Studies on Curing Kinetics and Thermal Behavior of Phosphorylated Epoxy Resin in the Presence of Aromatic Amide-Amines

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ABSTRACT: This article describes the synthesis of some novel aromatic amide-amine curing agents by reacting 1 mole of *p*-amino benzoic acid with 1 mole of each of 1,4-phenylene diamine (P), 1,5-diamino naphthalene (N), 4,4'-(9-fluorenyllidene)-dianiline (F), 3,4'-oxydianiline (O), and 4,4'-diaminodiphenyl sulphide (DS) and were designated as PA, NA, FA, OA, and SA, respectively. The aromatic amide-amines so synthesized were characterized with the help of spectroscopic techniques, viz., Fourier Transform Infrared, proton nuclear magnetic resonance, and carbon nuclear magnetic resonance. The curing kinetics of the epoxy resins obtained by reacting amines with diglycidyl ether of bisphenol-A blended with tris(glycidyloxy)phosphine oxide in a ratio of 3 : 2, respectively, were investigated by DSC technique using multiple heating rate method (5, 10, 15, 20°C/min). Activation energies were determined by fitting the experimental data into Kissinger and Flynn-Wall-Ozawa Kinetic models. The activation energies obtained through Flynn-Wall-Ozawa method were slightly higher than Kissinger method but were comparable. However, both the energies were found to be dependent on the structure of amines. The thermal stability and weight loss behavior of isothermally cured thermosets were also investigated using thermogravimetric analysis in nitrogen atmosphere. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 3612–3618, 2010

Key words: phosphorylated epoxy; curing; thermal stability; flame retardancy; amide-amines

INTRODUCTION

Epoxy resins because of having remarkable properties like fluidity, physical strength after cure, moisture and chemical resistance, and good adhesion to many substrate have been used for coating, casting, adhesive, electronic encapsulant, and aerospace composite matrix.[1,2] But it is crucial to improve the properties such as thermal stability, electrical properties and halogen free flame retardation to utilize them better in electronic and aerospace industry. Several approaches have been reported in the literature for the improvement of these properties, viz., by incorporating imido,[3–5] amido,[6] and maleimido groups[7,8] into the epoxy structure, using phosphorous flame retardant to replace traditional halogenated compound[9–11] either at polymerization stage or as flame retardant additive. However, organophosphorous compounds especially when used as reactive monomer have demonstrated to exhibit notable efficiency on improving flame retardancy of polymer through condensed mechanism.[12,13] Phosphorous

when combined with nitrogen showed a significant improvement in flame resistance.[14] Nitrogen is generally incorporated into the epoxy thermoset by using N-containing curing agents like diamines, polyamines, and imide/amide encappped with amines.

The epoxy resins are characterized by the presence of epoxide ring, which can undergo nucleophilic addition reactions with the compounds containing active hydrogen atoms including amines, amides, etc. During the curing process, epoxy prepolymer get converted into three-dimensional crosslinked network. Various chemical reactions that take place during the curing process determine the resin morphology, which, in turn, determines the properties of cured formulations.[15] Curing kinetics, curing rate, variation of rate at various temperature, and activation energy are useful for the study of epoxy applications. The kinetic characterization of the epoxy resins is a fundamental tool to understand the structure /property /processing relationships for the manufacturing of composites and their high-end usage.[16] The review of literature reveals that the curing kinetics of several epoxy-amine systems was studied by both dynamic and isothermal methods.[17,18]
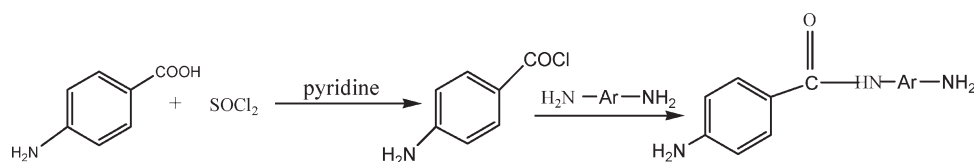
**Scheme 1** Reaction scheme of synthesis of amide-amine curing agents.

In this article, we synthesized aromatic amide-amines of different structure as epoxy curing agents by reacting 1 mole of *p*-aminobenzoic acid with 1 mole of 1,4-phenylene diamine (P), 1,5-diamino naphthalene (N), 4,4′-(9-fluorenylli-dene)-dianiline (F), 3,4′-oxydianiline (O), and 4,4′-diaminodiphenyl sulphide (DS) and designated them by putting suffix A as PA, NA, FA, OA, and SA, respectively. Various epoxy thermosets were obtained by reacting the amines stochiometricaly with diglycidyl ether of bisphenol-A (DGEBA) blended with synthesized phosphorylated epoxy resin, tris(glycidyloxy)phosphine oxide(TGPO) and their curing kinetics was investigated using Differential Scanning Calorimetry (DSC) and by applying Kissinger[19] and Flynn-Wall-Oza-wa's[20,21] dynamic kinetic methods. The thermal stabilities of cured polymers were investigated using thermo gravimetric analysis under nitrogen atmosphere.

EXPERIMENTAL

Materials

DGEBA (grade LY556, having epoxy EEW 177) was procured from Hindustan Ciba Geigy (Mumbai, India). Various diamines, i.e., 1,4-phenylene diamine (P), 1,5-diamino naphthalene (N), 4,4′-(9-fluorenylli-dene)-dianiline (F), 3,4′-oxydianiline (O), and 4,4′-diaminodiphenyl sulphide (DS) were purchased from Aldrich (Bangalore, India) and were used as received. *p*-amino benzoic acid (PABA), methanol, pyridine, thionyl chloride, and sodium bicarbonate were received from Merck (Darmstadt, Germany)

and were used as such. Phosphorylated epoxy (TGPO, EEW 120) was synthesized and characterized in our laboratory[22] and its structure is as follows:
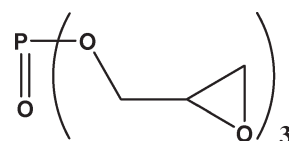
Synthesis of aromatic amide-amines

To a well-stirred solution of PABA (1.37 g, 0.01mol) in pyridine, 2 mL of thionyl chloride (SOCl_2) was added dropwise. After the complete addition, solution was further stirred for ∼ 3 h at room temperature to yield *p*-aminobenzoyl chloride. To this solution of *p*-aminobenzoyl chloride, was added dropwise a solution of *p*-phenylene diamine (1.08 g, 0.01 mol) in pyridine and the mixture was stirred for ∼ 5 h. The solution was then poured into ice-cold water (0–5°C) with constant stirring that resulted into the precipitation of the amide-amine. The precipitated brown colored solid was filtered and washed four times with 10% solution of NaHCO_3 to remove any unreacted acid. It was then washed twice with distilled water followed by methanol and then dried in vacuum oven at 80°C. This amide-amine (yield 80%) was designated as PA. Other amide amines were prepared by using the same procedure and different diamines, i.e., 1,5-diamino naphthalene (N), 4,4′-(9-fluorenyllidene)-dianiline (F), 3,4′-oxydianiline (O), and 4,4′-diamino-diphenyl sulphide (DS), and were designated as NA, FA, OA, and SA, respectively (Scheme 1) where Ar is
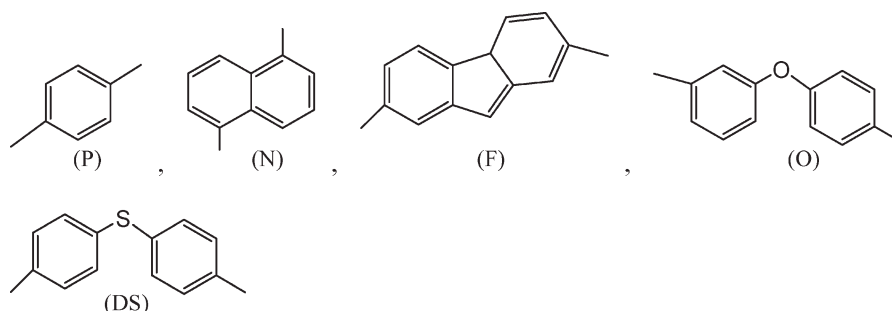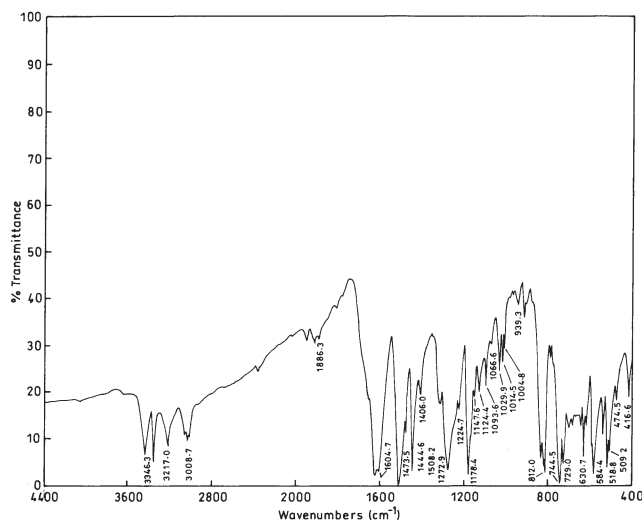
Figure 1 IR spectrum of an amide-amine FA.

Characterization

Synthesized amide-amines curing agents were characterized with the help of spectroscopic techniques, i.e., Fourier Transform Infrared (FTIR) Spectroscopy, Proton Nuclear Magnetic Resonance (^{1}H-NMR) Spectroscopy, and Carbon Nuclear Magnetic Resonance (^{13}C-NMR) Spectroscopy. FTIR spectra were recorded in KBr pellets using Shimadzu-8700 FTIR spectrophotometer. ^{1}H-NMR and ^{13}C-NMR spectra were recorded with a Bruker AVANCE II FT-NMR spectrophotometer at frequency of 400 MHz using deuterated dimethyl sulfoxide (DMSO-d_6) as a solvent and tetra methyl silane as an internal reference.

Curing studies

TA 2100 thermal analyzer having DSC 910 module was used for recording DSC scans at heating rates of 5, 10, 15, and 20°C/min. For curing studies phosphorylated polymer samples were prepared by homogenous and stoichiometric mixing of the blend (TGPO and DGEBA in 2 : 3) with each of synthesized amide-amines, i.e., PA, NA, FA, OA, and SA using a mixture of Dimethyl formamide (DMF) and ethyl methyl ketone as a solvent to generate various epoxy formulations. After the thorough mixing, the solvent was stripped off under vacuum and freshly prepared samples were used for recording DSC traces under nitrogen atmosphere at a programmed heating rate from room temperature upto 250°C. The epoxy samples have been designated by adding suffix EP to PA/ NA/FA/OA /SA.

Thermal stability

Isothermal curing of the samples, i.e., PAEP, NAEP, FAEP, OAEP, and SAEP as prepared earlier was done by heating them at 120°C (2 h) followed by postcure at 200 ± 10°C in an air oven. Thermal sta-

bility of the cured resins was evaluated by recording TG/DTG traces in the nitrogen atmosphere (flow rate 20 cm^3/min) using Perkin Elmer Diamond TG/DTA instrument. A heating rate of 20°C/min and powdered samples of the size 8 ± 2 mg were used in each experiment.

RESULT AND DISCUSSION

Structural analysis of amines

The amide-amines were obtained in ∼ 80–90% yield having colour range from brown to orange. These amines were insoluble in methanol, ethanol, and acetone but were soluble in amide solvents, viz., DMF and dimethyl acetamide.

Fourier Transform Infrared

Figure 1 shows the FTIR spectrum of amide-amines FA. Absorption band due to amide (—CONHR) was observed in all the samples from 1630 ± 10 cm^{-1}. Symmetrical stretch due to —NH (free —NH$_2$ and —NH of amide) were observed in the range of 3317 and 3450 cm^{-1}. Out of plane NH wagging was responsible for the band 1560 cm^{-1}. Absorption band due to (C—N) stretching vibration was observed in the range of 1402 ± 20 cm^{-1} (confirmed the occurrence of reaction).

Proton nuclear magnetic resonance

In the ^{1}H-NMR spectrum of amide-amines a characteristic signal due to amino proton was observed at $\delta = 3.6 \pm 0.5$ ppm. A broad singlet due to —NH proton of the amide group was observed at $\delta = 7.9 \pm 0.6$ ppm. A multiplet due to aromatic protons was observed in the range of $\delta = 6.5$– 8.0 ppm. A representative NMR of the amide-amines FA is shown in Figure 2.
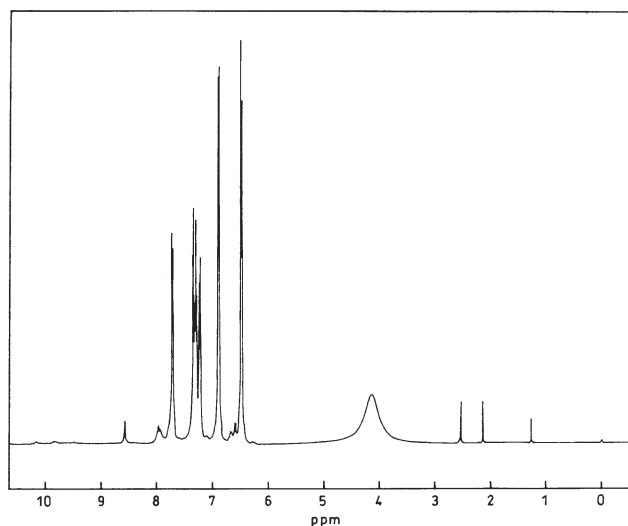

Figure 2 ^{1}H-NMR spectrum of an amide-amine FA.

Carbon nuclear magnetic resonance

Figure 3 shows the ^{13}C-NMR of the amide-amines FA. In the ^{13}C-NMR spectra of the amide-amines, characteristic signals due to Ar—NH$_2$ and amide carbon were observed at $\delta = 145 \pm 10$ ppm and $\delta = 152 \pm 8$ ppm. Multiplets due to aromatic carbons were observed in the range of $\delta = 110$ ppm to $\delta = 140$ ppm.

Curing studies

The curing reaction of epoxy resin depends on the structure and reactivity of curing agents. Not only the chemical structure of curing agents but also steric restrictions among different functional groups of the constituent components and the cure extension can also influence the cure kinetics. To evaluate the effect of structure of synthesized amide-amines on curing behavior of the blend, i.e., DGEBA and TGPO, DSC experiments were carried out. A broad exotherm was observed when the blend (DGEBA + TGPO) was cured with amide-amines of different structures. A typical DSC thermogram showing the curing of DGEBA and TGPO blend with amide-amine FA (at heating rate 10°C/min) is shown in the Figure 4. The exothermic transitions associated with the curing were characterized by following parameters:

- (T_i) is kick off temperature, where curing starts.
- (T_{onset}) is temperature where the first detectable heat was released this was obtained by extrapolation of the steepest portion of the curve.
- (T_p) is temperature on the peak of the exotherm.
- (T_f) is temperature at the end of the curing exotherm obtained by extrapolation of the curve.
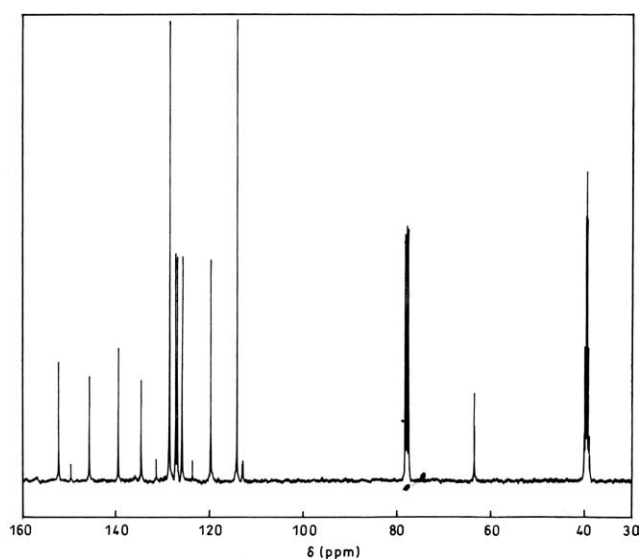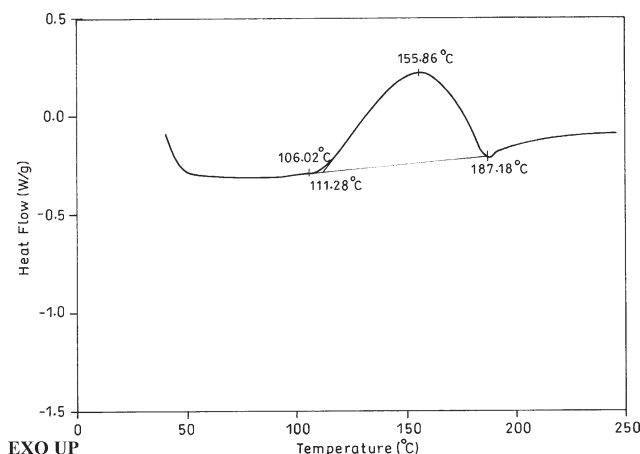

Figure 4 DSC thermogram of DGEBA + TGPO (3 : 2) cured by FA.

The characteristic curing temperatures for the samples are summarized in Table I. In all the samples, a curing exotherm was observed on curing. The curing of epoxy resin was proceeded by nucleophilic attack of amines on the oxirane carbon. A strong nucleophile can initiate the curing process at relatively lower temperature. Therefore, initial temperature of the exotherm may be used as criterion for evaluating the relative reactivities of various amines. The highest T_i value (comparing the temperatures at heating rate 10°C/min) was observed in the case of epoxy resin based on FA, which indicates its least reactivity as compared with others. This could be because of more complex mechanism of curing epoxy blend in the presence of a curing agent

Figure 3 ^{13}C-NMR spectrum of an amide-amine FA.

TABLE I
Results of DSC Scans of DGEBA + TGPO (3 : 2) in the Presence of Various Amide-Amine Curing Agents

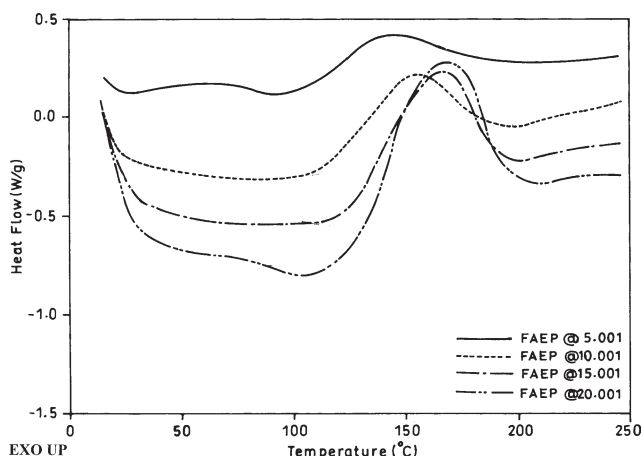| Sample designation	Heating rates (°C/min)	T_i (°C)	T_{onset} (°C)	T_{max} (°C)	T_f (°C)
PAEP	5	75.1	88.5	124.5	168.7
	10	90.1	104.3	150.2	234.3
	15	107.1	115.7	162.6	242.9
	20	117.2	125.7	175.0	245.8
NAEP	5	74.9	78.6	105.7	147.1
	10	85.8	97.1	137.2	218.6
	15	80.3	97.2	148.1	214.3
	20	94.3	100.1	152.9	237.2
FAEP	5	94.5	108.7	141.4	196.4
	10	106.0	111.3	155.9	187.2
	15	122.4	139.1	168.4	191.4
	20	111.4	123.2	172.2	208.9
OAEP	5	67.5	81.4	119.2	164.2
	10	83.9	85.3	138.1	174.9
	15	85.9	110.6	149.2	183.8
	20	81.7	120.8	151.2	190.8
SAEP	5	38.7	68.1	113.4	154.6
	10	77.5	106.4	150.3	182.7
	15	88.8	114.9	152.7	182.3
	20	91.7	117.0	158.2	215.7

Figure 5 DSC scans of FAEP amide-amines at different heating rates of 5, 10, 15, and 20°C /min.

having high molecular weight. This basically reduces the epoxy content per gram of the resin with increase in molecular weight of the amine. Therefore, the factors affecting the curing process are not only nucleophilicity of the amine but also diffusion process as well as reduced oxirane content.[14]

Curing kinetics

Kinetic parameters of curing reaction can be evaluated using dynamic DSC or isothermal method. In this study, dynamic method was used and DSC scans of various polymer samples were recorded at different heating rates, i.e., 5, 10, 15, and 20°C/min. Figure 5 shows the DSC scans (5, 10, 15, and 20°C/min) of thermoset FAEP. The characteristic curing temperatures for DGEBA and TGPO blend in the presence of amide-amines of different structure have been summarized in Table I. Kinetic analysis was performed by using two models, i.e., Kissinger method and Flynn-Wall-Ozawa method, which are based on the following assumptions.[16]

- The peak exothermic temperature T_P represents a point of constant conversion.
- The reaction follows the first order kinetics.
- The temperature dependence of the reaction constant obeys Arrhenius equation.

Kissinger method

According to Kissinger,[19] the activation energy can be obtained from the maximum reaction rate, where $[d(d\alpha/dt)]/dt$ is zero at a constant heating rate. The resulting relation can be expressed as:

$$\frac{d[\log(\phi/T_P^2)]}{d(1/T_P)} = -\frac{0.4342\,E_k}{R}$$

where ϕ is heating rate, E_k is activation energy, R is universal gas constant.

From the peak temperature and heating rates, the data for the plot of $-\log(\phi/T_P^2)$ against $(1/T_P)$ was obtained, and a linear plot as shown in Figure 6(a) was drawn. The activation energy was obtained from the slope of corresponding straight line (without the need to make any assumption about the conversion dependent function).

Flynn-Wall-Ozawa method

The thermal data was also analyzed using Flynn-Wall-Ozawa's method,[20,21] which is in accordance with the following equation.

$$\frac{d\log\phi}{d(1/T_P)} = -\frac{0.4567\,E_o}{R}$$

where ϕ is heating rate, E_o is activation energy, R is universal gas constant.

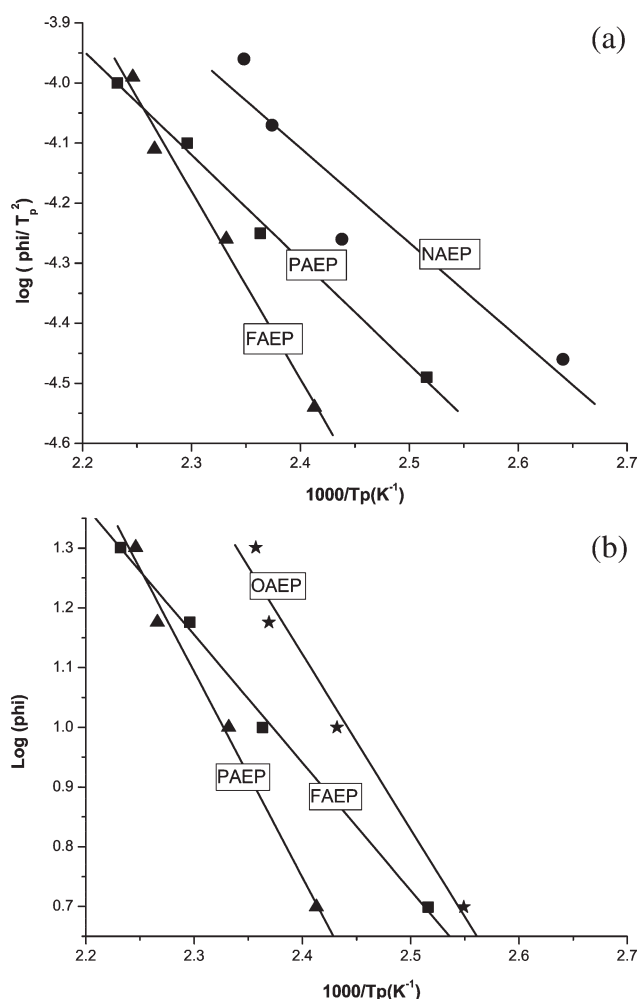**Figure 6** (a) Plots of $(\log\phi/T_P^2)$ vs. $(1/T_P)$ for the samples PAEP, NAEP, and FAEP. (b) Plots of log vs. $1/T_P$ for the samples PAEP, FAEP, and OAEP.

TABLE II
Activation Energies Obtained by Kissinger (E_k) and Flynn-Wall-Ozawa's (E_o) Methods for All Polymers

Sample designation	Activation energy (E_o) (kJ/mol)	Activation energy (E_k) (kJ/mol)
PAEP	38.94	33.39
NAEP	35.03	30.21
FAEP	62.73	59.85
OAEP	53.39	50.03
SAEP	36.01	31.90

Assuming a constant conversion at peak exothermic temperature, plot of log vs. $1/T_p$ were obtained and then activation energy was calculated taking slope of the line and then putting the value in equation as given earlier. Plot of log vs. $1/T_p$ are shown in Figure 6(b).

The activation energies hence obtained using both the methods were compared and the results are summarized in Table II. Activation energies calculated through Flynn-Wall-Ozawa method are slightly higher but not significantly different than those obtained by Kissinger method. However, the activation energies of the curing were found to be dependent on the structure of amide-amines. The value of activation energy was highest in the case of epoxy cured with FA, whereas it is lowest in the case which is cured with NA. This could be because of complex structure of FA leading to more steric restriction and hence attack on the oxirane ring than NA.

Thermal stability

TG/DTG traces of the epoxy resins cured isothermally with stoichiometric amounts of different amide-amines were recorded in nitrogen atmosphere [shown in Figure 7(a–c)]. The isothermal curing of epoxy polymers was done by heating them in an air oven for 2 h at 120°C followed by postcure at 200 ± 10°C. All the samples were stable upto 170 ± 20°C and started losing mass above this temperature. Single-step decomposition was observed in all the samples. The relative thermal stability of the cured resins was evaluated by comparing initial decomposition
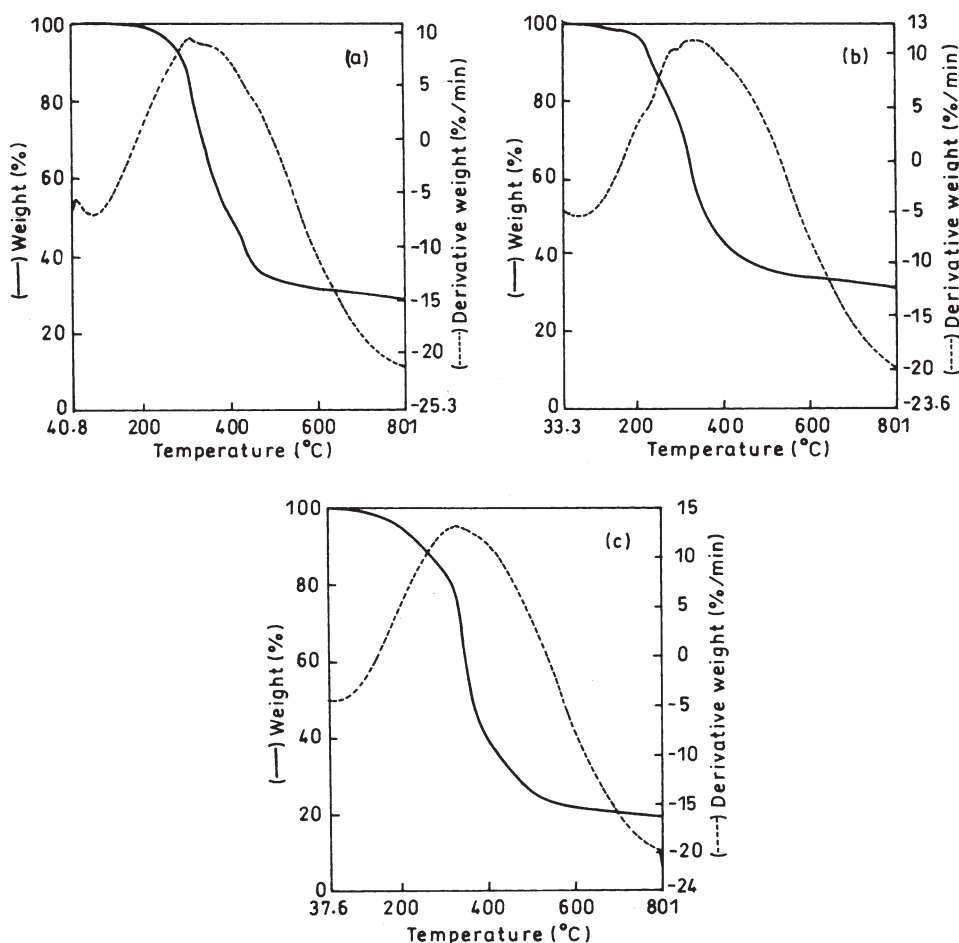

Figure 7 TG/DTG traces of cured epoxy resins under nitrogen atmosphere at the heating rate of 20°C /min of (a) PAEP, (b) NAEP, and (C) FAEP.

TABLE III
Results of Thermal Stability of Isothermally Cured Epoxy Resins at 20°C/min
Heating Rate Under Nitrogen Atmosphere

Sample designation	IDT (°C)	Tmax (°C)	FDT (°C)	% Age char yield (800°C)	Calculated LOI (%)
PAEP	175.3	337.8	619.4	28.6	28.9
NAEP	170.9	337.8	555.9	30.8	29.8
FAEP	160.2	353.9	604.3	21.2	25.9
OAEP	196.8	338.5	562.4	26.4	28.1
SAEP	177.4	334.8	560.2	27.5	28.5

temperature (IDT), temperature of maximum weight loss (Tmax), final decomposition temperature (FDT), and percentage char yield at 800°C. The results of TG/DTG scans are summarized in Table III. The degradation temperatures were found to be dependent on the structures of polymers, which is evident from the data in Table III. Epoxy blend (DGEBA + TGPO) cured with amide-amine FA showed relatively higher values of Tmax. All other samples had Tmax of 334 + 5°C. Highest value of percentage char yield was observed in the case of naphthalene-based epoxy resins because of the presence of stable aromatic ring, whereas it is least in the case of fluorenyllidene-based epoxy resins, which can be because of easier decomposition of five members embraced in two six-membered rings.

Char yield can be used as criteria for evaluating limiting oxygen index (LOI) of the resins in accordance with Van Krevelen and Hofytzer equation.[23]

$$LOI = 17.5 + 0.4 \, CR \text{ (where CR is char yield)}$$

All the epoxy resins except the sample based on amide-amine FA, i.e., FAEP showed the char yields > 28. These results clearly indicate the use of amide-amine based epoxy resins as flame-retardants.

CONCLUSIONS

From these results, it was concluded that five amide-amines were successfully synthesized and characterized. DSC studies showed that amide-amines FA mixing with blended DGEBA and TGPO (3 : 2) showed the higher values of T_i, T_{onset}, and T_p. The activation energies calculated by using both the methods (Kissinger and Flynn-Wall-Ozawa) also showed higher values for DGEBA + TGPO cured with FA (i.e., sample FAEP). Thermal stability of the sample NAEP (i.e., DGEBA + TGPO cured with NA) was the highest compared with others.

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