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Curing and thermal behaviour of diamide–diimide–diamines based on L-phenylalanine with epoxy blends containing phosphorus/silicon

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Abstract A series of diamide–diimide–diamines (DADIDAs) were synthesized by reacting diacid *N*,*N*'-(3,3',4,4'-benzophenone tetracarboxylic)-3,3'4,4' diimido-bis-L-phenylalanine (I) with different aromatic diamines *viz.* 1,4-phenylene diamine (PD), 1,5-diamino naphthalene (N), 4,4'-(9-fluorenyllidene)-dianiline (F), 4,4'-diaminodiphenyl sulphide (DS) and 3,4'-oxydianiline (O). The diacid (I) was synthesized by the condensation of 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA) with L-phenylalanine (PA) in a solution of glacial acetic acid and pyridine (3:2 v/v) at refluxing temperature. The resulting DADIDAs so synthesized were characterized with the help of elemental analysis (EA) and spectroscopic techniques, and were used as epoxy curing agents. Two epoxy blends (EP and ES) were prepared, each by mixing in an equivalent ratio of 2:3 of tris(glycidyloxy)phosphine oxide (TGPO) with diglycidyl ether of bisphenol-A (DGEBA) and 1,3-bis(3-glycidyloxypropyl)tetramethyl disiloxane (BGPTMSO) with diglycidyl ether of bisphenol-A (DGEBA), respectively. A series of new epoxy thermosets with good thermal stability were prepared by reacting EP/ES with synthesized DADIDAs stoichiometrically. Thermal properties of these epoxy resins were observed using the techniques viz. Differential scanning calorimeter (DSC) for curing behaviour and Thermogravimetric analysis (TGA) to study the thermal stability and mass loss behaviour. All the samples showed good thermal stabilities in terms of char yield (24.8–**52.7**) and calculated LOI (27.4–**38.6**), thereby demonstrate their effective use as flame retardant systems.

Keywords Phosphorylated epoxy · Siloxanes · Curing · Char yield · Thermal stability · Flame retardancy · Diamide–diimide–diamines

Introduction

The wide acceptances of epoxy resins in advanced composite matrices, surface coating, adhesives and semiconductor encapsulation applications due to their heat, solvent and chemical resistance, good mechanical and electrical properties and strong adherence to many substrates is well established [1–4], however, modified epoxy resins with better heat and moisture resistance are required for certain specific applications. For this reason, modifications of epoxy resins or curing agents in both backbone and pendant groups have therefore been continuously investigated to improve the thermal and physical properties of cured polymers [5–9]. Studies have been reported for improving the heat resistance of epoxy resins by increasing the crosslink density of cured epoxy resin or introducing bulky structures such as polyimides, urethane [10], or heterocyclic compounds such as hydroxy terminated imide-compounds [11, 12] and imide-acid [13, 14]. Polymers containing imide-structure have many excellent improved properties, such as good heat resistance, high char yield, high limited oxygen index and good flame proofing [15]. Therefore, the developments of these polymers have attracted extensive research interests during past few years [16–18].

Another modification proposed for increasing the flame retardancy in the epoxy resin is the introduction of phosphorous/silicon containing compounds, [19, 20] which has been evolved as an alternative to the halogen-based flame retardants having toxic effects. The phosphorus/silicon covalently bonds to the final epoxy network thereby

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imparts extra thermal stability. These compounds lead to the formation of carbonaceous char which protects the polymer surface from the flame action when burnt. phosphorous/silicon can be introduced in epoxy network either in the main chain by using phosphorous-oxiranes [21–23] or phosphorous-containing curing agents [24–26]. However, use of oxirane compound with phosphorus in the backbone of epoxy resins exhibited much better flame retardance and has overcome several drawbacks associated with the physical blend of the epoxy resins and the flame retardants.

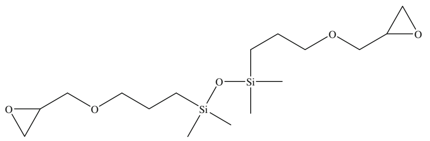
In the present study, the structural modification of the epoxy resin was done by introducing phosphorous/silicon in the main chain by blending conventional DGEBA with phosphorous/silicon containing oxiranes and using nitrogen containing cross linkers to study the synergistic effect of both nitrogen and phosphorous/silicon. For this purpose, a series of new curing agents containing nitrogen, diamide–diimides–diamines (DADIDAs), having preformed imide-rings were synthesized and characterized by spectroscopic techniques. The epoxy blends EP and ES containing P/Si oxirane, respectively, were then reacted stoichiometrically with the synthesized curing agents, and their thermal behaviour was investigated.

Experimental

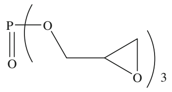
Materials

Diglycidyl ether of bisphenol-A (DGEBA, Grade LY556 having EEW 177) was procured from Hindustan Ciba Geigy Ltd. 1,3-Bis(3-glycidyloxypropyl)tetramethyl disiloxane (BGPTMSO, EEW180), 3,3’,4,4’-benzophenone tetracarboxylic dianhydride (BTDA), 1,4-phenylene diamine (PD), 1,5-diamino naphthalene (N), 4,4′-(9-fluorenyllidene)-dianiline (F), 4,4′-diaminodiphenyl sulphide (DS) and 3,4′-oxydianiline (O), all were purchased from Sigma-Aldrich and were used as received. L-Phenyl alanine (Merck) and glacial acetic acid (SRL) were used without any purification. Pyridine (Py, Merck) was purified by distillation under reduced pressure over calcium hydride. Dimethyl formamide (DMF, Merck) was dried under P_2O_5 and distilled under vacuum.

Structural formulas of 1,3-bis(3-glycidyloxypropyl)tetramethyl disiloxane (**1**, BGPTMSO, EEW 180) and synthesized [27] tris(glycidyloxy)phosphine oxide (**2**, TGPO, EEW 120) are shown as follows:



(1)



(2)

Synthesis of diamide–diimide–diamines (DADIDAs)

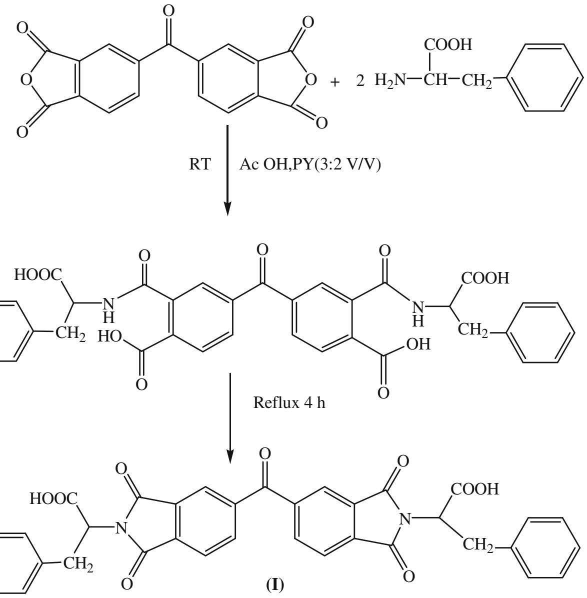
Diamide–diimide–diamines of different structures were synthesized in two steps:

Step 1: synthesis of diimide–diacid (DIDA)

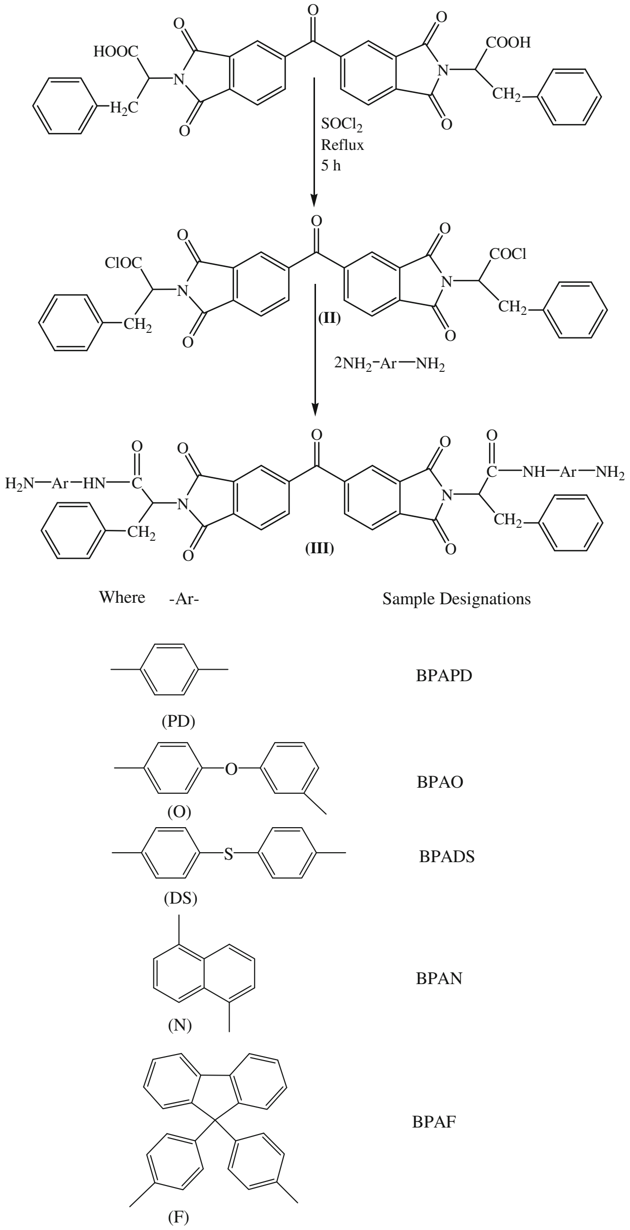
A mixture of dianhydride (BTDA, 3.22 g, 10 mmol) and L-phenylalanine (3.3 g, 20 mmol) in a solution of approximately 50 mL of glacial acetic acid and pyridine (3:2 v/v) was stirred over night and then refluxed for about 5 h to complete the condensation reaction between the amines and anhydride groups, as well as the subsequent cyclodehydration reaction (Scheme 1) [15]. The mixture of solvents was later removed under vacuum to leave a viscous residue which was dissolved in 100 mL of cold water, and then the solution was decanted. The subnatant mixture was then treated with 5 mL of concentrated HCl with continuous stirring to remove any entrapped pyridine. A light yellow amorphous solid was obtained, washed with water, filtered off and dried to give *N*,*N*’-(3,3′,4,4-benzophenone tetracarboxylic)-3,3’4,4’ diimido-bis-L-phenylalanine (**I**, yield 85%).

Step 2: synthesis of diamide–diimide–diamines (DADIDAs)

N,*N*’-(3,3′,4,4′-benzophenone tetracarboxylic)-3,3’4,4’ diimido-bis-L-phenylalanine (**I**, 3.0 g, 9 mmol) was condensed with 10 ml (an excess amount) of thionyl chloride by refluxing for about 5 h followed by stirring for another



Scheme 1 Synthesis of diimide–diacid (DIDA)



Scheme 2 Synthesis of diamide–diimide–diamines (DADIDA)

2 h at room temperature. The excess of thionyl chloride was removed by distillation, firstly by simple distillation and then by the use of dry benzene to give a dark yellow solid (**II**, diacid chloride).

The resulting compound (**II**) was dissolved in dimethyl formamide (DMF) and added drop-wise to the well-stirred solution of 1,4-phenylene diamine (PD, 18 mmol) in dry DMF The mixture was stirred for about 4 h at room temperature (Scheme 2). The resulting DADIDA was precipitated by pouring the mixture into ice-cold water with constant stirring and filtered. The product was washed with $NaHCO_3$ repeatedly to remove unreacted acid and then with copious amount of water and finally with hot methanol and then dried at 60 °C for 12 h in vacuum. Other DADIDAs were also prepared using the same procedure and different diamines and were designated using the prefix BPA to the diamines as given in Scheme 2.

Characterization

Structural characterization of the synthesized diamide–diacid (DIDA) and DADIDA was done using EA, Fourier transform infrared (FTIR) spectroscopy, nuclear magnetic resonance spectroscopy, i.e. ^{1}H NMR and ^{13}C NMR. Elemental analysis was carried out using Euro EA 3000 elemental analyzer. IR spectra were recorded in the range 4400–600 cm^{-1} by Shimadzu-8700 FTIR spectrophotometer in KBr pellets. ^{1}H NMR and ^{13}C NMR spectra were recorded with a Bruker AVANCE II FT-NMR spectrophotometer at frequency of 400 MHz using DMSO-d_6 (deuterated dimethyl sulfoxide)/$CDCl_3$ as a solvent and tetra methyl silane (TMS) as an internal reference.

Curing studies

Two blends of epoxy resins were prepared by homogenous mixing of tris(glycidyloxy) phosphine oxide (TGPO) with diglycidyl ether of bisphenol-A (DGEBA) (designated by EP) and 1,3-Bis(3-glycidyloxypropyl)tetramethyl disiloxane (BGPTMSO) with diglycidyl ether of bisphenol-A (DGEBA) (designated by ES); each in equivalent ratio of 2:3. Polymer samples were prepared by the reaction of stoichiometric amount of synthesized DADIDAs with EP and ES. The polymers so prepared were designated as BPAPD/EP, BPAO/EP, BPADS/EP, BPAN/EP, BPAF/EP and BPAPD/ES, BPAO/ES, BPADS/ES, BPAN/ES, BPAF/ES, respectively, with EP and ES. TA 2100 thermal analyzer having DSC 910 module was used for recording DSC scans to evaluate the curing behaviour of fresh samples prepared by using a mixture of dimethyl formamide (DMF) and ethyl methyl ketone as a solvent. The solvent was then stripped off under vacuum and samples of the size 4 ± 2 mg were used for recording DSC traces under nitrogen atmosphere at a programmed heating rate from room temperature to 300 °C.

Thermal stability

Various epoxy samples as prepared above were isothermally cured by heating at 180 °C (2 h) followed by post cure at 250 ± 10 °C in an air oven. Thermogravimetric data were obtained on Perkin Elmer Diamond TG/DTA instrument under nitrogen flowing at a rate of 20 cm^{3} min^{-1} to evaluate the thermal stability of the cured resins. The instrument was programmed at a heating rate of

10 °C min^{-1} and powdered samples of the size 6 ± 2 mg were used in each experiment.

Result and discussion

Structural characterization

The DIDA (I) was synthesized by the condensation reaction and subsequent cyclodehydration of L-phenylalanine (2 mol) with dianhydride (1 mol) in a mixture of acetic acid-pyridine (3:2) mixture. Dissolution of the residue in cold water resulted in the formation of semisolid. The semisolid was then treated with concentrated HCl to form a light yellow solid (85%). The resulting diimide-diacid (**I**) was then reacted with $SOCl_2$ (thionyl chloride) to convert it into diacid-dichloride (**II**, Scheme 1). The resulting compound then was condensed with aromatic diamines having Sulphur, Oxygen, phenyl, naphthalene and cardo group (Scheme 2). The DADIDAs were obtained in 76–90% yields having colour variation from dirty white to brown and were soluble in organic polar aprotic solvents such as *N*,*N*-dimethylacetamide (DMAc), *N*,*N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO) at room temperature, and were insoluble in solvents such as methylene chloride, ethanol, methanol and water. The chemical structures of the synthesized DADIDAs were confirmed using elemental analysis, IR, ^{1}H NMR and ^{13}C NMR spectroscopic techniques. The results of elemental analysis are given in Table 1, and the values were well agreed with those calculated theoretically.

In the FT-IR spectrum of Diamine–diacid (DIDA), the characteristic bands due to >C=O of imide groups appeared at 1778 and 1718 cm^{-1}, whereas the presence of O–H group was indicated by a broad band at 2900–3500 cm^{-1}. The absorption bands appeared at 3030 and 2925 cm^{-1} are related to the corresponding aromatic and aliphatic C–H stretching vibration, respectively. The IR spectra of all DADIDAs showed absorptions in the range of 3381–3436 cm^{-1} ($\nu_{N\text{–}H}$), two absorptions at 1724 ± 4 (ν_{symm} C=O) and 1780 ± 2 (ν_{asymm} C=O) of imide group, and 1674 ± 4 ($\nu_{N\text{–}H}$ amide) [28]. All the samples showed absorbance at 1352–1384 and 710–734 cm^{-1}, which suggested the presence of the imide heterocycle. In the ether containing DADIDA (i.e. BPAO), a strong absorption band due to ν (Ar–O–Ar) stretching vibration was observed at 1018 cm^{-1}. Figure 1a and b shows the FT-IR spectra of DIDA and BPAPD, respectively. Disappearance of strong acidic hydroxyl peak and the appearance of rather sharp peak at 3422 cm^{-1} (due to $\nu_{N\text{–}H}$) in IR spectrum of BPAPD confirmed a complete conversion of DIDA to DADIDA.

Table 1 CHN analytical data of diimide–diamide–dimines

Sample designation	Molecular formula	Yield (%)	Found (calculated) (%)		
			C	H	N
BPAPD	$C_{47}H_{36}N_6O_7$ (797)	76	70.76 (70.84)	4.54 (4.55)	10.61 (10.55)
BPAO	$C_{59}H_{44}N_6O_9$ (981)	83	72.91 (72.24)	5.01 (4.52)	8.25 (8.57)
BPADS	$C_{59}H_{44}N_6O_7S_2$ (1013)	80	70.46 (69.94)	4.16 (4.38)	8.76 (8.29)
BPAN	$C_{55}H_{40}N_6O_7$ (897)	85	73.98 (73.65)	5.11 (4.50)	9.29 (9.37)
BPAF	$C_{85}H_{68}N_6O_7$ (1285)	90	79.40 (79.42)	5.46 (5.33)	6.32 (6.54)

The ^{1}H NMR spectra of diimide–diacid showed a characteristics signal due to –COOH group at δ 10.5 ppm (singlet), and aromatic protons were observed in the range of 7.5–8.5 ppm. The ^{1}H NMR spectra of DADIDAs showed a broad peak due to amino group ($–NH_2$) in the range of δ 3.8–4.4 ppm. A singlet observed at $\sim\delta$ 8.00 ppm has been assigned to secondary amide group (–CONH). The signal of C–**H** of chiral centre of amino-acid moiety appeared at δ 4.2–4.7 ppm whereas the Signal due to methylene protons ($–CH_2$) was obtained at δ 2.0 [29]. The resonance of aromatic protons appeared in the range of δ 6.9–8.9 ppm, however, the signals due to aromatic protons of BTDA (δ 8.0–8.5) were down field than others. The proton integration area was consistent with the molecular formula (Fig. 2).

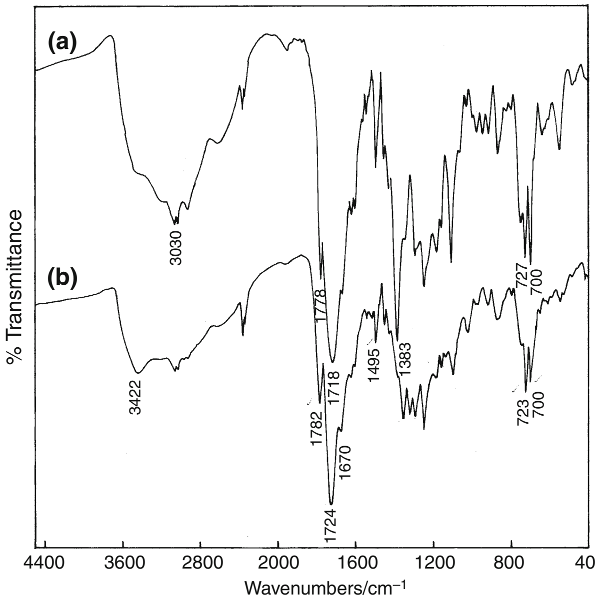


Fig. 1 **a** IR spectrum of diimide–diamine (DIDA); **b** IR spectrum of BPAPD

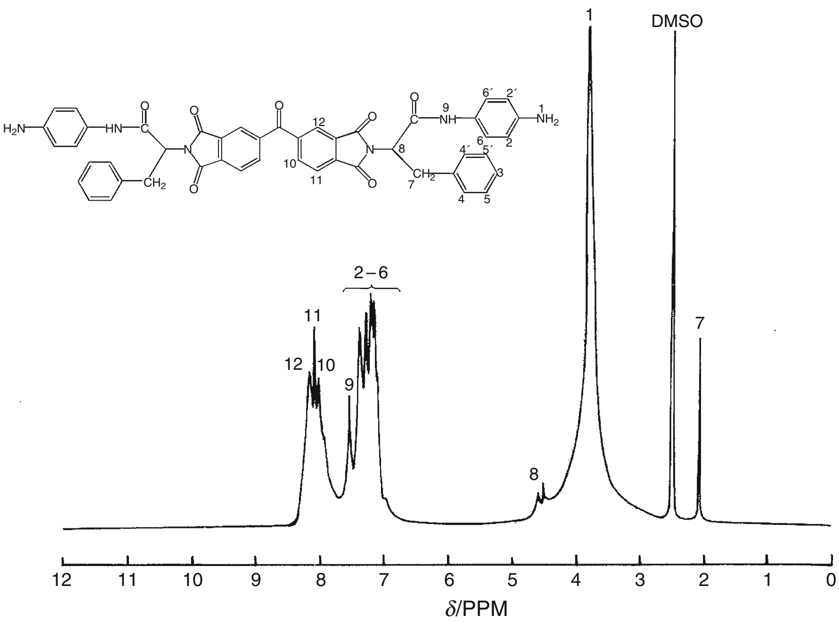


Fig. 2 ^{1}HNMR spectrum of a diamide–diimide–diamine BPAPD

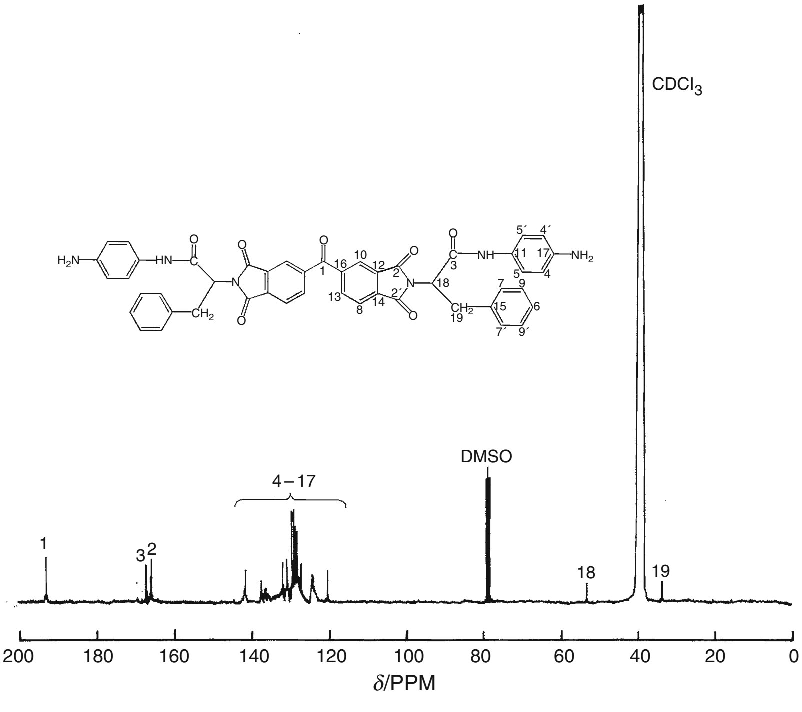


Fig. 3 ^{13}CNMR spectrum of a diamide–diimide–diamine BPAPD

In ^{13}C NMR spectrum of all DADIDAs, the peaks due to aromatic carbons were observed in the range of δ 107–150 ppm. The peaks due to –CH and –CH_2 of L-phenylalanine were appeared at δ 53–63 ppm and δ 31–34 ppm, respectively. The peaks due to carbonyl carbon (*C=O) of amide and imide groups appeared at δ 169 and δ 165 ppm, respectively, where as carbonyl carbon of benzophenone showed the signal at δ 193 ppm. A signal due to C–O–C in the spectra of BPAO was observed at δ 151 ppm, whereas in the spectrum of BPAF a characteristic signal due to carbon of cyclopentene ring was observed at δ 63 ppm (Fig. 3).

Curing studies

In order to evaluate the effect of structure and reactivity of the synthesized DADIDAs on curing behaviour of Epoxy blends, i.e. EP and ES, DSC (Differential Scanning

Calorimetry) studies were carried out using stoichiometric ratio of ES/EP and DADIDAs. In the DSC traces of all the samples, *two* broad exothermic transitions of curing were observed. The exotherm at lower temperature may be due to epoxy-amine reaction and the high temperature exotherm may be due to etherification as well as co-curing of resins. The exothermic transition associated with curing was characterised by determining,

- T_i = kick-off temperature, where curing starts, and this was taken as the temperature where the base line starts deviating
- T_o = temperature of onset of exotherm,
- T_p = temperature of peak position of exotherm,
- T_f = temperature of end of the exotherm,
- ΔH = heat of curing reaction.
  (T_o and T_f were obtained by extrapolation of the steepest portion of the exotherm)

The characteristic curing temperatures of the polymers were summarised in Table 2 (Fig. 4a, b). The curing of epoxy resin proceeds by the nucleophilic attack of amine on the oxirane carbon; hence, a stronger nucleophile can always increase the rate of curing process. The relative reactivity of various DADIDAs as curing agents was evaluated by comparing the peak temperature of exotherm (T_p). The higher value of T_p was observed with BPAO and BPADS for both the epoxy blends EP/ES. This behaviour of the curing agent may be attributed due to the presence of electron withdrawing ether or sulphide linkage, which in turn decreases the nucleophilicity of the amines. However, the curing of epoxy blends with these amines is a complex process and the phr (per hundred parts of resin) of amines used is significantly different with each other because of variation in the molecular masses. This basically reduces the epoxy content per gram of resin with the increase in the molecular mass of the amine. Therefore, the factors affecting the curing process are not only the nucleophilicity of the amine but also the diffusion processes as well as reduced oxirane content. [30] The DSC scan of isothermally cured epoxy thermosets, and the exothermic transition was absent which revealed their complete curing.

Thermal stability

Thermal stability of resin blends was evaluated by recording the TG/DTG traces of isothermally cured samples under nitrogen atmosphere and was found to be comparable in all the blends (Table 3). TG/DTG traces (Fig. 5) were characterized by determining extrapolated initial decomposition temperature (IDT), extrapolated final decomposition temperature (FDT), the temperature of maximum rate of mass loss (T_max) and percent Char Yield

Table 2 Results of DSC scans of EP/ES in the presence of stoichiometric amount of diamide–diimide–diamines at heating rate of 10 °C min^{-1}

Sample Designation	T_i/K	T_onset/K	T_p/K	T_f/K
BPAPD/EP	328.0	334.4	352.1	366.8
	412.3	414.8	446.3	475.6
BPAO/EP	371.1	392.6	405.0	450.0
	459.6	467.3	493.4	530.7
BPADS/EP	377.4	377.5	395.9	411.2
	439.3	457.1	503.3	521.3
BPAN/EP	341.2	341.8	355.8	370.4
	376.4	377.3	455.6	514.0
BPAF/EP	386.7	386.8	399.3	435.1
	444.0	445.1	492.0	512.2
BPAPD/ES	345.8	346.1	358.7	382.5
	403.4	404.3	442.2	494.1
BPAO/ES	379.9	380.1	412.6	448.2
	456.7	425.9	495.5	522.2
BPADS/ES	378.9	380.4	384.3	420.8
	425.1	425.9	443.4	483.8
BPAN/ES	343.7	343.9	356.5	372.5
	389.6	396.1	479.4	520.7
BPAF/ES	332.3	334.1	346.9	366.8
	417.3	427.1	466.1	525.8

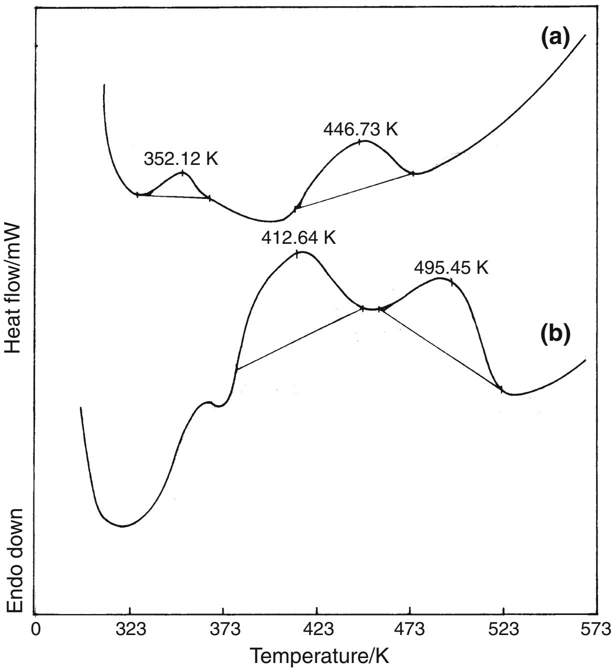


Fig. 4 DSC Scans at the heating rate of 10 °C min^{-1} of (*a*) EP in the presence of Stoichiometric amount of BPAPD. (*b*) ES in the presence of Stoichiometric amount of BPAO

Table 3 Results of TG/DTG traces of isothermally cured epoxy thermosets scanned at the heating rate of 10 °C min^{-1} under nitrogen atmosphere

Sample designation	IDT/K	T_{max}/K	FDT/K	% Age char yield (800 °C)	Calculated *LOI* (%)
BPAPD/EP	557.3	592.2	772.2	24.8	27.4
	807.4	876.5	964.9		
BPAO/EP	269.4	292.6	417.4	39.2	33.2
BPADS/EP	542.4	565.6	690.4	47.7	36.6
BPAN/EP	548.2	557.9	643.1	46.7	36.2
BPAF/EP	539.6	575.3	596.8	52.7	**38.6**
BPAPD/ES	543.0	569.7	643.3	25.3	27.6
BPAO/ES	567.7	595.16	698.7	27.4	28.5
BPADS/ES	548.4	562.4	750.3	26.1	27.9
BPAN/ES	563.6	590.6	728.1	42.7	34.6
BPAF/ES	553.3	569.2	701.4	36.6	32.1

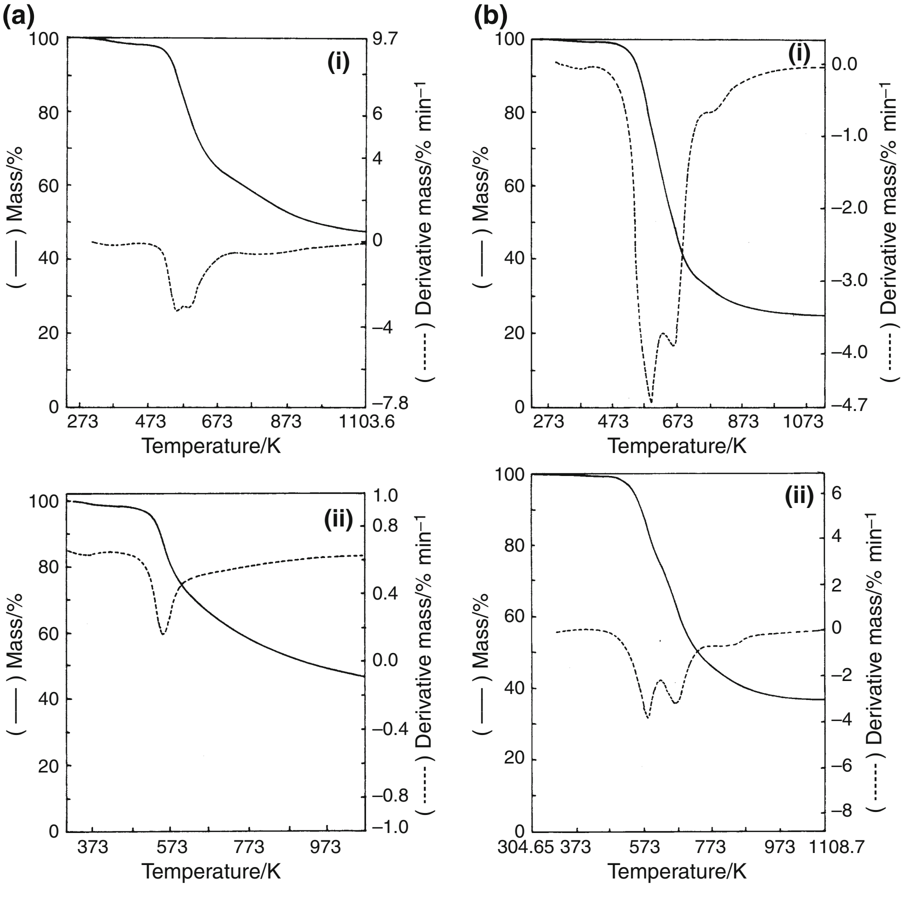


Fig. 5 TG/DTG traces at the heating rate of 10 °C min^{-1} under the nitrogen atmosphere of **a** EP cured isothermally with both BPADS and BPAN. **b** ES cured isothermally with both BPAPD and BPAF

at 800 °C. Single step decomposition was observed in all the samples except BPAPD/EP. All the samples were stable up to 267 °C, and a significant mass loss occurred between 300 and 450 °C.

Char yield can be used as criteria for evaluating limiting oxygen index (LOI) of the resins as shown in accordance with Van Krevelen and Hofytzer equation [31].

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

Increased char formation can limit the production of combustible carbo-containing gases, decreases the exothermicity due to pyrolysis reactions, as well as decreases the thermal conductivity of the burning materials. The blends having phosphorus in main chain, i.e. EP cured with

DADIDAs showed the better char yield than those having Silicon, i.e. ES cured with DADIDAs. However, most of the samples showed much improved percent char yield (36.6–52.7) and flame retardancy than using only DGEBA as base resin [32]; thereby demonstrating the Synergistic influence of Phosphorus/Nitrogen and Silicon/Nitrogen in epoxy resins.

The highest value of char yield obtained in the case of BPAF/EP may be primarily due to the compact network structure and then having phosphorus in main chain. Epoxy polymers having LOI higher than 28 can be classified as flame resistant. In the present study, all the samples except BPAPD/EP can effectively be used as flame retardant epoxy thermosets.

Conclusions

In this study, the synergistic effect of phosphorous/silicon with nitrogen on the flame retardancy of epoxy resin has been elaborated. For the same purpose, Phosphorus/Silicon was taken in main chain in the form of oxiranes and was blended with conventional epoxy resin DGEBA. Nitrogen was incorporated into the epoxy system in the form of DADIDA Curing agents, which were synthesized and characterized by Elemental Analysis and spectroscopic techniques. Curing behaviour of the epoxy blends with the synthesized curing agents was evaluated by Differential Scanning Calorimetry. The thermal stability and flame retardancy of the cured resins were determined by thermogravimetric analysis and some of the prepared blend resins showed much improvement in them in terms of Char yield (36.6–52.7) and LOI (32.1–38.6). The blends having phosphorus in main chain, i.e. EP cured with DADIDAs showed the better char yield than those having Silicon, i.e. ES cured with DADIDAs. The highest value of char yield was obtained in the case of BPAF/EP.

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