

Synthesis, Characterization of Phosphorus Containing Diamide-diimide-tetraamines Based on L-Tryptophan Amino Acid and Their Effect on Flame Retardancy of Epoxy Resins

Seema Agrawal and Anudeep Kumar Narula*

GGS Indraprastha University, Sector-16C Dwarka, Delhi 110078, India

Abstract The curing behavior of diglycidyl ether of bisphenol-A (DGEBA) with different phosphorus containing diamide-diimide-tetraamines (DADITAs) was studied by DSC. Eight DADITAs of varying structures were synthesized by reacting 1 mole of pyromellitic anhydride (PMDA)/3,3'-benzophenone tetracarboxylic dianhydride (BTDA)/1,4,5,8-naphthalene tetracarboxylic dianhydride (NTDA)/4,4'-oxydiphthalic anhydride (ODPA) with 2 mole of L-tryptophan (T) in a mixture of acetic acid and pyridine (3:2 *V/V*) followed by activation with thionyl chloride and then condensation with excess of phosphorus containing triamines tris(3-aminophenyl) phosphine (TAP) and tris(3-aminophenyl) phosphine oxide (TAPO). DADITAs obtained by reacting PMDA/BTDA/NTDA/ODPA with L-tryptophan followed by condensation with TAP/TAPO were designated as PTAP, PTAPO, BTAP, BTAPO, NTAP, NTAPO, OTAP and OTAPO respectively. The structural characterization of synthesized DADITAs was done by FTIR, ¹H-NMR, ¹³C-NMR, ³¹P-NMR spectroscopic techniques and elemental analysis. Thermal stability of the isothermally cured epoxy was investigated using dynamic thermogravimetry analysis. The glass transition temperature (*T_g*) was highest in DGEBA cured using PTAP. All epoxy thermosets exhibited excellent flame retardancy, moderate changes in *T_g* and thermal stability. Due to presence of phosphorus in curing agents, all epoxy resin systems met the UL-94 V-0 classification and the limiting oxygen index (LOI) reached up to 38.5, probably because of the nitrogen-phosphorus synergistic effect.

Keywords: Diamide-diimide-tetraamines; DGEBA; Curing behavior; Thermal stability; Flame retardancy.

INTRODUCTION

Epoxy resins have many attractive properties such as solvent and chemical resistance, low shrinkage, ease of cure and processing, good adhesive strength, excellent electrical and mechanical properties and ease of modification to optimize the properties^[1–6]. These epoxy resins have been widely used as adhesives, surface coatings, aerospace composite matrix, laminates, membranes, potting, encapsulant for semiconductors and insulating material for electronic devices^[7–11]. However, the common epoxy systems cannot satisfy the fields that require high thermal stability and flame retardancy. It is crucial to improve thermal stability, electrical properties and halogen free flame retardation of epoxy to utilize them better in electronic and aerospace industry. Several approaches have been reported for modification of the epoxy backbone to enhance the thermal properties and flame retardancy^[12–18].

Improvement in the thermal properties of epoxy resins by incorporating imides, amides, aromatic structures such as naphthalene, biphenyl, anthracene, pyrene, using phosphorus containing flame retardant to replace traditional halogenated compound, has been reported in literature either at the time of polymerization stage or as flame retardant additive^[19–27]. Incorporation of phosphorus and heterocyclic rings into the epoxy backbone leads

* Corresponding author: Anudeep Kumar Narula, E-mail: researchchemlab58@gmail.com

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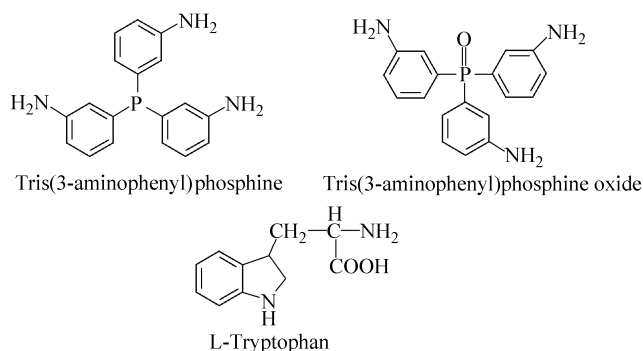
to an improvement in thermal stability and flame retardancy. New types of epoxy resins with adequate thermal stability and high char yield have been prepared by incorporating phosphine moiety and flexible ring in the backbone. Reaction of DGEBA (epoxy) with phosphorus containing amines gave products with superior stability and good flame retardancy.

We have recently reported DGEBA blended with two phosphorus containing epoxies tris(glycidyloxy) phosphine oxide (TGPO) and tris(glycidyloxy)phosphine (TGP) followed by curing with diamine curing agents^[28]. In present article curing behavior of DGEBA using phosphorus containing diamide-diimide-tetraamines is described. These epoxy thermosets are expected to exhibit required flame retardancy, high thermal stability and less fumes than conventional bisphenol-A type of epoxy resins.

EXPERIMENTAL

Materials

Diglycidyl ether of Bisphenol-A (DGEBA, grade LY556, having an epoxy equivalent 177) was procured from Hindustan Ciba Geigy Ltd. Pyromellitic anhydride (PMDA), 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA), 1,4,5,8-naphthalene tetracarboxylic dianhydride (NTDA) and 4,4'-oxydiphthalic anhydride (ODPA) all were purchased from Sigma Aldrich and used as received. L-tryptophan and glacial acetic acid were purchased from Merck and used without any purification. Pyridine (CDH) was purified by distillation under reduced pressure over calcium hydride. Methyl ethyl ketone (Merck) and thionyl chloride (Thomas baker) were used as received. Tris(3-aminophenyl)phosphine (TAP) and tris(3-aminophenyl)phosphine oxide (TAPO) were synthesized in laboratory as per reported procedure^[29]. Structures of all amines and L-tryptophan are shown in Scheme 1.



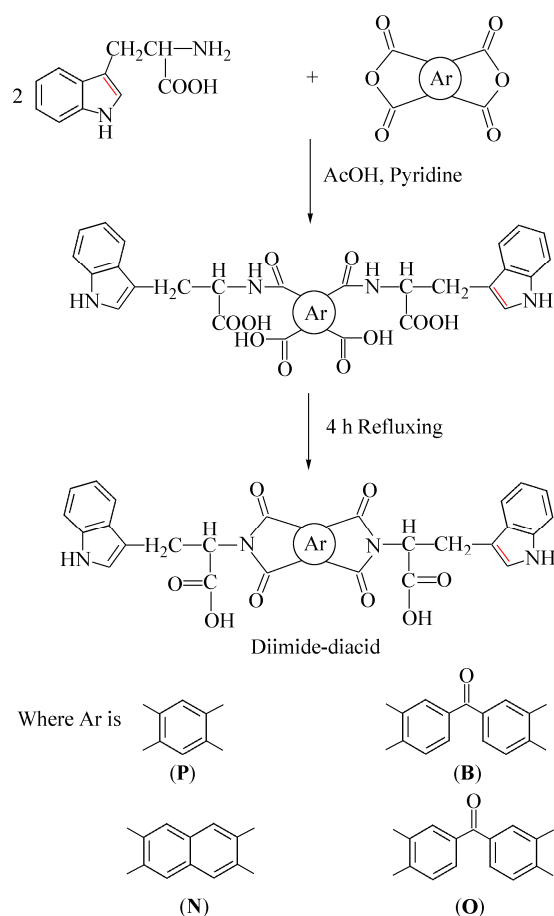
Scheme 1 Structures of phosphorus containing amines and L-tryptophan

Synthesis

Synthesis of diimide-diacids (DIDAs)

The dianhydride PMDA (4.36 g, 0.02 mol), L-tryptophan (8.17 g, 0.04 mol) and a mixture of acetic acid and pyridine (3:2 *V/V*) were placed in a 250 mL round bottom flask. The mixture was stirred overnight at room temperature and then refluxed for 5 h according to Scheme 2^[30]. The solvent was removed under reduced pressure and the residue was dissolved in 150 mL cold water and 8 mL concentrated HCl was added. The solution was stirred until a dark orange precipitate was formed. This precipitate was then filtered off and dried to give approximately 94% yields. This sample was designated as **P**.

Similarly, all other diimide-diacids were prepared by reacting BTDA/or NTDA/or ODPA with L-tryptophan and designated as **B**, **N** and **O** respectively.

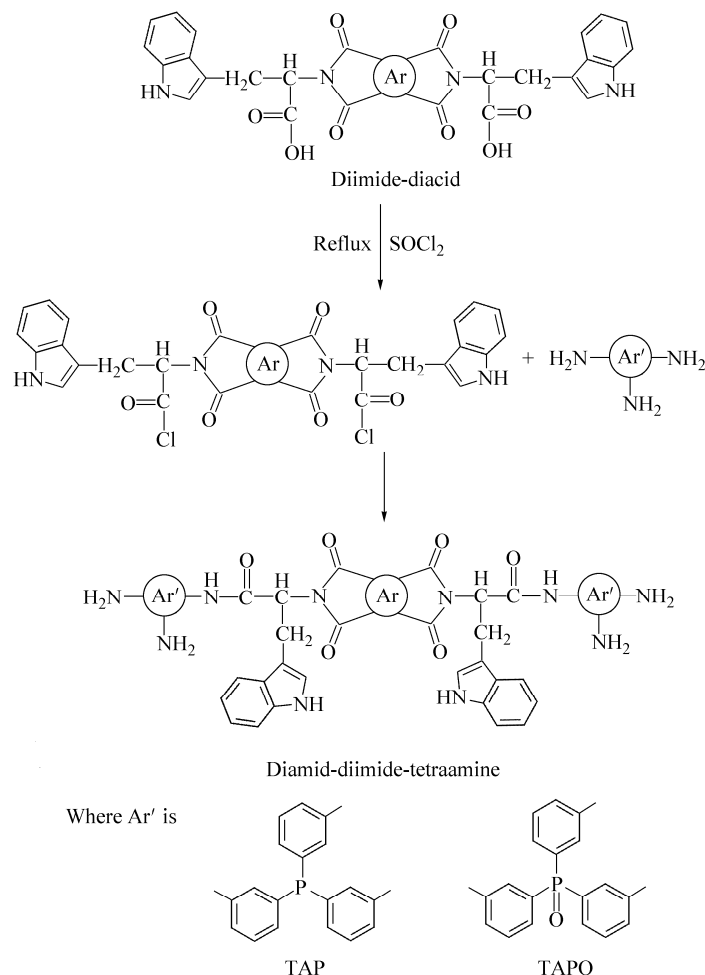
**Scheme 2** Synthesis of diimide-diacid*Synthesis of diamide-diimide-tetraamines (DADITAs)*

Diimide-diacidchloride of **P** was obtained by refluxing the mixture of diimide-diacid **P** (2.95 g, 0.005 mol) and excess of thionyl chloride for 5 h. The excess of thionyl chloride was removed by simple distillation and then by use of dry benzene. To the well stirred solution of tris(3-aminophenyl) phosphine (TAP) (3.07 g, 0.01 mol) in dry DMF, diimide-diacidchloride of **P** (3.07 g, 0.01 mol) in DMF was added dropwise and then stirred for 6 h at room temperature according to Scheme 3. The diamide-diimide-tetraamine was precipitated by pouring the reaction mixture into ice cold water with constant stirring. The product was washed with dil. NaHCO_3 to remove unreacted acid, then with water till neutral and finally with CH_3OH . It was dried in vacuum oven at 80°C and was designated as PTAP. Similarly, all other diamide-diimide-tetraamines were synthesized by reacting diimide-diacidchloride of **B**/or **N**/or **O** with phosphorus containing triamines.

Characterization

Structural characterization of diamide-diimide-tetraamines was done by Fourier transform infrared (FTIR), ^1H -NMR, ^{13}C -NMR, ^{31}P -NMR spectroscopy and elemental analysis. ^1H -NMR, ^{13}C -NMR and ^{31}P -NMR spectra were recorded on a BRUKER TOP-SPIN spectrophotometer (300 MHz) in DMSO-d_6 solution at room temperature. FTIR spectra were recorded using a Perkin Elmer RXI spectrophotometer. Perkin Elmer Diamond model was used for thermogravimetric analysis of epoxy thermosets. When running dynamic scans, it was done in Hi-Resolution mode, where the heating rate was automatically adjusted in response to changes in the rate of weight loss, which results in improved resolution, with an initial heating rate of 10 K/min under nitrogen atmosphere. Differential scanning calorimetric (DSC) analysis was performed on a 2100 thermal analyser having

DSC 910 module at a heating rate of 10 K/min under a reflux of nitrogen. T_g was taken as midpoint of the enthalpy transitions along the thermograms. Flammability (reaction to a small flame) was investigated by limiting oxygen index (LOI) tests using flammability tester as per the standard ASTM D 2863-77 procedure. Flammability rating was also determined by UL94 vertical tests where the sample size of 125 mm $\times$ 12.5 mm $\times$ 3 mm was used. Specimens were mounted vertically and a flame was introduced to the specimen at an angle of 45° for 10 s.



Scheme 3 Synthesis of diamide-diimide-tetraamine

Curing Studies

Rheometric analyser having DSC 910 module was used to record DSC scans at the heating rate of 10 K/min in nitrogen atmosphere. For curing studies the samples were obtained by mixing DGEBA with stoichiometric amounts of appropriate diamide-diimide-tetraamines dissolved in a minimum amount of low boiling solvent. The functionality of all curing agents was taken as four. Epoxy/amines systems were cured at 145 °C for 2 h, 170 °C for 1.5 h and 190 °C for 1.5 h respectively. Therefore these epoxy thermosets were allowed to cool slowly at room temperature in order to prevent cracking and then used for recording DSC traces. A sample size of (8 $\pm$ 1) mg was used in each experiment. The sample was designated by adding the prefix E to the sample designation of DADITAs.

Thermal Stability

Thermal stability of cured resins was evaluated by recording TG/DTG traces in nitrogen atmosphere (flow rate 60 mL/min). A heating rate of 10 K/min and sample size of (10 ± 2) mg was used in each experiment.

RESULTS AND DISCUSSION

Chemical Structure of DIDAs and DADITAs

These synthesized diamide-diimide-tetraamines were insoluble in chloroform, acetone and toluene but readily soluble in DMF, DMSO, NMP and DMAc. The structures of DIDAs and DADITAs were confirmed by common spectroscopic techniques and elemental analysis. Table 1 shows the results of CHN analysis of all DADITAs. The calculated values of CHN agreed well with the experimentally determined values. FTIR spectrum of the DIDAs shows bands at $3410\text{--}3440\text{ cm}^{-1}$ (due to O...H stretch), $(2930 \pm 3)\text{ cm}^{-1}$ (due to C...H stretch), $(1374 \pm 5)\text{ cm}^{-1}$ (due to C...N stretch) and $(1712 \pm 6)\text{ cm}^{-1}$ (due to C=O stretch of --COOH group). Since diimide-diacidchlorides (DIDACs) are more reactive than diimide-diacids towards substitution reactions therefore, DIDAs were converted to diimide-diacidchlorides (DIDACs) by using thionyl chloride. Figure 1 represents the FTIR spectrum of diimide-diacid **P**. As shown in Fig. 2(a) the ^1H -NMR spectrum of diimide-diacid, **P** presented signals in downfield region around $\delta = 8.42\text{--}8.95$ due to Ar—H proton. A singlet was obtained at $\delta = 11.1$ due to --COOH proton. Figure 2(b) shows the ^{13}C -NMR spectrum of diimide-diacid, **P**. In this spectrum, carbonyl carbon of imide group and carboxylic acid were observed at $\delta = 165.8$ and $\delta = 177.3$ respectively. Similar FTIR and NMR spectra were obtained for other diimide-diacid **B**, **N** and **O**.

Table 1. Elemental analysis of diamide-diimide-tetraamines

Sample designation	Molecular formula	Molecular weight	C (%)	H (%)	N (%)
PTAP	$\text{C}_{68}\text{H}_{54}\text{N}_{10}\text{O}_6\text{P}_2$	1169.2	C = 69.86, F = 69.78	C = 4.66, F = 4.61	C = 11.98, F = 12.04
PTAPO	$\text{C}_{68}\text{H}_{54}\text{N}_{10}\text{O}_8\text{P}_2$	1201.2	C = 67.99, F = 67.89	C = 4.53, F = 4.48	C = 11.66, F = 11.58
BTAP	$\text{C}_{75}\text{H}_{58}\text{N}_{10}\text{O}_7\text{P}_2$	1273.3	C = 70.75, F = 70.70	C = 4.59, F = 4.49	C = 11.00, F = 10.89
BTAPO	$\text{C}_{75}\text{H}_{58}\text{N}_{10}\text{O}_9\text{P}_2$	1305.3	C = 69.01, F = 69.11	C = 4.48, F = 4.60	C = 10.73, F = 10.81
NTAP	$\text{C}_{72}\text{H}_{56}\text{N}_{10}\text{O}_6\text{P}_2$	1219.2	C = 70.93, F = 70.67	C = 4.63, F = 4.69	C = 11.49, F = 11.58
NTAPO	$\text{C}_{72}\text{H}_{56}\text{N}_{10}\text{O}_8\text{P}_2$	1251.2	C = 69.11, F = 68.89	C = 4.51, F = 4.73	C = 11.19, F = 10.97
OTAP	$\text{C}_{74}\text{H}_{58}\text{N}_{10}\text{O}_7\text{P}_2$	1261.3	C = 70.47, F = 70.50	C = 4.64, F = 4.74	C = 11.11, F = 11.23
OTAPO	$\text{C}_{74}\text{H}_{58}\text{N}_{10}\text{O}_9\text{P}_2$	1293.3	C = 68.72, F = 68.66	C = 4.52, F = 4.44	C = 10.83, F = 10.85

A series of eight DADIDAs compounds were prepared by the reaction of diimide-diacidchlorides with two different phosphorus containing triamines in the presence of DMF through condensation reaction. The FTIR spectrum of diamide-diimide-tetraamine OTAPO shown in Fig. 3(a), exhibited absorption bands at 3390 cm^{-1} (due to N—H stretch), characteristic absorption bands around 1721 cm^{-1} and 1780 cm^{-1} (typical of imide carbonyl symmetrical and asymmetrical stretching), 1665 cm^{-1} (due to amide C=O stretch) and 1378 cm^{-1} (due to imide C...N stretch). The peak at 1209 cm^{-1} is attributed to P=O absorption.

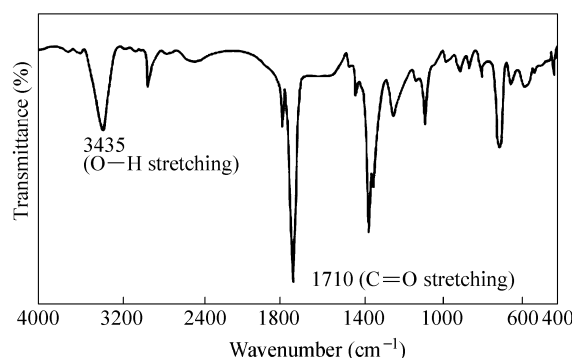


Fig. 1 FTIR spectrum of diimide-diacid **P**

A representative ^1H -NMR spectrum of diamide-diimide-tetraamine, OTAPO is shown in Fig. 3(b). In this spectrum, the existing aromatic protons resonate in the region $\delta = 6.45\text{--}8.56$. Among the aromatic protons, the protons adjacent to the imide ring appeared at the farthest downfield because of the resonance of imide ring. A broad peak due to amine ($-\text{NH}_2$) groups was observed at $\delta = 4.12$. A sharp peak at $\delta = 9.92$ was appeared due to $-\text{NH}$ proton present in pyrrole ring and a singlet due to secondary amide ($-\text{CONH}$) groups also observed at $\delta = 8.16$.

Figure 4(a) represents ^{13}C -NMR spectrum of diamide-diimide-tetraamine OTAPO. The spectrum showed signals for carbonyl carbons of amide group and imide ring at $\delta = 169.3$ and $\delta = 167.2$ respectively. Carbons of benzene ring appeared between $\delta = 108.2\text{--}154.3$. The spectral data corresponding to other carbon atoms was in good agreement with the proposed structure of polymer. ^{31}P -NMR spectrum of diamide-diimide-tetraamine OTAPO shows a characteristic peak at $\delta = -23.3$, represented in Fig. 4(b).

Above characterizations confirm that the target product was synthesized successfully.

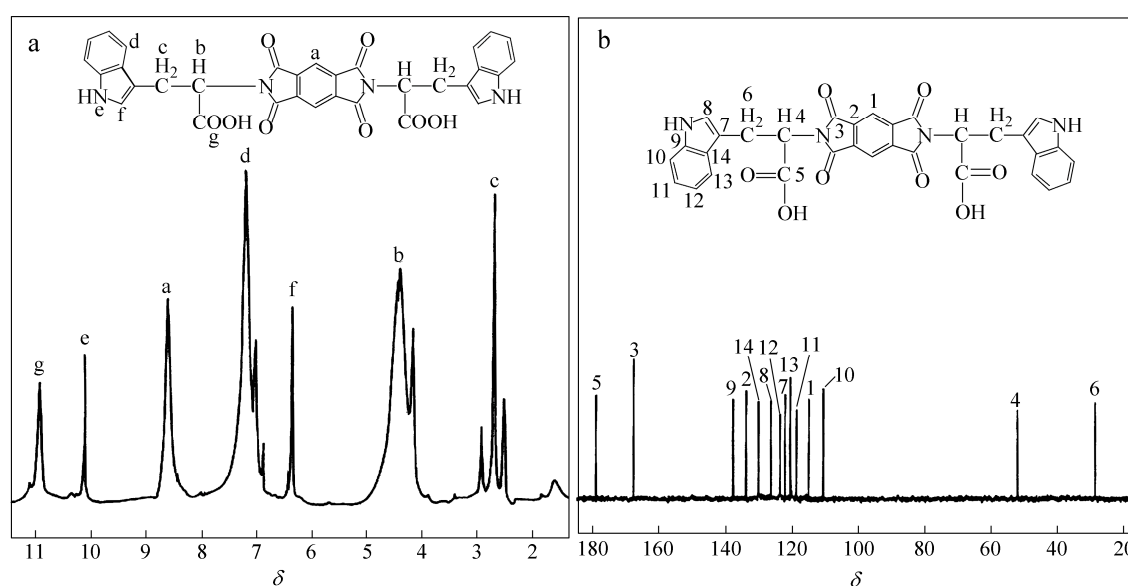
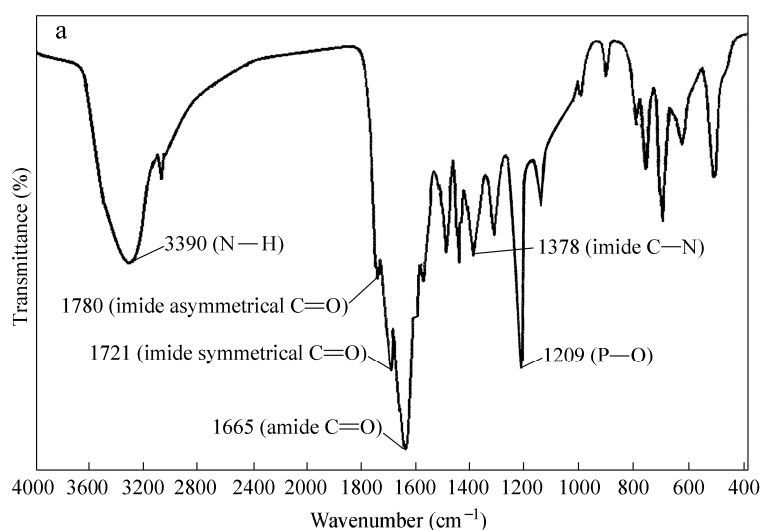


Fig. 2 (a) ^1H -NMR spectrum and (b) ^{13}C -NMR spectrum of diimide-diacid P



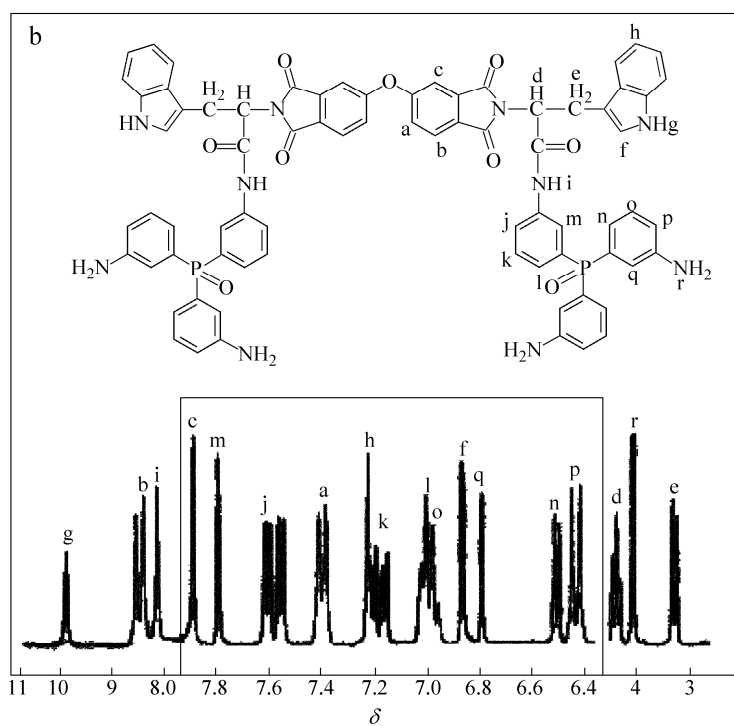
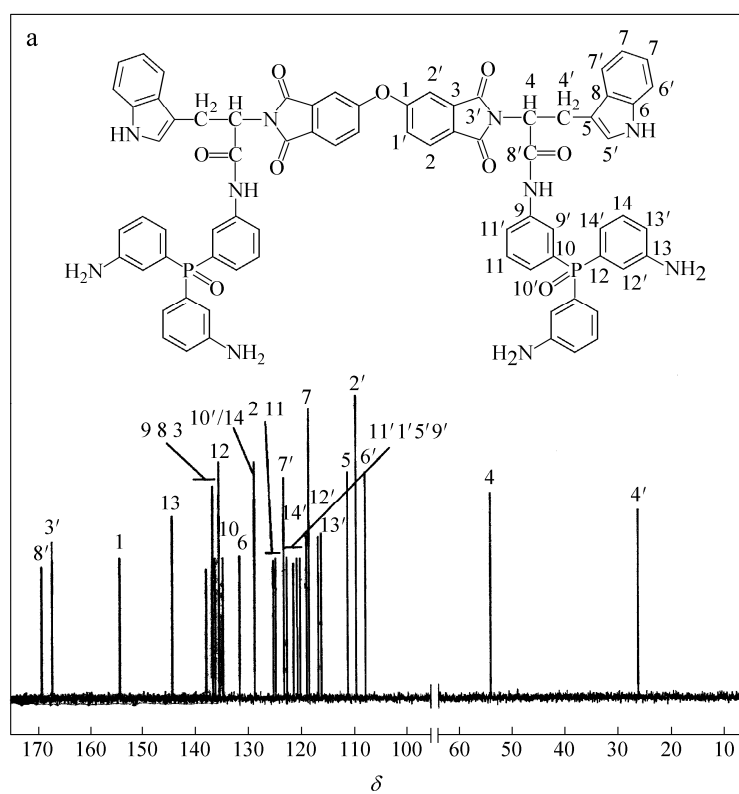


Fig. 3 (a) FTIR spectrum and (b) ^1H -NMR spectrum of diamide-diimide-tetraamine, OTAPO



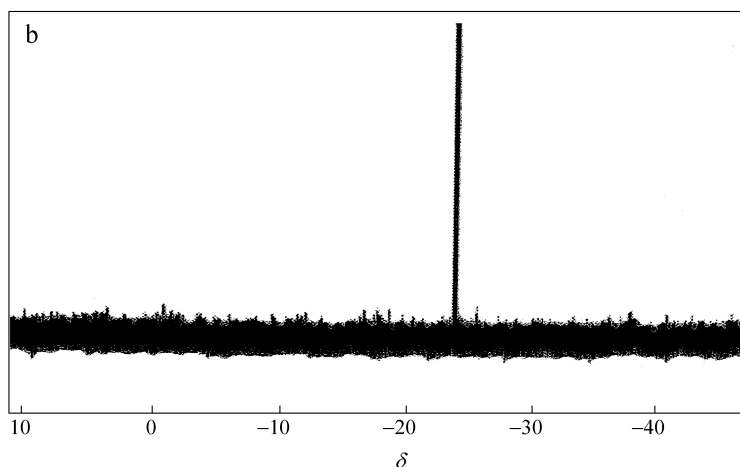


Fig. 4 (a) ^{13}C -NMR spectrum and (b) ^{31}P -NMR spectrum of diamide-diimide-tetraamine OTAPO

Thermal Properties of Cured Epoxy Resins

T_g of epoxy thermosets

The effect of structure and molecular size of DADITAs on the curing behavior was monitored by recording DSC traces at a heating rate of 10 K/min under nitrogen atmosphere. As shown in Fig. 5(a) and Table 2, the glass transition temperature (T_g) of cured epoxy resins gradually decreased from 149 °C to 96 °C with increasing percentage of phosphorus in curing agents. As curing agent as well as additive, diamide-diimide-tetraamines will decrease T_g s of epoxy resins for that the bulky and non-coplaner phosphorus containing phenylene groups could increase the intermolecular distance and that backbone of curing agent was not rigid to conjugate structure but rather a flexible structure, which was convenient to molecular motion and formation of T_g ^[31–32]. Therefore, diamide-diimide-tetraamines in epoxy thermosets could provide motion space to groups of epoxy resin and make T_g s of the thermosets decreased.

Thermogravimetric analysis (TGA)

TGA is widely used to evaluate the thermal stability and thermal degradation behavior of polymers^[33]. TGA curves of the cured epoxy resins E/PTAP, E/BTAP, E/NTAP and E/OTAP under nitrogen atmosphere at the heating rate of 10 K/min, are represented in Fig. 5(b). All data are summarized in Table 2. As shown in Fig. 5(b), the onset degradation temperatures of cured epoxy resins decreased with increasing phosphorus content under nitrogen, which may attributed to the poorer stability of P—C bond than common C—C bond which leads to low crosslink density of phosphorus containing epoxy resins^[34–36]. All the epoxy thermosets were highly stable and their 5% decomposition temperature was found in the range of 344 °C to 435 °C. Thermal stability was highest for epoxy cured by NTDA anhydride based DADITAs which may be due to the presence of more compact structure *i.e.* six membered imide rings in NTDA, although the thermal stabilities decreased with increasing phosphorus content. Furthermore it was obvious that all the cured epoxy resins under nitrogen atmosphere showed one stage decomposition processes.

However, it was noticed that the residual char yields of cured epoxy resins increased with increasing phosphorus content. It means that phosphorus containing curing agents could enhance the thermal stability and resins charring properties during combustion. The result was deduced that the triphenyl phosphorus structure and nitrogen had a synergistic effect in condensed phase to promote charring of thermosets. The residual char yield of E/OTAPO was 37.6% at 700 °C which was much higher than that of E/OTAP, which was 35.7%, due to higher phosphorus content in E/OTAPO. The char layer played an important role in improving the flame retardancy of phosphorus containing cured epoxy resin^[37–38]. Furthermore, the char yields increased with increasing phosphorus content, which was consistent with the flame retardancy of the system characterized by LOI measurement and UL94 test discussed below.

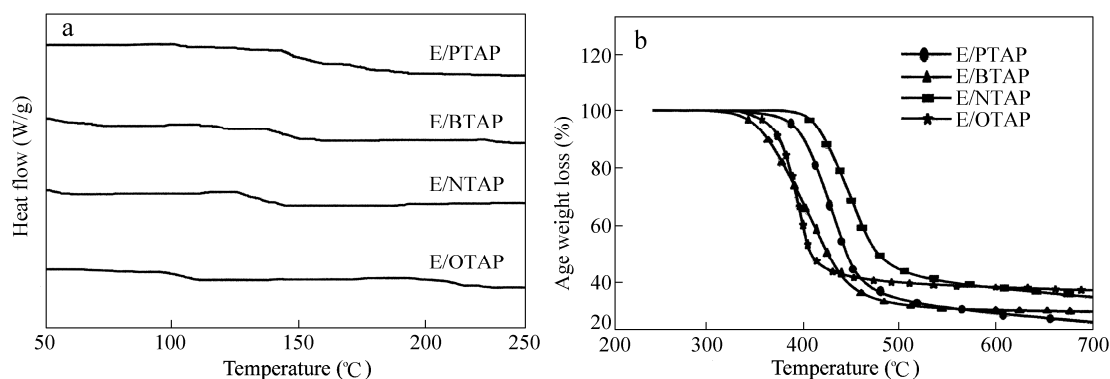


Fig. 5 (a) DSC scans of epoxy thermosts E/PTAP, E/BTAP, E/NTAP and E/OTAP and (b) TGA of epoxy thermosts E/PTAP, E/BTAP, E/NTAP and E/OTAP at heating rate of 10 K/min under nitrogen atmosphere

Table 2. Thermal properties of cured epoxy resins

Sample	T_g (°C)	$T_{-5\%}$ (°C)	T_{max} (°C)	Char yield at 700 °C (%)
E/PTAP	149	389	457	24.7
E/PTAPO	147	380	438	27.8
E/BTAP	138	358	424	26.6
E/BTAPO	142	366	432	29.4
E/NTAP	135	410	476	32.4
E/NTAPO	137	435	498	33.6
E/OTAP	102	367	329	35.7
E/OTAPO	96	344	397	37.6

Flame Retardant Properties

The flame retardant properties of all the samples were examined by LOI and UL94 test. All data are summarized in Table 3. It could be seen that LOI values of all epoxy thermosts significantly increased from 28.9 to 38.5 as the phosphorus content increase in epoxy network. This indicated that incorporating phosphorus containing groups was very effective in improving the flame retardancy of epoxy resins. The results could be related with P/N/P-C ratio in thermosts and an optimal P/N/P-C ratio will bring better flame retardant performance of thermosts instead of higher phosphorus content.

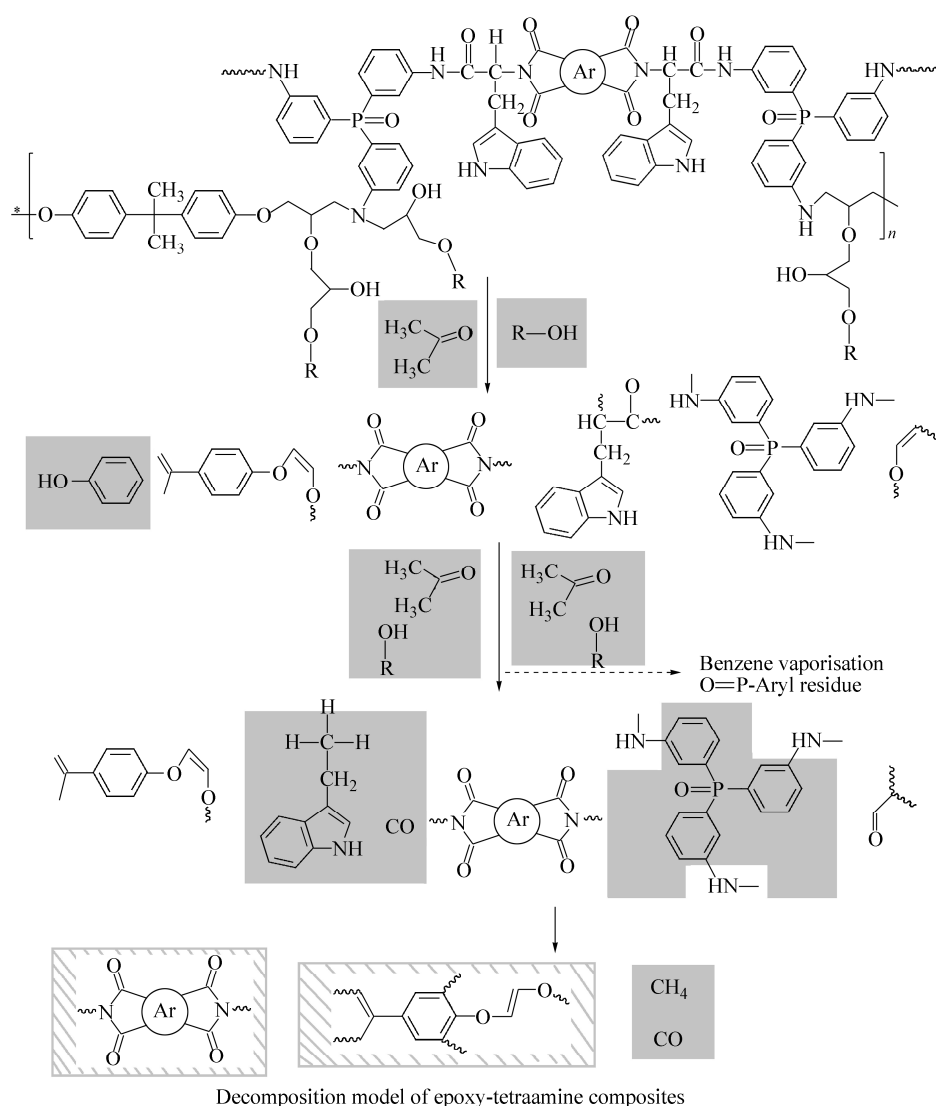
Table 3. The LOI value and results of UL94 test

Sample	DGEBA (g)	Tetraamine (g)	P (wt%)	N (wt%)	LOI	Dripping	UL94 rating
E/PTAP	35.4	29.0	1.54	3.47	29.2	No	V-0
E/PTAPO	35.4	30.0	1.55	3.50	28.9	No	V-0
E/BTAP	35.4	31.8	1.55	3.50	32.7	No	V-0
E/BTAPO	35.4	32.6	1.55	3.50	33.3	No	V-0
E/NTAP	35.4	30.5	1.55	3.50	34.4	No	V-0
E/NTAPO	35.4	31.3	1.55	3.50	34.1	No	V-0
E/OTAP	35.4	31.6	1.55	3.51	36.1	No	V-0
E/OTAPO	35.4	32.4	1.55	3.50	38.5	No	V-0

UL94 test exhibited that all epoxy thermosts had UL94 V-0 flammability rating. We could deduce that the excellent charring interaction of triphenyl phosphine groups enhanced the flame retardant efficiency of epoxy thermosts and that of nitrogen in backbone and triphenyl phosphorus groups in curing agents, jointly to exert the synergistic flame retardant function on thermosts. The reason was that the diamide-diimide-tetraamines curing agents increased the thermal stability as well as had outstanding charring property can promote materials to forming stronger char layer. The char layer deduced the exothermicity caused by the pyrolysis reaction and thermal conductivity of surface radiated from flame and thus, keep the samples no dripping and improve the flame retardancy of the epoxy resin thermosts^[32].

Mechanism of flame retardation and synergistic effect of P-N

Phosphorus based flame retardants in general, react in condensed phase producing phosphoric acid and polyphosphoric acid^[39] which favors char forming reactions. Triphenyl phosphine oxide and triphenyl phosphine have been shown to break down in the flame to small molecular species such as PO, P₂, HPO₂ etc. The synergistic property probably occurs due to formation of the P and N containing intermediates, which are better phosphorylating agents than those of the related phosphorus compounds without nitrogen^[40]. The epoxy network breaks first at nitrogen bonds, because the binding force of nitrogen-aliphatic carbon bonds is lower than the binding force of C—C and C—O bonds^[41–42]. The detailed analysis of decomposition also demonstrated benzene as a decomposition product and phosphoryl component in the residue. Consequently, an alternative minor decomposition pathway is presumed in which triphenyl phosphine oxide units decompose, decreasing the decomposition steps and increasing the residue amount. Thus, the main decomposition pathway results in the release of phosphorus-containing volatiles, whereas traces of the phosphorus remain in the condensed phase due to a side decomposition pathway. Scheme 4 describes the main decomposition pathway of epoxy-tetraamine.



Scheme 4 Decomposition model of epoxy-tetraamine (n = molecular structure of simplified monomer unit, R = connection to bisphenol A units, zig-zag line = char formation/cross-linking, dashed background = proved residue structures, grey background = proved gaseous decomposition products)

CONCLUSIONS

New phosphorus containing flame retardant curing agents were synthesized and their structures were confirmed by FTIR, NMR and elemental analysis. The introduction of diamide-diimide-tetraamines groups into DGEBA network may improve the thermal stability as compared to other amines. All epoxy thermosets exhibited moderate changes in T_g and thermal stability. The degradation temperature and char yield of NTDA based epoxy thermosets was higher than those of the other thermosets which might be due to presence of more compact structure *i.e.* naphthalene. The diamide-diimide-tetraamines containing epoxy polymers were observed to have good char yield on pyrolysis. Since higher char yield indicates good flame retardancy. Utilization of appropriate amounts of diamide-diimide-tetraamines in the epoxy system may yield resins with better flame retardance. The char layer of E/OTAPO was more stable at a much higher temperature.

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