Synthesis, Characterization, and Curing of {2,6−Bis-[2-(bis-oxiranylmethyl-amino)-methylbenzyl]-phenyl}-bis-oxiranylmethylamine (BPBOMA)

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ABSTRACT: The curing behavior of epoxy resin prepared by reacting epichlorohydrin with amine functional aniline acetaldehyde condensate (AFAAC) was investigated using AFAAC as a curing agent. The epoxy resin, {2,6-bis-[2-(bis-oxiranylmethyl-amino)-methylbenzyl]-phenyl}-bis-oxiranylmethylamine (BPBOMA), was characterized by FTIR and ^{1}H-NMR spectroscopy, viscosity measurement, and determination of epoxy content. Analysis of the curing reaction was followed by differential scanning calorimetry (DSC) analysis. To investigate the curing kinetic with AFAAC, dynamic DSC scans were made at heating rates of 5, 10, 15, and 20°C/min. The activation energy and frequency factor of the AFAAC formulation were evaluated. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 3168–3174, 2006

Key words: kinetics, activation energy; differential scanning calorimetry (DSC); crosslinking

INTRODUCTION

To improve cure response and provide better crosslinking, many multifunctional epoxy resins have been synthesized, and commercialized[1] resins based on N,N,N',N'-tetraglycidyldiaminodiphenylmethane are resinous materials with good rheology and high functionality that are useful in high-strength and high-performance applications.[1,2] As the properties of the final thermoset depend on not only the structure of the epoxy resin but also the type and amount of curing agent, it is essential to understand the kinetic behavior of the curing reaction. Differential scanning calorimetry (DSC) is a valuable technique for investigating the kinetic parameters of the curing reaction of thermosetting polymer.[3,4] This article reports the synthesis of a hexafunctional epoxy resin (BPBOMA) from the reaction of amine functional aniline acetaldehyde condensate (AFAAC) and epichlorohydrin and an investigation of its curing reaction using a new curing agent such as AFAAC. DSC was also used to investigate the curing reaction. In addition, the kinetic parameters of the BPBOMA resin with amine functional aniline acetaldehyde condensate (AFAAC) were evaluated using the Ozawa and Kissinger equations.

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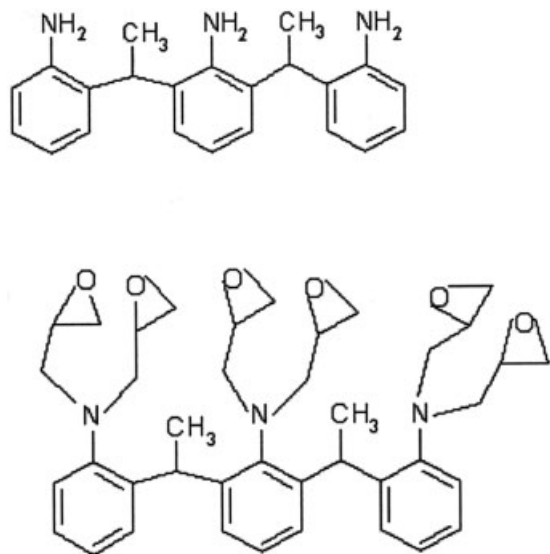
EXPERIMENTAL

Materials

Epichlorohydrin (Fluka Chemie AG, Buchs, Switzerland) was used as received. The aniline and acetaldehyde used in this work were obtained from Merck Fine Chemicals (Mumbai, India). Reagent-grade acetic acid, hydrobromic acid (48% in water), crystal violet indicator solution (0.1% solution in acetic acid), primary-standard-grade sodium carbonate dried to a constant weight at 120°C–140°C, and reagent-grade chlorobenzene were obtained from Fluka and Merck Fine Chemicals. The chemical structures of AFAAC and BPBOMA are presented in Scheme 1.

Synthesis of AFAAC

Amine functional aniline acetaldehyde condensate (AFAAC) was synthesized from the reaction of aniline and acetaldehyde (mol ratio 1.25 : 1) in an acidic medium. Aniline (153 mL, 1.64 mol) was first mixed with an amount of HCl sufficient for the medium to reach a pH of 4. Then the pale-yellow-colored liquid mixture was added to a three-necked flask and stirred at 30°C. Next the acetaldehyde (1.31 mol) was added to the flask at fixed intervals of 10 min. Stirring continued for 4 h, after which the product was washed first with 2% NaOH first and then with water until the mixture became neutral. Finally, the red-colored liquid product was dried in an oven at 90°C. The product yield was 90%.

Scheme 1 Chemical structures of AFAAC and BPBOMA.

Synthesis of BPBOMA

{2,6-Bis-[2-(bis-oxiranylmethyl-amino)-methylbenzyl]-phenyl}-bis-oxiranylmethylamine (BPBOMA) was synthesized from epichlorohydrin and AFAAC by the following method.[5] Epichlorohydrin (600 mL) was placed in a 1-L three-necked flask fitted with a condenser and a nitrogen inlet. The flask was warmed to 70°C, and then AFAAC (50 g) was added. The temperature was maintained at 75°C for 10 h, after which the epichlorohydrin was stripped under reduced pressure. The resulting viscous product was dissolved in methanol (150 mL), and the contents were warmed to 55°C followed by the dropwise addition of 40% (w/v) aqueous sodium hydroxide over 1 h. The contents were stirred for an additional 0.5 h. Methanol was stripped off, and the product was extracted in methyl ethyl ketone (MEK), washed with water several times and then with hot water, and dried over anhydrous sodium sulfate. The MEK was stripped off to get the pure resin (121.5 g/mol epoxy equivalent weight). The product yield was 85%.

Characterization of AFAAC and BPBOMA

FTIR spectroscopic analysis

The FTIR spectrum of the neat resin sample between KBr discs was obtained with a Thermo-Nicolate Nexus-870 FTIR spectrometer.

^{1}H-NMR spectroscopic analysis

The ^{1}H-NMR spectrum was recorded on a Bruker AC 200 spectrometer. Sample was dissolved in deuterated chloroform, and TMS was used as the internal standard.

Viscosity measurement

Viscosity measurement was carried out with TA instruments (model AR1000, Newcastle, DE) in a parallel plate configuration (40 mm in diameter, 1-mm gap) at various shear rates at 30°C for AFAAC and at temperatures ranging from 30°C to 80°C for BPBOMA.

Amine equivalent of AFAAC

Amine equivalent or amine equivalent weight (AEW) is defined as the weight of the amine in grams that contains 1 g equivalent of amine. The AEW was determined by the nonaqueous titration method (perchloric acid method). A small amount (300 mg) of accurately weighed AFAAC was added to a conical flask and dissolved in 20 mL of chlorobenzene and 10 mL of glacial acetic acid. Four drops of 0.1% solution of crystal violet in glacial acetic acid was added. Then the resulting purple-colored solution was titrated with 0.1N HClO$_4$ solution in acetic acid to a bluish-green end point. A blank titration without AFAAC was done.

The amine equivalent weight was calculated from the following equation:

$$AEW = \frac{(W) \times (1000)}{(S-B) \times (N)}$$

where W is the weight of the sample, S is the HClO$_4$ used in the titrating sample (in mL), B is the HClO$_4$ used in the titrating blank (in mL), and N is the normality of the HClO$_4$.

Epoxy content of BPBOMA

Epoxide equivalent or epoxy equivalent weight (EEW) is defined as the weight of the resin in grams that contains 1 g equivalent of epoxy. The EEW was determined by the hydrogen bromide method[6] and was calculated from the following equation:

$$EEW = \frac{(W) \times (1000)}{(S - B) \times (N)}$$

where w is the weight of the sample, S is the HBr used in the titrating sample (in mL), B is the HBr used in the titrating blank (in mL), and N is the normality of the HBr.

Differential scanning calorimetry

Differential scanning calorimetry (DSC) was conducted on a Mettler DSC 25 module attached to a Mettler TC 114000 thermal analyzer using the variable peak exotherm method to determine the kinetic parameters of different resin formulations. All measure-
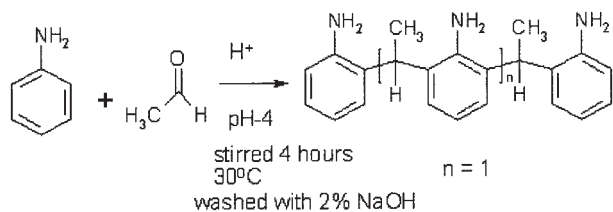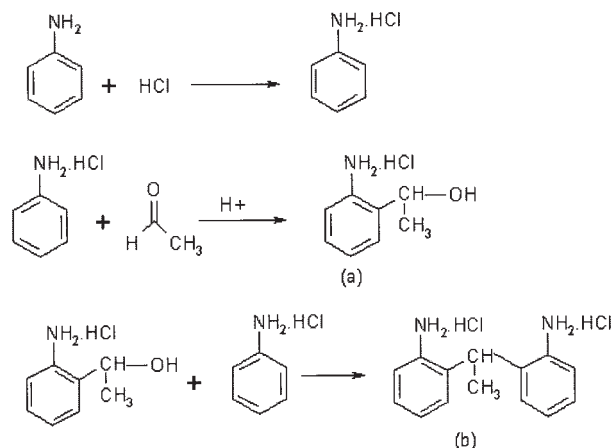
Scheme 2   Reaction details of aniline and acetaldehyde.

ments were carried out under a nitrogen flow (100 mL/min) at a constant heating rate and using an alumina crucible with a pinhole. Dynamic scans were conducted at heating rates of 5°C, 10°C, 15°C, and 20°C/min. AFAAC (20 phr) was added to the BP-BOMA resin and mixed thoroughly for 15 min. The clear viscous solution was then subjected to DSC analysis.

RESULTS AND DISCUSSION

Synthesis of AFAAC

The AFAAC was synthesized from the reaction of aniline and acetaldehyde in the acid medium. The details of the reaction are given in Scheme 2. In this reaction, first 1 mol aniline hydrochloride reacted with acetaldehyde in the presence of acid to give intermediate (a). Then intermediate (a) reacted with 1 mol aniline hydrochloride to give intermediate (b), which then reacted with acetaldehyde and aniline hydrochloride by the same mechanism to produce AFAAC, as shown in Scheme 3. The formation of the product was demonstrated by the AEW of AFAAC (from amine titration) and by the aliphatic and aromatic proton ratios (from NMR). The AEW of AFAAC determined by amine titration was 112, which was close to the 109 from the molecular weight obtained from
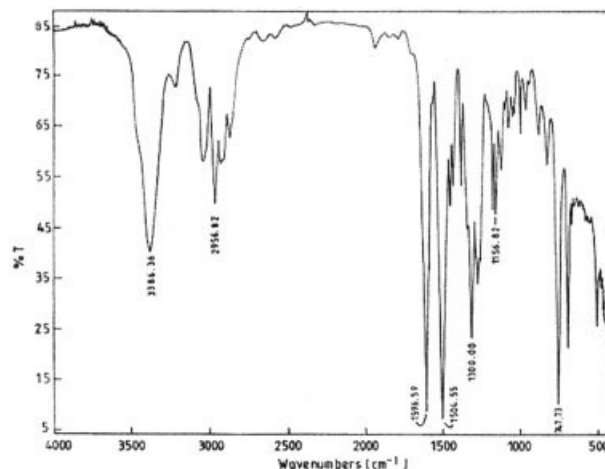

Figure 1   FTIR of AFAAC.

the structure, which confirmed the formation of AFAAC. The titration method used was supported by determining the AEW of a known diamine such as diaminodiphenylmethane, whose AEW, 97, was in good agreement with the theoretical value. The reaction of AFAAC led to a mixture of oligomers with an average n of 1, which has been proved by TLC.

Synthesis of BPBOMA

The BPBOMA was synthesized from the reaction of epichlorohydrin and AFAAC as described in the Experimental section. The details of the reaction are shown in Schemes 4 and 5. The reaction involved a two-step mechanism. In stage (a) the epoxide group of the epichlorohydrin (ECH) reacted with the amine group for the formation of the chlorohydrin amine. In stage (b) the chlorohydrin amine was dehydrochlorinated by the NaOH solution, forming the glycidyl amine together with sodium chloride and water. The BPBOMA was produced by the repetition of this process in which an epoxide group was expected to replace six hydrogen atoms of three —NH_2 groups.
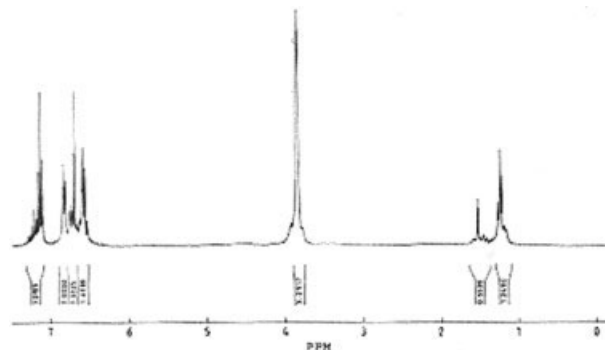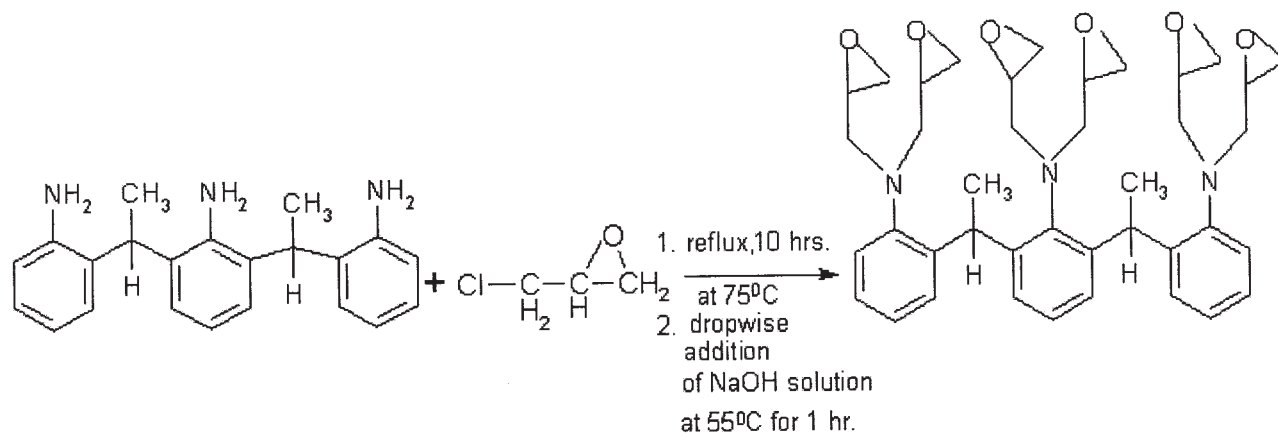

Scheme 3   Reaction mechanism of aniline and acetaldehyde.


Figure 2 ^{1}H-NMR of AFAAC.

Scheme 4

Spectroscopic analysis of AFAAC

In the FTIR spectrum (Fig. 1), the characteristic peaks at 3386 and 1505 cm^{-1} are responsible for N—H stretching and N—H bending, respectively. The aromatic and aliphatic C—H stretching at 3030 and 2957 cm^{-1}, respectively, confirmed the presence of aromatic and aliphatic moieties in the probable structure. This was further supported by the peaks at 1360 and 1596 cm^{-1}, which resulted from C—N aromatic stretching and C=C aromatic ring stretching, respectively.

The ^{1}H-NMR spectrum (Fig. 2) shows the 11 aromatic protons in the region from 6.7 to 7.5 ppm. The doublet at 1.5 ppm and the quartet at 1.2 ppm resulted from methyl and methylene protons, respectively. The amine protons appeared at 3.8 ppm as a singlet. All these peaks support the expected structure of AFAAC, as the peak area ratio of aliphatic to aromatic protons (5.1 : 4.1; i.e., 1.26 : 1) was almost same as the ratio of the number of aliphatic and aromatic protons (14 : 11; i.e., 1.27 : 1).

Epoxy equivalent of BPBOMA

The epoxy equivalent of BPBOMA was 121.5. The expected number of epoxy groups in the reaction
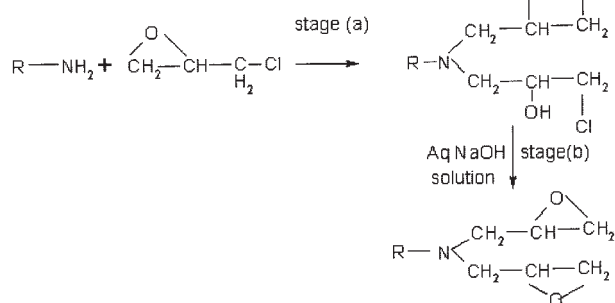
product of AFAAC and epichlorohydrin (BPBOMA) was 6 and the expected EEW was 112, but the epoxy equivalent of 121.5 indicates incomplete epoxidation, also shown by the presence of an unreacted —NH group in the resin (FTIR spectrum of BPBOMA). So the actual degree of epoxidation was 5.5, which was obtained from the epoxy equivalent value (121.5) and the molecular weight of the reaction product of AFAAC and epichlorohydrin (667) calculated from the probable molecular formula, $C_{40}H_{49}N_3O_6$ (shown in Scheme 4).

Spectroscopic analysis of BPBOMA

The FTIR spectrum (Fig. 3) shows that because of the epoxide group, the characteristic absorption band was observed at 965 cm^{-1}. A broad absorption band was observed around 3421 cm^{-1}, which may be a result of the —NH— stretch. As the epoxy equivalent of BPBOMA was less than 6, it may have had lower functionality because of an unreacted —NH— group in
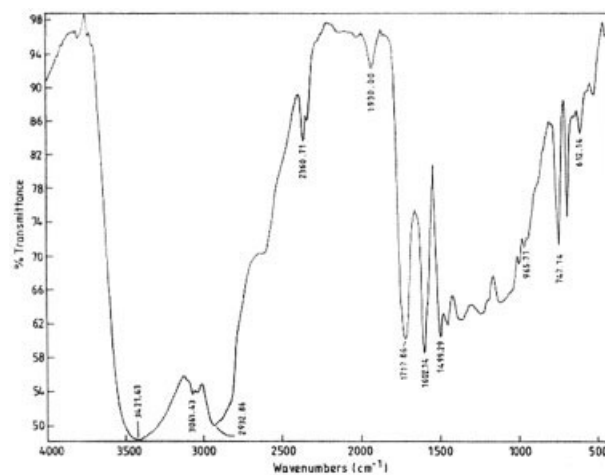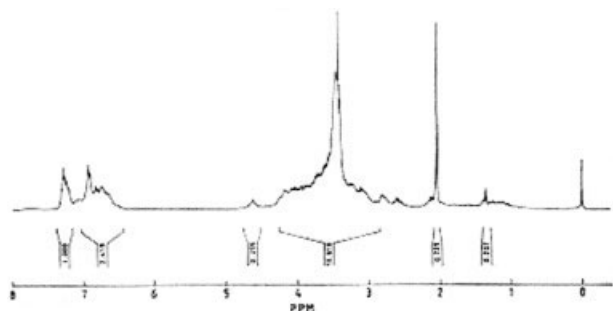

Scheme 5

Figure 3 FTIR of BPBOMA.

Figure 4 ^{1}H-NMR of BPBOMA.

this resin. Further confirmation of this —NH— group was the appearance of a strong absorption band at 1500 cm^{-1} from —NH— bending.

From the ^{1}H-NMR spectrum (Fig. 4), it is clear that the 11 aromatic protons were in the region from 6.7 to 7.5 ppm. The doublet at 1.5 ppm and the quartet at 2.6 ppm were the result of methyl and methylene protons, respectively. The protons of epichlorohydrin were in the region of 3.2–4 ppm as multiplate. The unreacted amine protons appeared at 4.6 ppm as a singlet. All these peaks confirmed the expected structure of BP-BOMA.

Viscosity of AFAAC

The results for viscosity of AFAAC are shown in Table I. It appears that the AFAAC displayed nearly Newtonian behavior, with an average viscosity of 148.8 cp.

Viscosity of BPBOMA

The viscosity of BPBOMA at different temperatures is shown in Figure 5, from which it is clear that the product was highly viscous relative to AFAAC at 30°C, confirming the reaction of amine and ECH. The resin also was Newtonian at each temperature. This was also evident from Figure 6, in which the viscosities of BPBOMA at a constant shear rate (49.99 s^{-1}) have been plotted against the temperatures that produced viscosity decreases. This temperature dependence shows Arrhenius dependence, which is shown in Figure 7, according to the equation[7]

TABLE I
Viscosity of AFAAC

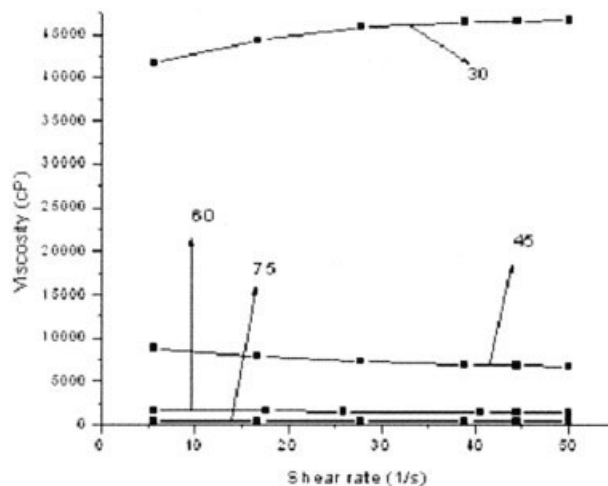| Shear rate (s^{-1})	Viscosity (cP)	Average viscosity (cp)
4.580	147.4	
9.120	148.8	
22.74	149.1	
31.82	149.1	148.8
45.44	149.3	
49.98	148.9	

Figure 5   Viscosity curves of BPBOMA at 30°C, 45°C, 60°C, and 75°C.

$$\eta = A \exp(-Q/RT) \qquad (1)$$

where η is the viscosity, R is the gas constant, T is the absolute temperature, A is a constant, and Q is the activation energy. Q was calculated from the slope of the graph of log η versus $1000/T$ (Fig. 7) at a constant shear rate (49.99 s^{-1}) and fitting it to a straight line. The activation energy (Q) calculated from eq. (1) was 51.32 kJ/mol.

Standard Deviation of the Viscosity of BPBOMA

Using the viscosities at a constant shear rate of 49.99 s^{-1} at temperatures of 30°C, 45°C, 60°C, 75°C, 90°C, and 100°C (from Fig. 6), the standard deviation of viscosity was calculated as 18,530 Cp. When also calculated by taking the viscosity at different shear rates for each temperature studied separately (from Fig. 5),
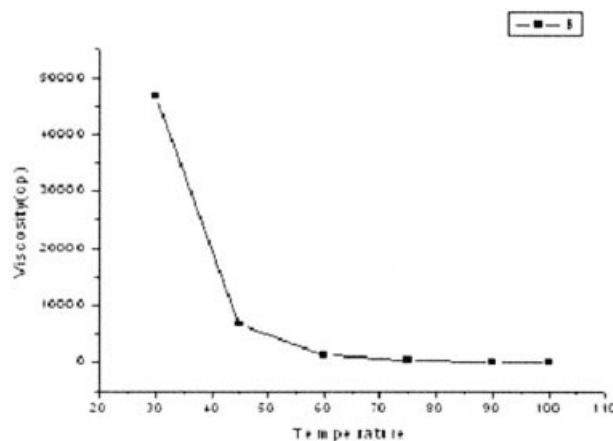

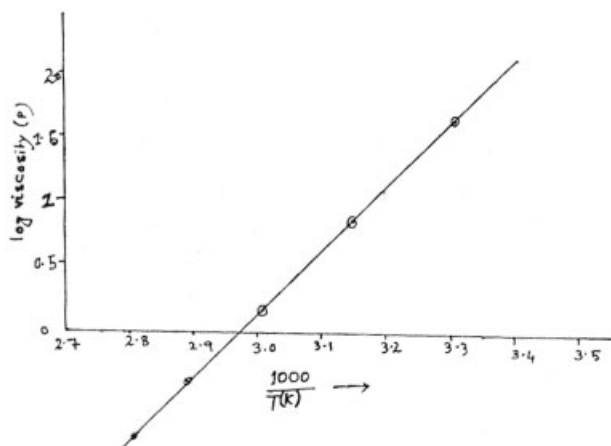**Figure 6**   Viscosity versus temperature curve of BP-BOMA at a shear rate of 49.99 s^{-1}.

Figure 7 Plot of log viscosity (p) versus $1000/T$ of BP-BOMA at a shear rate of 49.99 s^{-1}.

the standard deviation of viscosity was found to be 1910, 812, 131, 20, 6, and 4 Cp at 30°C, 45°C, 60°C, 75°C, 90°C, and 100°C, respectively.

DSC analysis

Investigation of the curing behavior was followed by DSC. Figure 8 shows the DSC scans of a curing formulation pertaining to four heating rates: 5°C, 10°C, 15°C, and 20°C/min. The initiation temperature (T_i), peak exothermic temperature (T_{max}), completion temperature (T_f), and heat of cure (ΔH) for each heating rate are given in Table II.

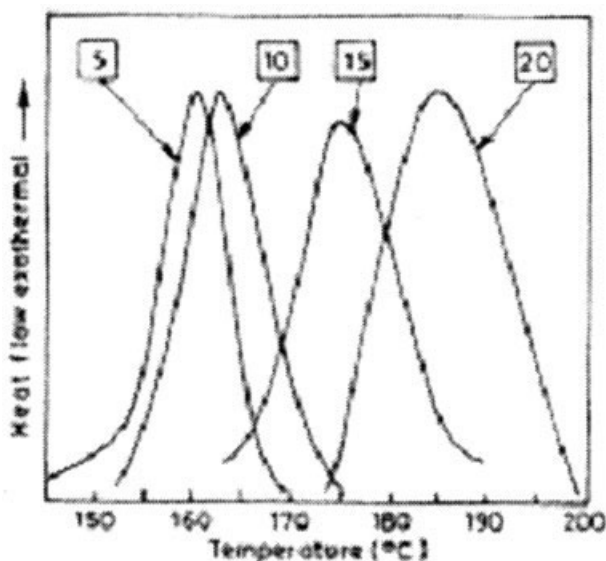The kinetic parameters were calculated by employing the Ozawa and Kissinger equations[8–9]

TABLE II
DSC Results for BPBOMA Cured with 20 phr of AFAAC

Heating rate (°C/min)	T_i (°C)	T_{max} (°C)	T_f (°C)	ΔH (J/g)
5	145	160	170	4.309
10	152	162	175	2.827
15	165	174	189	1.249
20	172	185	200	1.687

$$E_a = -R\Delta \ln \beta / 1.052\Delta(1/T_{max})$$

$$-\ln[\beta/T_{max}^2] = E_a/RT_{max} - \ln[AR/E_a] \quad (2)$$

where E_a is the activation energy, R is the gas constant, β is the heating rate, $\ln A$ is the frequency factor, and T_{max} is the peak exotherm temperature of the corresponding β. These were obtained from a variable peak exotherm of epoxy formulation. The variable peak exotherm was shown in Figure 8. The E_a from the Kissinger equation was calculated from the slope of the graph of $-\ln[\beta/T_{max}^2]$ versus $1/T_{max}$ and fitting it to a straight line. The graph between $-\ln[\beta/T_{max}^2]$ and $1/T_{max}$ for epoxy formulation is shown in Figure 9. The kinetic parameters, that is, the energy of activation (E_a) and the frequency factor ($\ln A$), calculated from the Kissinger equation were 55.12 kJ/mol and 7.12 min^{-1}, respectively. The conversion profiles are shown in Figure 10. As shown in Figure 8, the peak exotherm temperature (T_{max}) varied in a predictable manner with the heating rate. The maximum rate of conversion occurred at the peak exothermic temperature for each heating rate.

CONCLUSIONS

The cure kinetics of a new resin BPBOMA containing almost six epoxy groups with a new triamine AFAAC
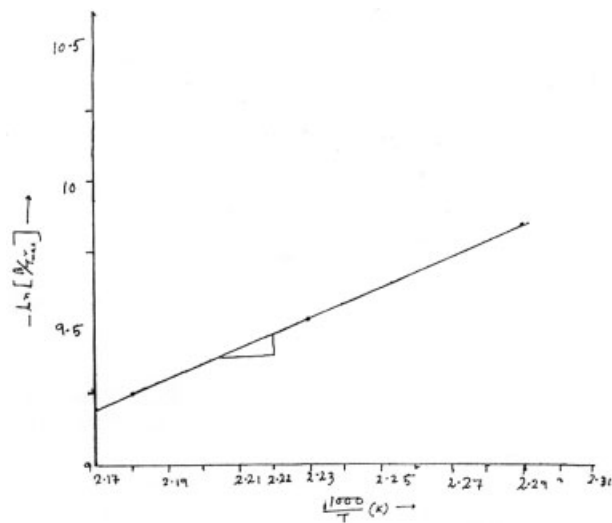

Figure 8 DSC scans of four heating rates (5, 10, 15 and 20°C/min).

Figure 9 Graph of $-\ln[\beta/T_{max}^2]$ versus $1000/T$ (K).
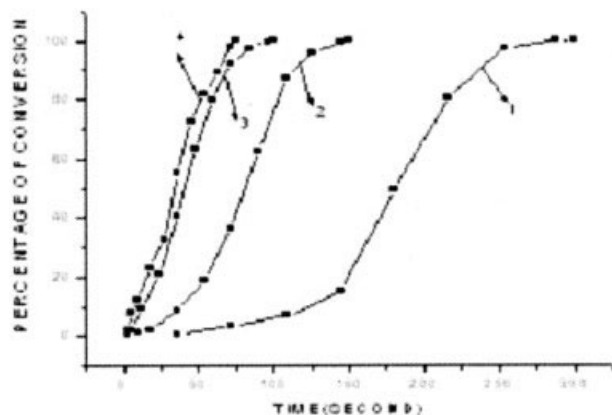
Figure 10   Plot of percentage conversion versus time (1: 5°C/min; 2: 10°C/min; 3: 15°C/min; 4: 20°C/min).

as the curing agent was investigated by DSC analysis. The AFAAC was successfully used as a curing agent for BPBOMA, as the DSC curves showed a complete curing exotherm. The curing exotherm conversion profiles showed that the maximum rate of conversion occurred at peak exotherm temperature. Other kinetic parameters also were evaluated with the Ozawa and Kissinger equations.

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