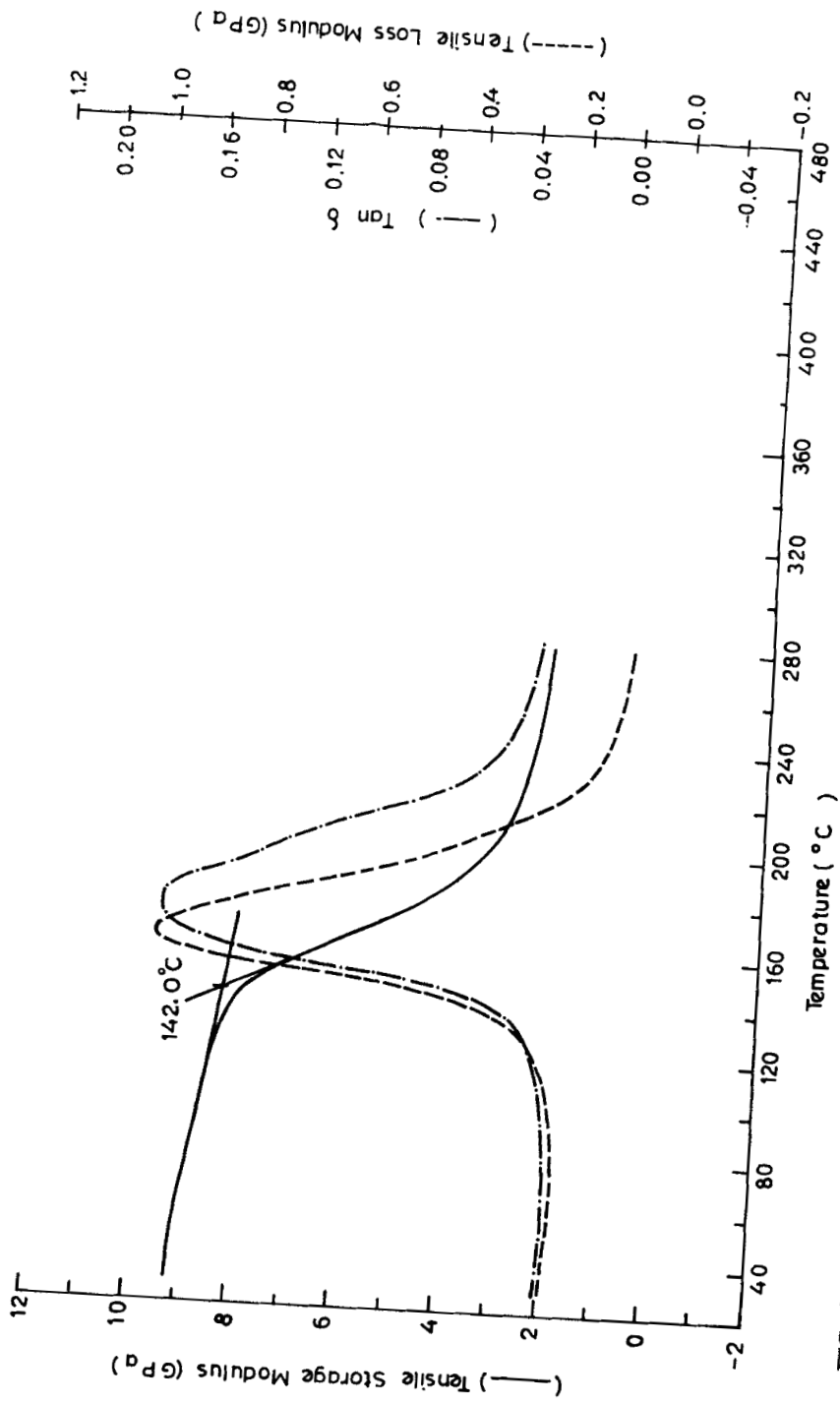


FIG. 8. DMA trace of fiber glass-reinforced epoxy-BAPO laminate.

TABLE 3. Properties of Glass Fiber-Reinforced Epoxy Resin/Amine Composites

Curing agent	BAPO	DDS
Resin content	24.5 ($\pm 1.5\%$)	25.7 ($\pm 0.5\%$)
Void content	5.8 ($\pm 9.0\%$)	6.2 ($\pm 2.5\%$)
LOI (% oxygen)	39.8 ($\pm 2\%$)	25.9 ($\pm 2\%$)
Flexural strength, MN/m ²	621.1 ($\pm 4\%$)	448.4 ($\pm 4\%$)
Flexural modulus, GN/m ²	28.6 ($\pm 4\%$)	26.8 ($\pm 4\%$)
Shear strength, MN/m ²	53.5 ($\pm 5\%$)	42.5 ($\pm 5\%$)

TABLE 4. Effect of Heat Aging and Boiling-Water Treatment on Mechanical Properties of Epoxy-Glass Fiber Laminates

Property rested	Amine used	Heat aging for 100 h	Percent variation from original upon	
			Boiling water treatment	
			100 h	200 h
Flexural strength, MN/m ²	BAPO	+7	-	-
	DDS	-1.6	-	-
Flexural modulus, GN/m ²	BAPO	+5	-	-
	DDS	-3.7	-	-
Shear strength, MN/m ²	BAPO	+4.6	-27.7	-46.2
	DDS	+2.9	-20	-24.6

epoxy/amine composites are given in Table 4. A weight loss of 0.65% in the BAPO composites and 0.39% in the DDS composites was observed on thermal aging. On boiling water treatment, however, gains of 0.51% after 100 h and 1.14% after 200 h were noted in the BAPO system, while in the DDS system gains of 0.29% after 100 h and 0.95% after 200 h were observed.

The mechanical properties of BAPO-cured epoxy composite increase on thermal aging, which can be understood on the basis of the stresses

released on heating at 185°C. Immersing epoxy composites in water produces a variety of types of damage with regard to its mechanical properties. The deterioration in the mechanical properties in the presence of water is primarily due to delamination. The water migrates to the interface of the fiber and matrix resin, thereby decreasing the interfacial bond. The decrease in shear strength was more in laminates based on BAPO than those based on DDS.

CONCLUSIONS

On the basis of these observations, it can be concluded that DGEBA can be cured at a lower temperature with BAPO than with DDS. Cured resin gave higher char yields and exhibited better thermal stability when BAPO was used as the curing agent instead of DDS. Glass fabric-reinforced composites based on DGEBA/BAPO had better flexural and interlaminar shear strength than DGEBA/DDS resins. Marginal variation in the mechanical properties of the composites was observed on heating at 185°C for 100 h. However, boiling water treatment for 100 h and 200 h resulted in a substantial decrease in shear strength of these composites.

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