

CURING KINETICS AND THERMAL STABILITY OF EPOXY BLENDS CONTAINING PHOSPHOROUS-OXIRANE WITH AROMATIC AMIDE-AMINE AS CURING AGENTS

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Abstract This article describes the synthesis of a series of aromatic amide-amines and their potential use as epoxy hardeners. These amines were synthesized by the reaction of L-phenylalanine (PA) with diamines of different structures *i.e.* 1,4-phenylene diamine (PD), 1,5-diamino naphthalene (N), 4,4'-(9-fluorenylidene)-dianiline (F), 4,4'-diaminodiphenyl sulphide (DS) and 3,4'-oxydianiline (O) in a stoichiometric ratio (1:1). Structural characterization of synthesized amide-amines was done with the help of elemental analysis and spectroscopic techniques *viz.* FT-IR, ¹H-NMR and ¹³C-NMR. An epoxy blend was prepared by mixing tris(glycidyloxy) phosphine oxide (TGPO) with conventional epoxy *i.e.* diglycidyl ether of bisphenol-A (DGEBA) in an equivalent ratio of 2:3 to incorporate phosphorous into the main chain. The curing kinetics of the epoxy blend with synthesized aromatic amide-amines was investigated by non-isothermal DSC technique using multiple heating rate method (5, 10, 15 and 20 K/min.). The activation energies were determined by fitting the experimental data into Kissinger and Ozawa kinetic models. The activation energies obtained through Ozawa method were slightly higher than those of 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 (TGA) in nitrogen atmosphere. All the samples showed improved thermal stability in terms of char yield than using only amines as hardeners.

Keywords: Phosphorylated epoxy; Amide-Amines; Curing kinetics; Char yield; Thermal stability.

INTRODUCTION

Epoxy resins are widely used as encapsulating materials in the electronic/electrical industries and advanced composite matrices for structural laminates, owing to their high tensile strength and modulus, good chemical and corrosion resistance and excellent dimensional stability. However, the common epoxy systems cannot satisfy the need of high thermal and flame resistance for these applications^[1–3]. Several techniques and approaches for structural modification of epoxy have been employed in improving the flame retardancy of epoxy polymers which include the incorporation of halogen and/or phosphorus into the polymer backbone. But the incorporation of halogen into polymers is not preferred because the toxic, corrosive gases produced during their combustion are increasingly becoming an area of concern to environmental legislators^[4–7]. As a result, phosphorus, nitrogen, and silicon compounds have been evolved as non-toxic flame retardants for epoxy resins. Organophosphorus compounds when compared to phosphorus-free epoxy resins, show a lower thermal stability, with a reduced initial decomposition temperature, but exhibit a multi-step degradation with a higher final char yield^[8–10]. During the first degradation step, a thermally stable char is formed and serves as an outer layer to prevent the further degradation of the bulk and thus improve the flame retardancy. Incorporating covalently bonded phosphorus into epoxy resins could be achieved using phosphorus-containing oxirane compounds or curing agents. As a reactive-

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type flame retardant, the oxirane compound with phosphorus in the backbone of epoxy resins exhibits much better flame retardance and overcomes several drawbacks associated with the physical blend of the epoxy resins and the flame retardants. However, the combination of different types of flame retardants can lead to a synergistic improvement in the fire retardance of epoxy resins^[11–14]. Literature survey revealed that a significant improvement of flame-retardance efficiency was observed when phosphorus and nitrogen elements existed simultaneously in the curing system of epoxy resins. Nitrogen is generally incorporated into the epoxy thermoset by using *N*-containing curing agents like diamines, polyamines and imide/amide encapped with amines. Aromatic polyamides are thermally stable high performance thermoplastics due to their outstanding rigidity in the backbone, but this unique feature makes them insoluble in organic solvents. However, the solubility of polyamides can be increased by carrying out structural modifications^[15]. Therefore, it was found to be interesting to utilize the structurally modified thermally stable aromatic amide-linkage into the epoxy resin in the form of curing agent.

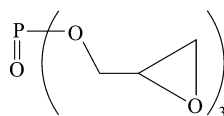
The optimum performance properties including thermal stability and flame retardancy can be obtained by cross-linking the epoxy resins into a three-dimensional and infusible network, which in-turn are strongly influenced by the functionality, structure and compositions of both epoxy monomer and the curing agent^[16]. Curing kinetics, variation of rate at various temperatures, activation energy of curing and other kinetic data provide the information for the curing cycles of epoxies, which ensures that the adequately cured epoxy is able to meet the requirements of its end use. Kinetic characterization of thermoset resins is fundamental in understanding structure/property/processing relationships for manufacturing and utilization of high performance composites^[17, 18]. Therefore it was important to study the reactivity of synthesized curing agents toward the newly tailored epoxy blend to establish the structure-property relationship.

In this article, we synthesized partially aromatic amide-amines of different structure having amino-acid as well as only one amide linkage to make them soluble in common organic solvents and used them as epoxy curing agents. The amide-amines were synthesized by reacting 1 mol of *N*-protected phenylalanine (PA) with 1 mol of 1,4-phenylene diamine (PD), 1,5-diamino naphthalene (N), 4,4'-(9-fluorenylidene)-dianiline (F), 3,4'-oxydianiline (O) and 4,4'-diaminodiphenyl sulphide (DS) and designated them by putting suffix PA as PDPA, NPA, FPA, OPA and SPA respectively. In our efforts to prepare a thermal stable epoxy system, an epoxy blend was prepared by mixing phosphorylated epoxy resin, TGPO [tris(glycidyloxy)phosphine oxide] with DGEBA (Diglycidyl ether of bisphenol-A) in an equivalent ratio of 2:3 to incorporate phosphorous in main chain. Epoxy polymers were obtained by reacting the amide-amines stoichiometrically with this blend and their curing kinetics was investigated using Kissinger^[19] and Flynn-Wall-Ozawa's^[20, 21] dynamic kinetic methods. The thermal stabilities of cured polymers were evaluated using thermo gravimetric analysis under nitrogen atmosphere.

EXPERIMENTAL

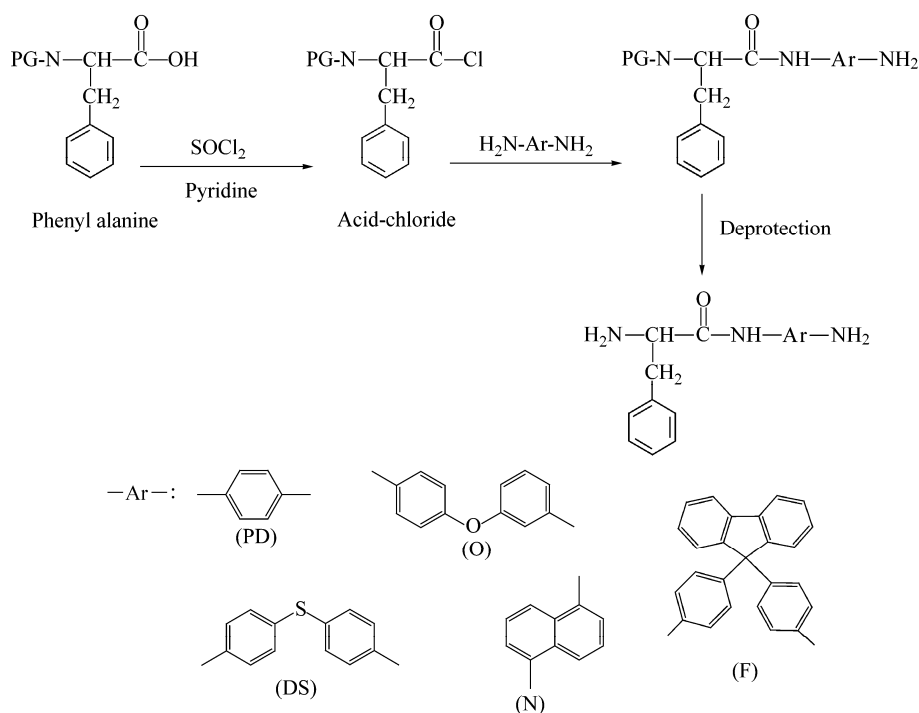
Materials

Diglycidyl ether of bisphenol-A (DGEBA of grade LY556, EEW 177, Hindustan Ciba Geigy Ltd.), diamines of different structures *i.e.* 1,4-phenylene diamine (PD), 1,5-diamino naphthalene (N), 4,4'-(9-fluorenylidene)-dianiline (F), 3,4'-oxydianiline (O) and 4,4'-diaminodiphenyl sulphide (DS) all of Sigma-Aldrich Co. were used as received. Protected amino-acid L-phenylalanine (SRL), methanol (CDH), pyridine (Thomas Baker), thionyl chloride (Thomas Baker) and sodium bicarbonate (CDH) were used as received. Phosphorylated epoxy *i.e.* tris(glycidyloxy)phosphine Oxide (TGPO, EEW 120) was synthesized^[8] and characterized in our laboratory, the structure of TGPO^[22] is as follows:



Synthesis of Aromatic Amide-Amines

N-protected L-phenylalanine (10 mmol) in *ca.* 10 mL of pyridine, placed under nitrogen in a three necked flask was stirred well to ensure its complete dissolution. To this solution 2 mL of thionyl chloride (SOCl_2) was added dropwise, and the reaction mixture was further stirred for about 3 h at room temperature to yield the acid chloride. The excess of thionyl chloride was removed by distillation, first by simple distillation and then by use of dry benzene. A solution of 4,4'-diaminodiphenyl sulphide (DS, *ca.* 10 mmol) in dry DMF was added drop wise into the solution of acid chloride (*ca.* 10 mmol) in dry DMF with continuous stirring and then was stirred for about 5 h. The solution was then poured into ice-cold water ($0-5^\circ\text{C}$) with constant stirring, and amide-amine precipitated out as dirty white colored solid. The solid was filtered and washed three times with 10% solution of NaHCO_3 to remove any unreacted acid. Finally it was washed with water till neutral, then with CH_3OH followed by deprotection^[23]. The product obtained was then dried in vacuum oven at 80°C . This amide-amine (yield 76%) was designated as SPA. Other amide amines based on L-phenylalanine were prepared by using the same procedure and different diamines. The amide-amines based on L-phenylalanine were designated by putting suffix PA to the letter designation of diamines of different structures *i.e.* 1,4-phenylene diamine (PD), 3,4'-oxydianiline (O), 4,4'-diaminodiphenyl sulphide (DS), 1,5-diamino naphthalene (N) and 4,4'-(9-fluorenylidene)-dianiline (F) such as PDPA, SPA, OPA, NPA and FPA (Scheme 1).



Scheme 1 Reaction scheme of synthesis of amide-amine curing agents

Characterization

Structural characterization of the synthesized amide-amine curing agents was done with the help of elemental analysis, Fourier transform infrared (FTIR) spectroscopy, proton nuclear magnetic resonance ($^1\text{H-NMR}$) spectroscopy and carbon nuclear magnetic resonance ($^{13}\text{C-NMR}$) spectroscopy. Elemental analysis was carried out using a Euro EA 3000 elemental analyzer. FTIR spectra were recorded in KBr pellets using a Shimadzu-8700 FTIR spectrophotometer. $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra were recorded with a Bruker AVANCE II FT-NMR spectrophotometer using DMSO-d_6 (deuterated dimethyl sulfoxide) as solvent and tetra methyl silane (TMS) as an internal reference.

Curing Studies

TA 2100 thermal analyzer having DSC 910 module was used for recording DSC scans to evaluate the curing behavior of the DGEBA (diglycidyl ether of bisphenol-A) blended with TGPO [tris(glycidyloxy)phosphine oxide] in the ratio of 3:2. Various epoxy polymer samples were prepared by homogenous and stoichiometric mixing of the blend with each of synthesized amide-amines *i.e.* PDPA, NPA, FPA, OPA and SPA using a mixture of dimethyl formamide (DMF) and ethyl methyl ketone as a solvent. The solvent was then stripped off under vacuum, and freshly prepared samples of the size (4 ± 2) mg were used for recording DSC traces under nitrogen atmosphere at a programmed heating rate from room temperature upto 300°C. The epoxy samples have been designated by adding suffix EP to PDPA/ NPA/FPA/OPA /SPA. In order to determine the activation energy for the curing reaction of the blend with stoichiometric amounts of amide-amines multiple heating rate methods (5, 10, 15, 20 K/min) of Kissinger and Ozawa were used.

Thermal Stability

Various epoxy samples *i.e.* PDPAEP, NPAEP, FPAEP, OPAEP and SPAEP as prepared above were isothermally cured by heating at 150°C (2 h) followed by post curing at (200 ± 10) °C in an air oven. To evaluate the thermal stability of the cured resins TG/DTG experiments were performed using a Perkin Elmer Diamond TG/DTA instrument in the atmosphere of nitrogen (flow rate 20 cm³/min). A heating rate of 10 K/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 *ca.* 70%–80% yield having color range from dirty white to dark brown. These amines were insoluble in methanol, ethanol and partially soluble in acetone, but were soluble in amide solvents like dimethyl formamide (DMF) and dimethyl acetamide (DMAc). The structure of amide-amines was confirmed by elemental analysis and common spectroscopic techniques. Table 1 shows the result of CHN analysis. The calculated values of CHN agreed well with the experimentally determined values.

Table 1. Results of C, H and N of aromatic amide-amines based on L-phenylalanine

Sample designation	Molecular formula	Found (calculated) (%)		
		C	H	N
PDPA	C ₁₅ H ₁₇ N ₃ O (255)	70.8 (70.6)	6.5 (6.7)	16.2 (16.5)
OPA	C ₂₁ H ₂₁ N ₃ O ₂ (347)	71.9 (72.6)	5.99 (6.09)	12.4 (12.1)
SPA	C ₂₁ H ₂₁ N ₃ OS (363)	69.2 (69.4)	5.9 (5.8)	11.4 (11.6)
NPA	C ₁₉ H ₁₉ N ₃ O (305)	74.6 (74.7)	6.5 (6.3)	13.9 (13.8)
FPA	C ₃₄ H ₂₉ N ₃ O (496)	82.6 (82.4)	5.7 (5.9)	8.6 (8.5)

In the FTIR spectra of amide-amines, symmetrical stretching vibration due to $-\text{NH}_2$ was observed in the range of 3336–3444 cm⁻¹. The absorption bands due to amide-I and amide-II were observed at (1630 ± 20) cm⁻¹ and 1506–1595 cm⁻¹ in all the samples whereas the absorption bands appearing at 1404–1492 cm⁻¹ can be assigned to $\nu(\text{C}-\text{N})$ stretching vibrations. Out of plane NH wagging is responsible for a broad band of medium intensity in the range of 800–666 cm⁻¹. A band due to aromatic $\nu(\text{C}-\text{H})$ stretching was also obtained in these spectra at the usual positions. In the case of amide-amine OPA strong absorption bands due to Ar–O–Ar linkage were obtained at 1024 cm⁻¹. A typical FTIR spectrum of SPA along with spectrum of PA is shown in Fig. 1.

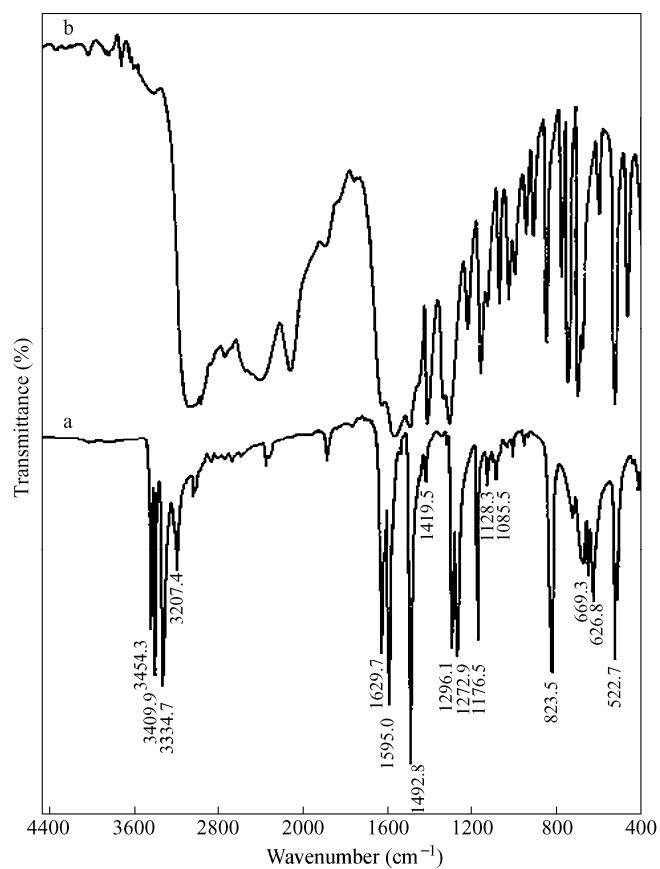


Fig. 1 IR spectra of amide-amine SPA (a) and amino-acid PA (b)

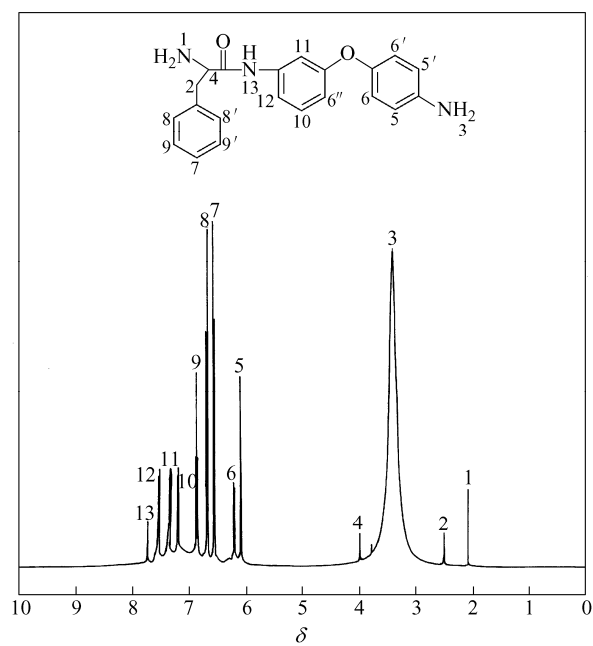


Fig. 2 ^1H -NMR spectrum of amide-amine OPA

In the ^1H -NMR spectrum of amide-amines, characteristic signal due to hydrogen of amide group was observed at $\delta = 7.7\text{--}8.1$. A singlet was observed at $\delta = 3.4 \pm 0.1$ for aromatic $-\text{NH}_2$ group whereas $-\text{NH}_2$ group of phenylalanine showed a singlet at $\delta = 2.0$. Multiplets due to aromatic protons were observed at $\delta = 6.4\text{--}8.0$. A characteristic signal due to methylene protons ($-\text{CH}_2$) was observed at $\delta = 2.5 \pm 0.2$ and the signal due to methine proton ($-\text{CH}$) was observed at $\delta = 3.9 \pm 0.1$. The proton integration area was consistent with the molecular formula. An H-NMR spectrum of OPA is shown in Fig. 2.

Figure 3 shows the ^{13}C -NMR spectrum of FPA amide-amine. In the ^{13}C -NMR spectra of amide-amines, characteristic signals due to aromatic carbons were observed at $\delta = 103\text{--}149$. Characteristic signals due to chiral carbon ($-\text{CH}$) was observed at $\delta = 60\text{--}63$ whereas the signal due to $-\text{CH}_2$ was overlapped with signal of DMSO and was observed at $\delta = 40$. In the case of sample OPA, a singlet due to $\text{C}-\text{O}-\text{C}'$ of $\text{Ar}-\text{O}-\text{Ar}'$ was also observed at $\delta = 160$ whereas an additional signal at $\delta = 65.0$ was observed for a carbon of cyclopentane ring in the spectrum of FPA. All the samples showed singlets due to carbon of $\text{Ar}-\text{NH}_2$ and amide carbon at $\delta = 145\text{--}152$ and $\delta = 170 \pm 2$, respectively.

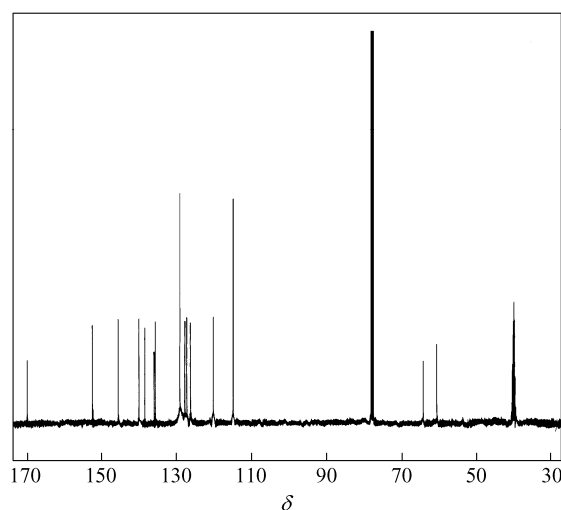


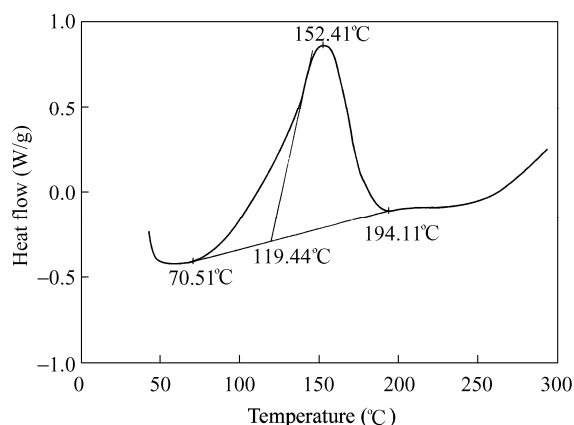
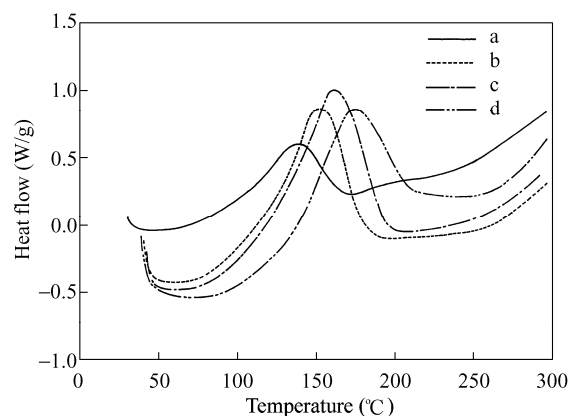
Fig. 3 ^{13}C -NMR spectrum of amide-amine FPA

Curing Studies

The curing reaction of the epoxy resin depends on the structure and reactivity of the curing agent. The curing of epoxy resin proceeds by the nucleophilic attack of amine on the oxirane carbon, and would thus depend on nucleophilic character of amines. When amines having higher nucleophilicity are used, the onset temperature of curing is expected to be lower. It was interesting to understand the effect of structure of amide-amines on the curing behavior of the blend. In the DSC scans of the blend with stoichiometric amounts of amide-amines, a broad exotherm due to curing reaction was observed in the temperature range of $67\text{--}282^\circ\text{C}$ (Table 2, Fig. 4). The exothermic transition associated with curing was characterised by determining T_i (kick-off temperature of curing), T_{onset} (temperature of onset of exotherm), T_p (temperature of peak position of exotherm) and T_f (temperature of the end of the exotherm). In the present studies the reactivities of curing agents on the basis of onset temperatures (T_i and T_{onset}) of curing (at 10 K/min) of the blend were compared and found to be depended on the amine structure and were in the order $\text{SPA} > \text{OPA} > \text{FPA-NPA} > \text{PDPA}$. The high reactivity of SPA is due to the presence of an electron withdrawing sulphur in the structure which makes it better nucleophiles than other amines. The least reactivity of PDPA is attributed to the presence of resonance effect ($+R$), because of which electrons of nitrogen are not readily available for nucleophilic attack.

Table 2. Curing parameters obtained from DSC scans of DGEBA + TGPO (3:2) in the presence of various amide-amine curing agents

Sample designation	Heating rates (K/min)	T_i (°C)	T_{onset} (°C)	T_{max} (°C)	T_f (°C)
PDPAEP	5	126.4	128.3	169.2	235.7
	10	142.3	149.4	206.4	247.1
	15	156.1	161.2	222.13	265.4
	20	165.8	168.2	238.2	282.2
NPAEP	5	100.9	108.9	136.13	197.7
	10	113.9	115.2	166.3	256.8
	15	128.9	135.9	168.8	255.7
	20	134.5	143.7	212.7	254.7
FPAEP	5	106.3	119.3	137.5	199.5
	10	112.2	119.8	141.6	209.9
	15	112.8	138.9	151.9	236.7
	20	119.6	126.9	170.3	242.1
OPAEP	5	103.8	108.5	128.3	226.7
	10	104.8	110.0	136.7	213.1
	15	107.8	113.5	149.9	224.9
	20	117.4	132.5	169.6	248.9
SPAEP	5	66.9	110.1	139.6	170.8
	10	70.5	119.4	152.4	194.1
	15	83.84	129.9	161.9	202.6
	20	119.9	145.5	176.4	226.0

**Fig. 4** DSC thermogram of DGEBA + TGPO (3:2) cured by SPA**Fig. 5** DSC scans of SPA amide-amines at different heating rates of (a) 5, (b) 10, (c) 15 and (d) 20 K/min

Curing Kinetics

Kinetic parameters of the curing reactions can be obtained from dynamic DSC scans or isothermal methods. In the present study kinetic analysis was performed using dynamic kinetic models, and DSC scans were recorded at different heating rates *i.e.* 5, 10, 15 and 20 K/min for all the samples. Figure 5 shows the DSC scans of the amide-amine SPA cured with EP at different heating rates. The activation energies of curing reaction were calculated using Kissinger and Ozawa methods, both of these methods are based on the assumptions that: (1) The peak exothermic temperature T_p represents a point of constant conversion; (2) The reaction follows the first order kinetics; (3) The temperature dependence of the reaction constant obeys Arrhenius equation.

According to the Kissinger method, the activation energy can be obtained from the equation expressed as

$$\frac{d[\ln(\phi/T_p^2)]}{d(1/T_p)} = -\frac{E}{R} \quad (1)$$

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

From the peak temperature (T_p) and heating rates, the scatter graph of $-\ln(\phi/T_p^2)$ against $(1/T_p)$ was drawn, as shown in Fig. 6(a), the straight line has been drawn according to the method of least square. The activation energy was obtained from the slope of corresponding straight line. (Without the need to make any assumption about the conversion dependent function)

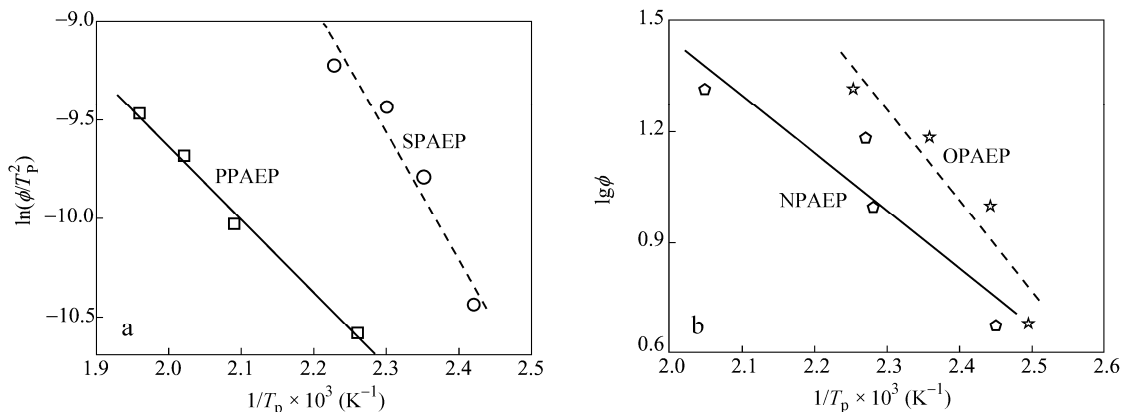


Fig. 6 (a) Plots of $(\ln\phi/T_p^2)$ versus $(1000/T_p)$ for the samples PDPAEP and SPAEP; (b) Plots of $\lg\phi$ versus $1000/T_p$ for the samples NPAEP and OPAEP

In Ozawa's method, the relationship between the heating rate and T_p is given as

$$\lg\phi = \lg(AE/R) - \lg f(x) - 2.315 - 0.4567 E/RT_p$$

or

$$\lg\phi = A' - 0.4567 E/RT_p \quad (2)$$

where $f(x)$ is a conversion dependent term. Thus, for a given conversion, the relationship between $\lg\phi$ and $1/T_p$ should be a straight line. The scatter plots of $\lg\phi$ and $1/T_p$ were drawn as shown in Fig. 6(b), in which linear fits were made to experimental data points. From the slope of straight lines activation energies were calculated. The activation energies thus calculated from the above methods were found to be dependent on the structure of amines and were summarized in Table 3. The values of activation energies calculated by Kissinger method (23.3–53.8 kJ/mol) were lesser than the values calculated by Ozawa's (28.3–58.2 kJ/mol) but were comparable. The activation energies calculated by using both methods (Kissinger and Ozawa) showed higher values for DGEBA + TGPO cured with SPA and FPA.

Table 3. Curing activation energies calculated from Kissinger and Ozawa's methods for all polymers

Sample designation	Activation energy (kJ/mol)	
	Ozawa's method	Kissinger's method
PDPAEP	36.6	30.9
NPAEP	28.3	23.3
FPAEP	55.7	51.3
OPAEP	44.6	39.8
SPAEP	58.2	53.8

Thermal Stability of Cured Network

TGA/DTG traces of isothermally cured epoxy resins with various amines were recorded in N_2 atmosphere as shown in Figs. 7(a–d). The relative thermal stability of cured resins was evaluated by comparing the initial

decomposition temperature (T_i), final decomposition temperature (T_f) and temperature of maximum rate of mass loss (T_{max}) and percent char yield at 800°C (Table 4). Single step decomposition was observed in all samples except in FPAEP. Two step decomposition of FPAEP can be explained due to degradation of a five membered ring embraced in two six member phenyl rings. All the cured thermosets were stable in the range of 259–322°C and major weight loss occurred after this. As expected, the thermal stability of this newly tailored epoxy composition decreased in terms of IDT but the value of percent char yield increased than the case when we used only amines as curing agent^[22]. Phosphorylated epoxy resins generally increase the flame retardancy by producing phosphorous rich thermostable char. Isothermally cured epoxy thermosets FPAEP and SPAEP after TGA experiment left behind the lowest percentages of char yield of 19.4 and 19.3 respectively at 800°C, whereas NPAEP showed highest char yield of 45.5. The highest value of char yield obtained in the case of NPAEP may be due to the compact network structure. Increased char formation can limit the production of

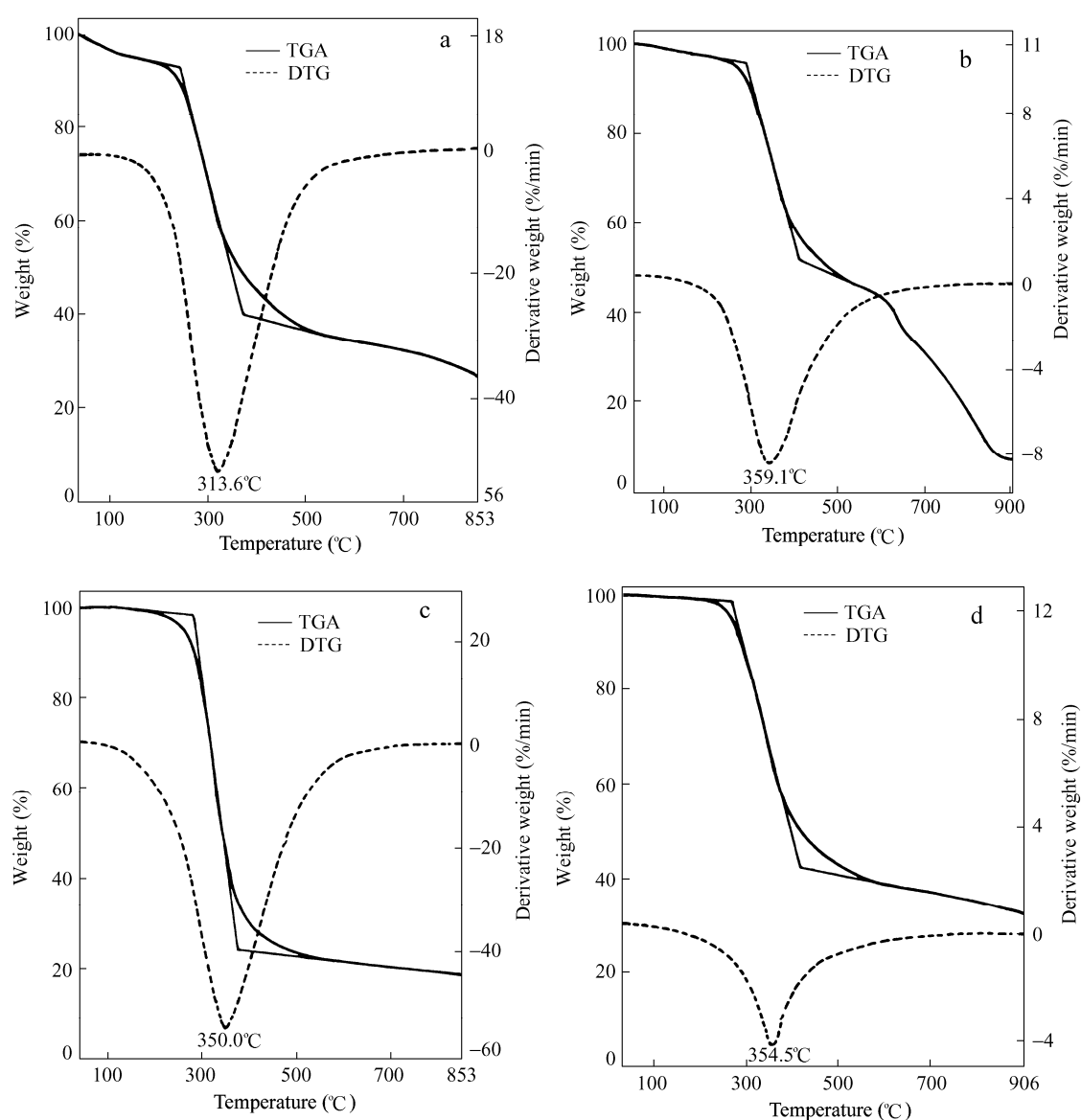


Fig. 7 TGA/DTG traces of cured epoxy resins under nitrogen atmosphere at the heating rate of 10 K/min of (a) PDPAEP, (b) FPAEP, (c) SPAEP, (d) OPAEP

combustible carbo-containing gases, decreases the exothermicity due to pyrolysis reactions, as well as decrease the thermal conductivity of the burning materials^[24].

Table 4. Results of thermal stability of isothermally cured epoxy resins at 10 K/min heating rate under nitrogen atmosphere

Sample designation	IDT (°C)	$T_{\max}$ (°C)	FDT (°C)	% Age char yield (800°C)	Calculated LOI (%)
PDPAEP	259.1	313.6	359.1	28.9	29.1
NPAEP	300.0	331.8	386.4	45.5	35.7
FPAEP	322.7	359.1	395.4	19.4	25.3
SPAEP	304.5	350.0	372.7	19.3	25.2
OPAEP	281.8	354.5	402.0	34.3	31.2

The ability to form char is related to the flammability of a polymer. The higher the amount of residual char after combustion, the lower the amount of combustible material available to perpetuate the flame and the greater is the degree of flame retardance of the material^[25]. Van Krevelen^[26] proposed that the char residue on pyrolysis is linearly proportional to the oxygen index for halogen-free polymer. We used the same for evaluating theoretical values of LOI ($\text{LOI} = 17.5 + 0.4 \text{ CR}$, CR is char yield).

Epoxy polymers having LOI higher than 28 can be classified as self extinguishing and flame resistant. In the present study epoxy samples PDPAEP (LOI = 29.1), NPAEP (LOI = 35.7) and OPAEP (LOI = 31.2) can be treated as flame resistant.

CONCLUSIONS

A series of amide-amines containing phenylalanine were successfully synthesized and characterized by elemental analysis and spectroscopic techniques. Curing studies by DSC revealed that the blend (DGEBA and TGPO in 3:2) when cured with amide-amines PDPA showed the higher values of T_i , T_{onset} and T_p and hence was found to be least reactive. The activation energies calculated by using both the methods of Kissinger and Ozawa showed higher values for DGEBA + TGPO cured with SPA and FPA. Amide-amides curing agents showed improved thermal stability in terms of char yield. The sample NPAEP (*i.e.* DGEBA+ TGPO cured with NPA) showed maximum char yield suggesting better flame retardancy.

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