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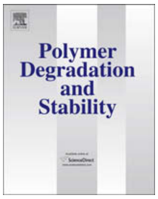

Synthesis, characterization, thermal properties and flame retardancy of a novel nonflammable phosphazene-based epoxy resin

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ABSTRACT

Hexakis(4-hydroxyphenoxy)-cyclotriphosphazene (PN–OH) was synthesized through nucleophilic substitution of the chloride atoms of hexachlorocyclotriphosphazene and reduction of the aldehyde groups, and its chemical structure was characterized by elemental analysis, ^{1}H and ^{31}P NMR, and Fourier transform infrared (FTIR) spectroscopy. A new phosphazene-based epoxy resin (PN-EP) was successfully synthesized through the reaction between diglycidyl ether of bisphenol-A (DGEBA) and PN–OH, and its chemical structure was confirmed by FTIR and gel permeation chromatography. Four PN-EP thermosets were obtained by curing with 4,4′-diaminodiphenylmethane (DDM), dicyandiamide (DICY), novolak and pyromellitic dianhydride (PMDA). The reactivity of PN-EP with the four curing agents presents an increase in the order of DDM, PMDA, novolak and DICY. An investigation on their thermal properties shows that the PN-EP thermosets achieve higher glass-transition and decomposition temperatures in comparison with the corresponding DGEBA ones while their char yields increase significantly. The PN-EP thermosets also exhibit excellent flame retardancy. The thermosets with novolak, DICY and PMDA achieve the LOI values above 30 and flammability rating of UL94 V-0, whereas the one with DDM reaches the V-1 rating. The nonflammable halogen-free epoxy resin synthesized in this study has potential applications in electric and electronic fields in consideration of the environment and human health.

1. Introduction

Epoxy resins are widely applied as advanced composite matrices in electronic/electrical industries where a remarkable flame-retardant grade is required, but the fire risk is a major drawback of these materials [1]. There are two approaches to achieve flame retardancy for polymers generally known as the "addition" and the "reaction", and the latter is given much attention recently [2]. Traditionally, brominated reactive compounds [3] are used as co-monomers with epoxy resins to obtain fire-retardant materials. However, flame-retardant epoxy resins containing bromine can produce corrosive and obscuring smoke and may give super-toxic halogenated dibenzodioxins and dibenzofurans with deleterious effects on the environment and human health. Recently, in consideration of environmental problems, researches for halogen-free fire-retardant epoxy resins have received a great deal of attention [4,5]. Phosphorylation is considered to be one of the most efficient methods to confer flame retardancy on epoxy resins [6–8], whereas phosphate-based epoxy resins could possess excellent flame retardancy only when using amine curing agents. Some studies indicated that the flame-retardant efficiency significantly improved when phosphorus and nitrogen existed simultaneously in the curing system of epoxy resin. Therefore, the phosphorus–nitrogen synergistic effect on flame retardancy is very interesting [9].

In recent years, there has been considerable interest in the phosphazene-based family of materials because they not only have a wide range of thermal and chemical stabilities, but also can provide improved thermal and flame-retardant properties to polymers and their composites [10–15]. Hexachlorocyclotriphosphazene is a versatile starting oligomer for the synthesis of phosphazene-based polymers. The chlorine groups attached to the phosphorus atoms are easily substituted by various nucleophiles to form reactive cyclotriphosphazenes. Cyclotriphosphazene, as a ring compound consisting of alternating phosphorus and nitrogen atoms with two substituents attached to the phosphorus atoms, exhibits unusual thermal properties such as flame retardancy and self-extinguishability [16,17]. Cyclotriphosphazene has several advantages as a reactive flame-retardant functional oligomer. First, the flexible synthetic methodology can be developed for preparation of cyclotriphosphazene-based copolymer with various substituents, which allows us to obtain multifunctional initiators or terminators with ease. Second, thermal and nonflammable properties of the

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cyclotriphosphazene moieties can be conferred to the resulting polymers, especially, of low molecular weights [12,13,18–20]. Therefore, when cyclotriphosphazenes are incorporated into the network of thermoset polymers, they can increase the thermal property and flame retardancy of the polymers because of phosphorous and nitrogen flame-retardant synergy. The reason is that the thermal decomposition of the phosphazene-based polymers is an endothermic process, and phosphate, metaphosphate, polyphosphate generated in the thermal decomposition form a nonvolatile protective film on the surface of the polymer to isolate it from the air; meanwhile, the inflammable gases released such as CO_2, NH_3 and N_2 cut off the supply of oxygen so as to achieve the aims of synergistic flame retardancy [21–24]. The phosphazene-based polymers have more effective flame retardancy than any other flame-retardants, making them a new focus [25–29]. However, the phosphazene-based polymers used as a flame-retardant component with epoxy resins are seldom reported [28]. In this study, we developed a novel nonflammable halogen-free epoxy resin by incorporating the cyclotriphosphazene group, and investigated the thermal property and flame retardancy of this thermoset resin with various curing agents.

2. Experimental

2.1. Materials

Hexachlorocyclotriphosphazene ($N_3P_3Cl_6$) was purchased from Shanghai Jiachen Chemical Co. Ltd., China. The epoxy resin (diglycidyl ether of bisphenol-A, DGEBA) with an epoxide equivalent weight (EEW) of 184–194 g/equiv. was kindly supplied by Wuxi Bluestar Epoxy Co., China. Triphenylphosphine, sodium hydride (NaH), sodium borohydride ($NaBH_4$), 4-hydroxybenzaldehyde, tetrahydrofuran (THF), acetone, 4,4′-diaminodiphenylmethane (DDM), pyromellitic dianhydride (PMDA), dicyandiamide (DICY) and novolak were purchased from Beijing Chemical Reagent Co., China.

2.2. Synthesis of hexakis(4-aldehydephenoxy)-cyclotriphosphazene

A suspension of sodium 4-aldehydephenoxide in dry THF was prepared by mixing 274 g NaH (70 wt.% diluted in oil) and a solution of 976 g 4-hydroxybenzaldehyde in 500 mL THF in a reactor with mechanical stirring, reflux condensation and a nitrogen inlet. Subsequently, 348 g $N_3P_3Cl_6$ was dissolved in 400 mL THF and added dropwise into the flask over a period of 60 min, and then the reaction system was maintained at 65 °C for 48 h. Some light-brown powders as hexakis(4-aldehydephenoxy)-cyclotriphosphazene (PN–CHO) were collected after recrystallization with ethyl acetate, and the yield was 72.6 wt.%.

2.3. Synthesis of hexakis(4-hydroxyphenoxy)-cyclotriphosphazene

$NaBH_4$ (56 g) was added into a reactor containing a solution of 200 g PN–CHO in 500 mL THF/methanol mixture. The reaction system was stirred at room temperature for 14 h. Some white solids as hexakis(4-hydroxyphenoxy)-cyclotriphosphazene (PN–OH) were obtained after recrystallization with 90 vol.% alcohol, and the yield was 81.3 wt.%.

2.4. Synthesis of phosphazene-based epoxy resins

DEGBA (1000 g) was added into a reactor and stirred for 2 h at the temperature of 120 °C under a nitrogen atmosphere, and then 318 g PN–OH with the equivalent ratio to DGEBA of 1:14 and appropriate amount of triphenlyphosphine (0.3 wt.%) as a catalyst were added. The reaction mixture was maintained at 175 °C for 5 h. And some light-yellow gel-like phosphazene-based epoxy resin (PN-EP) was obtained with a yield of 86.4%.

2.5. Curing procedure of the PN-EP

The synthesized PN-EP and DGEBA as a control were cured using 4,4′-diaminodiphenylmethane (DDM), dicyandiamide (DICY), novolak and pyromellitic dianhydride (PMDA) as curing agents. The epoxy resin was dissolved in appropriate amount of acetone, and then the curing agent with an equivalent ratio to PN-EP of 1:1 and 2-methylimidazole (0.2 wt.%) as a curing accelerator were added into this solution. The mixture was stirred constantly to be a homogeneous solution and then was kept in a vacuum oven at 50 °C for 1 h to remove the solvent. The curing process was carried out in terms of the curing conditions determined by the DSC tracings of the respective curing systems as listed in Table 1. In the end of the curing procedure, the cured system was cooled gradually to room temperature to avoid stress crack.

2.6. Characterization

Elemental analysis was carried out using a Heraeus CHN-O rapid elemental analyzer with acetanilide as a standard. ^1H and ^{31}P nuclear magnetic resonance (NMR) spectra were obtained by a Bruker AV-600 NMR spectrometer at 300 MHz using dimethyl sulfoxide (DMSO)/D_2O as solvent with tetramethylsilane and phosphoric acid as external standards, respectively. Fourier transform infrared (FTIR) spectra were obtained using a Nicolet 205 FTIR spectrometer with the scanning number of 30. EEWs of the synthesized PN-EPs were measured by HCl/acetone chemical titration method. Gel permeation chromatography (GPC) was performed by a Waters 515 GPC with THF as a solvent at a flow rate of 1.0 mL/min. The number average molecular weights (M_n) and weight average molecular weights (M_w) were obtained from the analysis of the GPC data.

The curing systems of PN-EPs with various curing agents and the glass-transition temperature (T_g) of the cured samples were determined using a TA instrument Q100 differential scanning calorimeter (DSC) under a N_2 atmosphere at a heating rate of 10 °C/min with the sample weights about 10 mg. Thermogravimetric analysis (TGA) was carried out on a TA instrument Q50 thermal gravimetric analyzer at a heating rate of 10 °C/min from 50 to 600 °C under a N_2 atmosphere. UL94 horizontal and vertical burning tests were carried out in terms of the method proposed by Underwriter Laboratory. Three horizontally clipped samples (127 × 12.7 × 1.6 mm) were ignited by a butane burner with a butane flow of 105 mL/min. The samples would achieve the flammability rating of UL94 HB if the burning speed was less than 75 mm/min and each of them extinct before it reached 100 mm. Five samples hung vertically over some surgical cotton were ignited by the butane burner with the same flow. The samples would achieve the UL94 V-0 flammability rating if the combustion of each sample did not last for 10 s and the cotton below the tested sample could not be ignited by the sparks. Limiting oxygen index (LOI) measurement was performed using a HD-2 oxygen index apparatus with a magneto-dynamic oxygen analyzer according to ASTMD D-2863. The sample (65 × 3.0 × 0.5) was

Table 1
Curing programs of PN-EP cured with various curing agents.

Curing system	Curing temperature (°C)	Curing time (min)	Postcuring temperature (°C)	Postcuring time (min)
PN-EP/DDM	120	60	150	180
PN-EP/DICY	160	30	190	60
PN-EP/novolak	140	60	170	180
PN-EP/PMDA	180	60	200	180

clamped vertically in the center of the combustion column and was ignited by a butane burner with a mixture of oxygen and nitrogen continuously going through a flow rate of 10 L/min. The flammability was determined by the minimum concentration of oxygen for supporting the combustion.

3. Results and discussion

3.1. Synthesis of phosphazene-containing oligomers

PN-EP was considered as an epoxide-functionalized material containing cyclotriphosphazene. As depicted in Fig. 1, a phosphazene-containing oligomer, PN–CHO, was synthesized first by the reaction of $N_3P_3Cl_6$ with 4-hydroxybenzaldehyde, and then the other one, PN–OH, was obtained by the reduction of PN–CHO with excessive $NaBH_4$.

The chemical structures of the two phosphazene-containing oligomers synthesized in this study were characterized by elemental analysis, ^1H NMR, ^{31}P NMR and FTIR spectroscopy. The calculated elemental contents of PN–CHO in terms of the formula ($C_{42}H_{30}N_3O_{12}P_3$) were C, 58.42; H, 3.48; N, 4.88; O, 22.30; P, 10.80; and the analyzed data show that C, H, N, O and P are 58.49, 3.75, 4.97, 22.32 and 10.73, respectively. For PN–OH, the analyzed data were C, 57.45; H, 4.72; N, 4.85; O, 22.04; P, 10.66; while the calculated values in terms of the formula ($C_{42}H_{42}N_3O_{12}P_3$) were C, 57.73; H, 4.81; N, 4.81; O, 21.99; P, 10.65. It is found that elemental analysis of the synthesized PN–CHO and PN–OH is both in good agreement with the calculated values. The ^{31}P NMR spectra of $N_3P_3Cl_6$, PN–CHO and PN–OH (Fig. 2) show an intense single peak for each at $\delta = 0.58$ ppm ($J = 376.52$ MHz), $\delta = 7.9778$ ppm ($J = 464.54$ MHz) and $\delta = 9.2517$ ppm ($J = 454.48$ MHz), respectively. These results indicate the presence of a phosphazene unit. However, the different chemical shifts between them exhibit the occurrence of the substitution and reduction reaction. Furthermore, as shown in Fig. 3, the ^1H NMR spectrum of PN–CHO shows a single peak at $\delta = 9.847$ ppm due to the aldehyde group (s, 6H, $J = 454.48$ MHz); $\delta = 7.211$ ppm (d, 12H, $J = 372.15$ MHz) and $\delta = 7.824$ ppm (d, 12H, $J = 325.88$ MHz), as the two doublets prove the presence of the phenol ring. In the ^1H NMR spectrum of PN–OH, the chemical shifts corresponding to the phenol ring protons are found at $\delta = 6.831$ ppm (d, 12H, $J = 185.59$ MHz) and $\delta = 7.217$ ppm (d, 12H, $J = 183.54$ MHz); the single peak attributable to the hydroxyl proton appears at $\delta = 5.208$ ppm (t, 6H, $J = 119.52$ MHz); the doublet found at $\delta = 4.478$–4.487 ppm (d, 12H, $J = 201.37$ MHz) corresponds to the methylene protons. The single peaks at $\delta = 3.314$ ppm and $\delta = 2.515$ ppm appear in both of the two ^1H NMR spectra corresponding to D_2O and DMSO, respectively.

The FTIR spectra of $N_3P_3Cl_6$, PN–CHO and PN–OH were displayed in Fig. 4. It is observed that the strong absorption peak between 1266.00 and 1200.81 cm^{-1} corresponds to the P=N stretching, while the absorption peaks at 600.25 and 521.49 cm^{-1} corresponding to the P–Cl bond in the spectrum of $N_3P_3Cl_6$ disappear in the spectra of PN–CHO and PN–OH. Instead, the absorption peak at 1015.60 cm^{-1} indicates the formation of the P–O linkage, and the strong absorption peaks at 1168.25 cm^{-1} and 958.91 cm^{-1} reveal the presence of a phosphazene structure (P–O–Ph). The spectrum of PN–CHO shows the absorption peaks at 2823.64 and 1706.95 cm^{-1} illustrating the presence of the aldehyde group (–CHO), whereas in the spectrum of PH–OH, these two absorption peaks disappear, and a strong absorption peak at 3380 cm^{-1} takes place corresponding to the hydroxyl stretching (–OH).

3.2. Synthesis of phosphazene-based epoxy resins

The PN-EP was synthesized by the reaction between PN–OH and DGEBA using triphenylphosphine as a catalyst. Theoretically, a

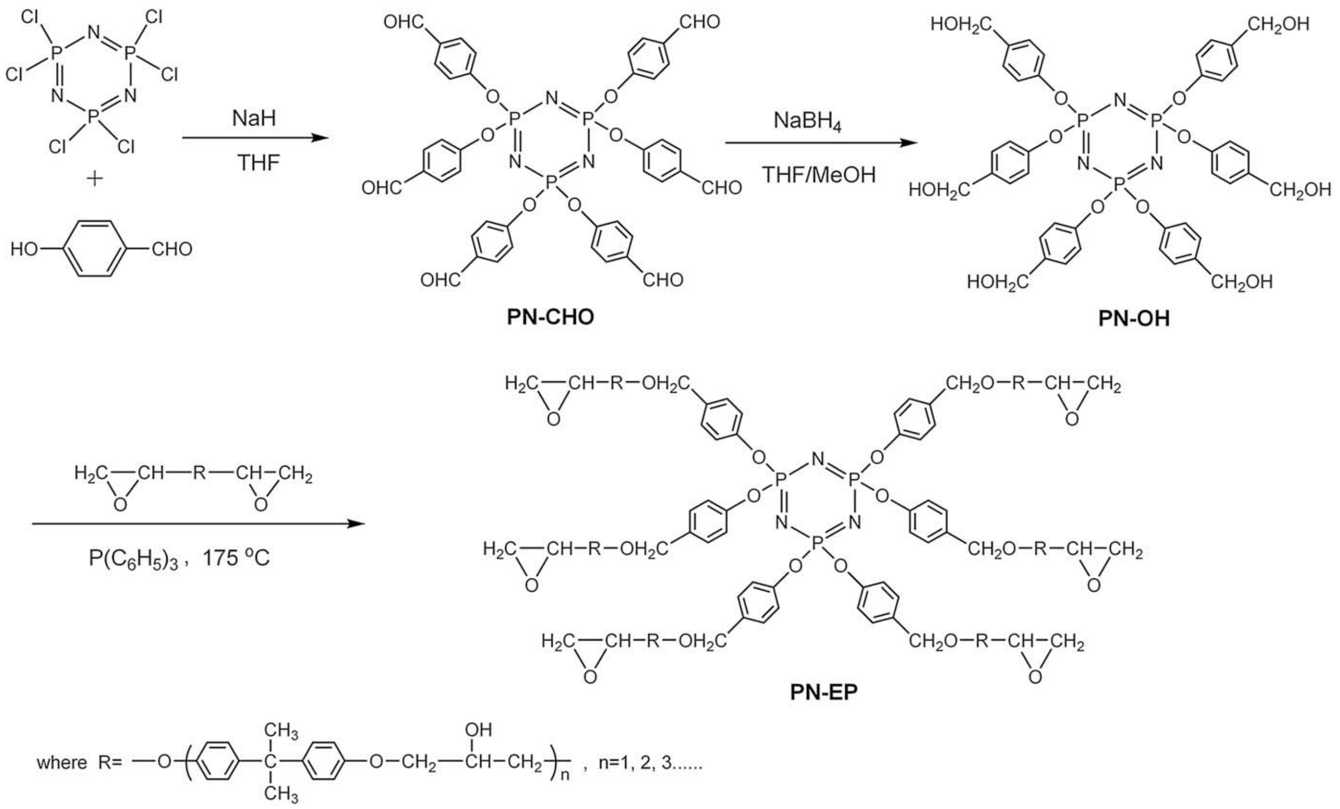

Fig. 1. Schematic procedure of synthesis for PN-EP.

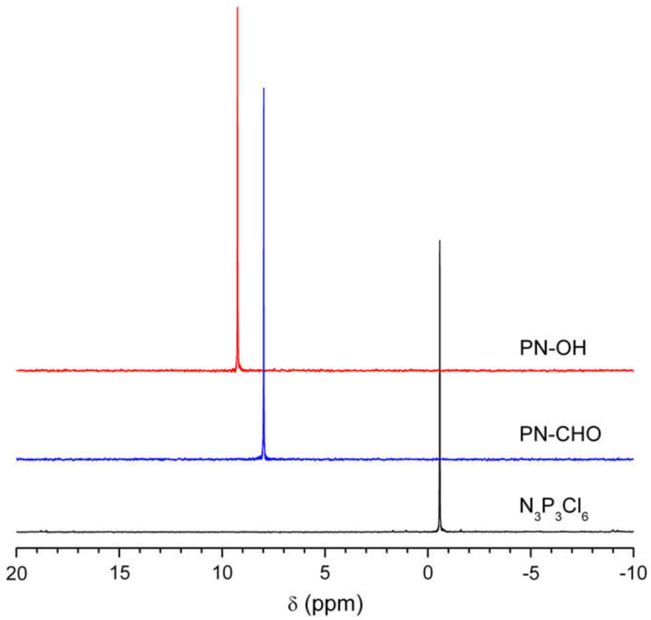

Fig. 2. ^{31}P NMR spectra of $N_3P_3Cl_6$, PN–CHO and PN–OH.

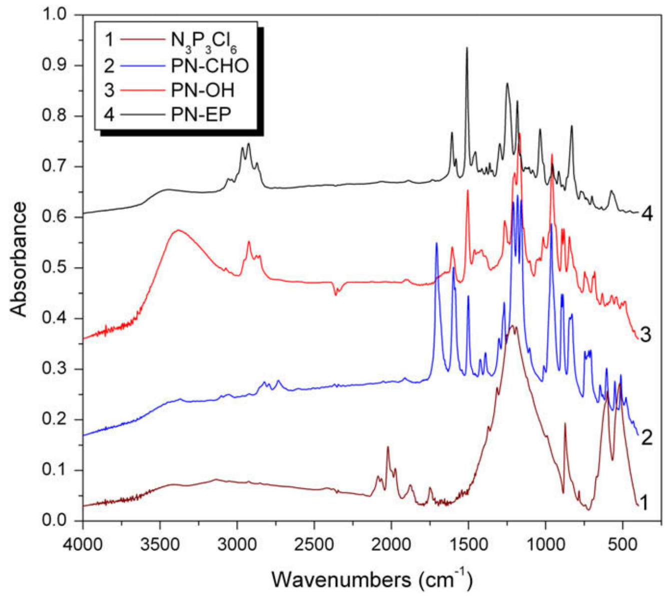

Fig. 4. FTIR spectra of $N_3P_3Cl_6$, PN–CHO, PN–OH and PN-EP.

PN–OH molecule reacts with six DGEBA molecules, resulting in an EEW of 538 g/equiv. for the obtained PN-EP. In order to achieve the complete reaction of the hydroxyl groups on PN–ON with epoxy ones, excessive DGEBA was introduced; therefore, the theoretical EEW of synthesized product is actually 489 g/equiv. In this experiment, the EEW was 487 g/equiv. measured by HCl/acetone chemical titration method. The experimental result is so close to the theoretical one, indicating the perfect completion of the reaction between PN–OH and DGEBA. Furthermore, the contents of phosphorus and nitrogen were calculated to be 2.62% and 1.18%, respectively.

The structure of PN-EP was confirmed using FTIR spectroscopy, and its spectrum is shown in Fig. 4. It can be found that the absorption peaks at 1248.34, 915.50 and 830.93 cm^{-1} indicate the presence of the epoxy group. The absorption peaks at 1183.46 and 1456.13 cm^{-1} correspond to the P–O–Ph bond. And the absorption peak at 1248.46 cm^{-1} reveals the presence of the phosphazene structure. The performance of the reaction for PN-EP was also verified by the GPC diagrams as shown in Fig. 5. It could be observed that, for DGEBA, the main distribution peaks at 357 and 770 appear in the diagram with percentages of 86.1 and 13.9, respectively. PN–OH has an M_n of 680 and an M_w of 866 from the evaluation of GPC. And for PN-EP, the distribution peaks at the molecular weights of 357 and 923 weaken sharply to the percentages of 16.0 and 3.8, respectively, but that of 2910 with a percentage of 80.2 appears in the GPC diagram. It is also found that PN-EP possesses an M_n of 2960 and an M_w of 4021, respectively. Meanwhile, the M_n of PN-EP can be calculated with the

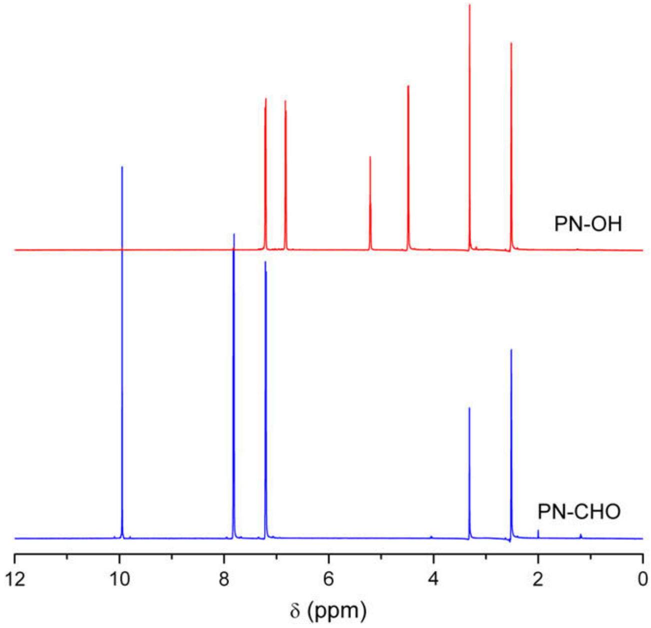

Fig. 3. ^{1}H NMR spectra of $N_3P_3Cl_6$, PN–CHO and PN–OH.

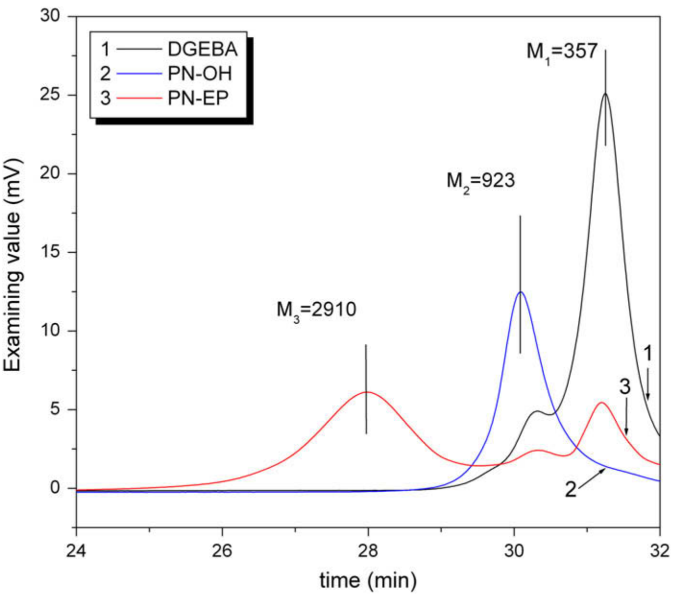

Fig. 5. GPC diagrams of DGEBA, PN–OH and PN-EP.

reaction formula to be 3225 in theory. The fact that the experimental data are less than the theoretical one is ascribed to the excessive DGEBA in the reaction system.

3.3. Reactivity of the phosphazene-based epoxy resin

Curing reactions of PN-EP with various curing agents were studied by DSC, and the typical DSC thermograms are shown in Fig. 6, which presented a single exothermic peak corresponding to the curing reaction for each curing system in homopolymerization. Reactivity of the four curing systems is determined by initial curing temperatures shown as the starting temperatures at the exothermic peaks. As shown in Fig. 6, it can be observed that the starting exothermic temperatures increase in the order of DDM, PMDA, novolak and DICY, indicating that the reactivity of these curing agents with PN-EP decrease in the same order. The curing reaction of epoxy resin with amine is considered to occur via a nucleophilic attack of the electronic donating group in the epoxy group. Generally, the oxirane ring is easy to react with a nucleophile [28,30]. It is reasonable that the highest reactivity of DDM among all the curing agents with PN-EP is attributed to the strongest electronic donation. PMDA has a lower reactivity with PN-EP than DDM due to its weaker nucleophilicity of anhydride oxygen than that of amino nitrogen. However, the reactivity of PMDA is higher than the other two curing agents, since the conjugation effect of phenyl ring enhances the nucleophilicity of anhydride oxygen. In the case of DICY, the strong polarity of cyano groups decreases the electron density, and consequently, reduces the nucleophilic attack of the amine nitrogen, resulting in a lowest reactivity with PN-EP among the four curing agents. In addition, the reaction rates of these curing systems can be estimated from the width of exotherms in Fig. 6, which demonstrates an increase in the order of PMDA, novolak, DDM and DICY. It is noticed that the PN-EP/DICY curing system shows a narrow exotherm, indicating that the low steric hindrance in the DICY molecules results in a rapid curing reaction. Conversely, the other three systems present the broad exotherms, which implies that the strong steric hindrance in the curing agents caused by the high density of phenyl ring leads to lower reaction rates [31,32].

3.4. Thermal properties

T_g is an important parameter for thermoset epoxy resins, and in most cases, the service temperature of epoxy-based materials is below their T_g. Therefore, studies on the mechanism of T_g variation and the prediction of T_g decline are critical for the engineering design and application of epoxy resins [33]. T_gs of PN-EP cured with the four curing agents were also measured by DSC. The DSC thermograms of all the samples are displayed in Fig. 7, and the results are summarized in Table 2, in which the corresponding data for the DGEBA thermosets as controls were also listed. It is noticed that the PN-EP/novolak thermoset exhibits a higher T_g than the other three, which may be attributed to its high cross-linking density. However, T_gs of PN-EP/DDM and PN-EP/PMDA curing systems are higher than those of PN-EP/DICY one, owing to their high rigidity. It is also found that each of the PN-EP curing systems has a higher T_g in comparison with the data for the DGEBA thermosets using corresponding curing agents. Obviously, the incorporation of the multifunctional cyclotriphosphazene rings into the epoxy molecules can increase the motion barrier of the PN-EP molecules, and thus, improve the T_gs of the PN-EP thermosets. Furthermore, it is noteworthy that these phosphazene-based epoxy thermosets have T_gs above 130 °C, which suggests that they all could be applied potentially to the FR-4 type copper-clad laminates [34].

Thermal stabilities of the PN-EP thermosets with various curing agents were evaluated by TGA with a temperature range from the room temperature to 600 °C. Fig. 8 shows the behaviors of the thermal degradation for these thermosets, and the obtained data are summarized in Table 2, in which the corresponding data from the DGEBA thermosets as the controls are also listed. The temperature at rapid weight loss is an important parameter to characterize the thermal stability of the thermosets. It can be defined as the decomposition temperature, under which the thermoset lose its weight most rapidly during the whole degradation process. The peaks in differential curves of Fig. 8(b) indicate these characteristic temperatures. All the TGA thermograms indicate that water or solvent has been successfully removed from the curing systems because there is no weight loss below 100 °C. PN-EPs cured with DICY, novolak and DDM present one-step degradation, while the decomposition of the PN-EP/PMDA thermoset occurs through

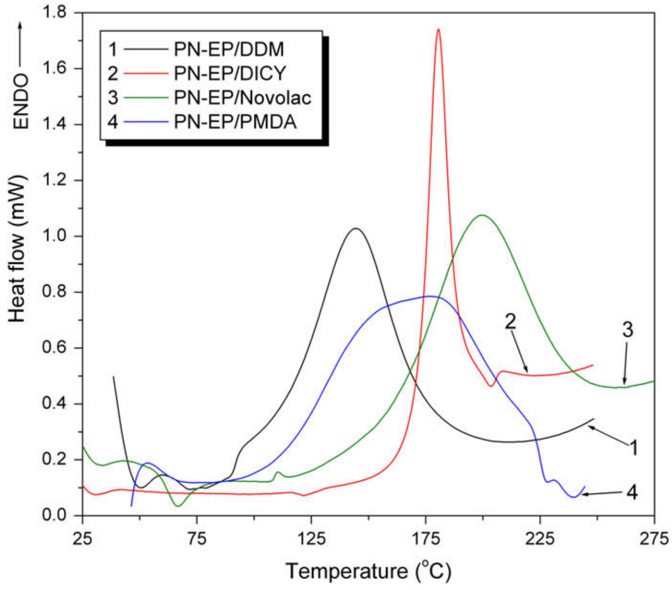

Fig. 6. DSC thermograms of the curing reaction of PN-EP with various curing agents.

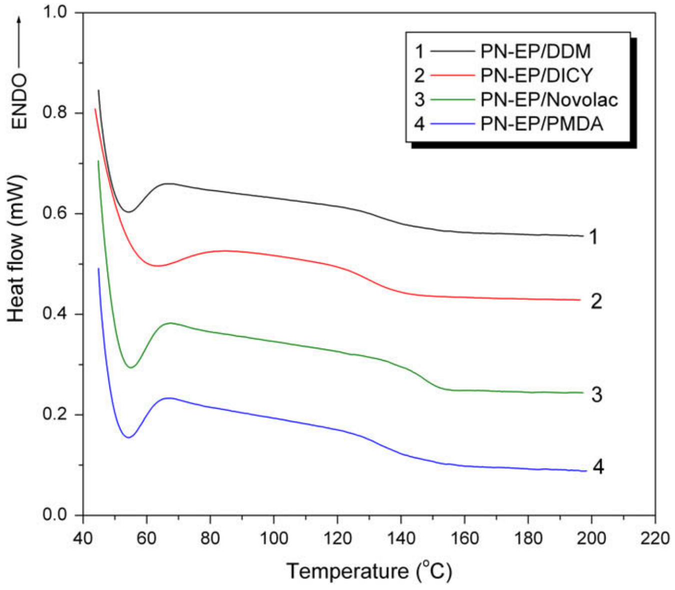

Fig. 7. DSC thermograms of the PN-EP thermosets with various curing agents.

Table 2
Thermal properties of PN-EP and DGEBA cured with various curing agents.

Curing system	T_g (°C)	Temperature at characteristic weight loss (°C)		Temperature at rapid weight loss (°C)	Char yield at 600 °C (wt.%)
		3 wt.%	10 wt.%		
DGEBA/DDM	132.7	281.6	385.4	395.5	9.4
PN-EP/DDM	137.5	270.7	373.8	396.9	23.5
DGEBA/DICY	129.6	325.1	362.4	402.5	7.6
PN-EP/DICY	133.8	322.4	365.8	408.8	42.4
DGEBA/novolak	135.4	362.1	390.5	401.7	8.7
PN-EP/novolak	144.6	378.6	400.1	409.4	56.2
DGEBA/PMDA	131.5	259.4	352.6	385.6	8.1
PN-EP/PMDA	138.2	238.2	340.8	387.3	54.6

two-step weight loss. Compared with the control thermosets using corresponding curing agents, the PN-EP ones exhibit lower temperatures at 3 wt.% and 10 wt.% weight loss, which results from the initial degradation of the unreacted PN-EP or the curing agent at relatively low temperature. The volume of the PN-EP molecule is huge in comparison with that of the DGEBA one, which generates a steric hindrance effect. In practice, hydroxyl groups in PN-EP are difficult to achieve complete reaction with the curing agent. However, the temperature at the rapid weight loss of the PN-EP thermoset is higher than that of the corresponding control one. This result indicates that the thermal stabilities of the PN-EP curing systems are improved after the covalent incorporation of cyclotriphosphazene moieties into the epoxy resin. Furthermore, it is also noticed that the char yields of the PN-EP thermosets are much more than those of the control ones. This result indicates that the incorporation of cyclotriphosphazene into the epoxy resins can increase the char yield significantly because of the formation of phosphorus-rich char during the decomposition of the cyclotriphosphazene moieties. This result plays an important role to improve the flame retardancy of the phosphazene-based epoxy resins [33]. It can be deduced that the formation of the phosphorus-rich char in the decomposition of the PN-EP thermosets not only increased the weight loss temperature at the rapid degradation region but also resulted in a high char yield. This high phosphorus-rich char yield can limit the production of combustible carbon-containing gases, reduce the exothermicity caused by the pyrolysis reactions and the thermal conductivity of the surface burning material, and thus, improve the flame retardancy of the epoxy resins.

It is also observed from Table 2 that the thermal stabilities of PN-EP cured with different curing agents are improved in the order of PMDA, DDM, DICY and novolak by comparing the temperatures for rapid weight loss. The high decomposition temperature of the PN-EP/novolak thermoset is ascribed to its high cross-linking density. However, the PN-EP/PMDA thermoset exhibits a comparatively poor thermal stability as well as a two-step degradation, in which the first step is attributed to a characteristic decomposition of the joint epoxy resin structure or the unreacted curing agent caused by the steric hindrance of PMDA [35]. In addition, the char yields of the PN-EP thermosets with different curing agents decrease in an order of novolak, PMDA, DICY and DDM. Apparently, the PN-EP/DDM thermoset has the least char yield among them. This result is ascribed to the methyl groups in DDM, which act as electronic donators. These methyl groups weaken the linkages of oxygen atoms with others in the PN-EP molecules and reduce the bond energy of P–O–Ph. In this case, the P–O–Ph bonds become easily broken down, and the pyrolysis of the thermoset is promoted. The pyrolysis of the thermoset is so drastic as to reduce the phosphorus-rich residue.

In order to learn more about the degradation mechanism of the PN-EP thermosets, the residues obtained from the TGA measurements were evaluated by FTIR. Fig. 9 illustrates the FTIR spectra of the pyrolysis residues of the PN-EP thermosets with various curing agents. These residues after pyrolysis almost present the same spectra, in which the absorption peaks at 1593, 1439, and 752 cm^{-1}, corresponding to aromatics and polyaromatics are characteristic for the carbonized polymers. A series of bands between 1258 and 1123 cm^{-1} are attributed to the combination of stretching vibrations of the P═N and P–O–C bonds. Moreover, the broad absorptions between 887 and 743 cm^{-1} are characteristic of the P–O–Ph bonds. These results indicate that the pyrolysis residues of these PN-EP thermosets seem to consist of cross-linked phosphorous oxynitride and carbonized aromatic networks.

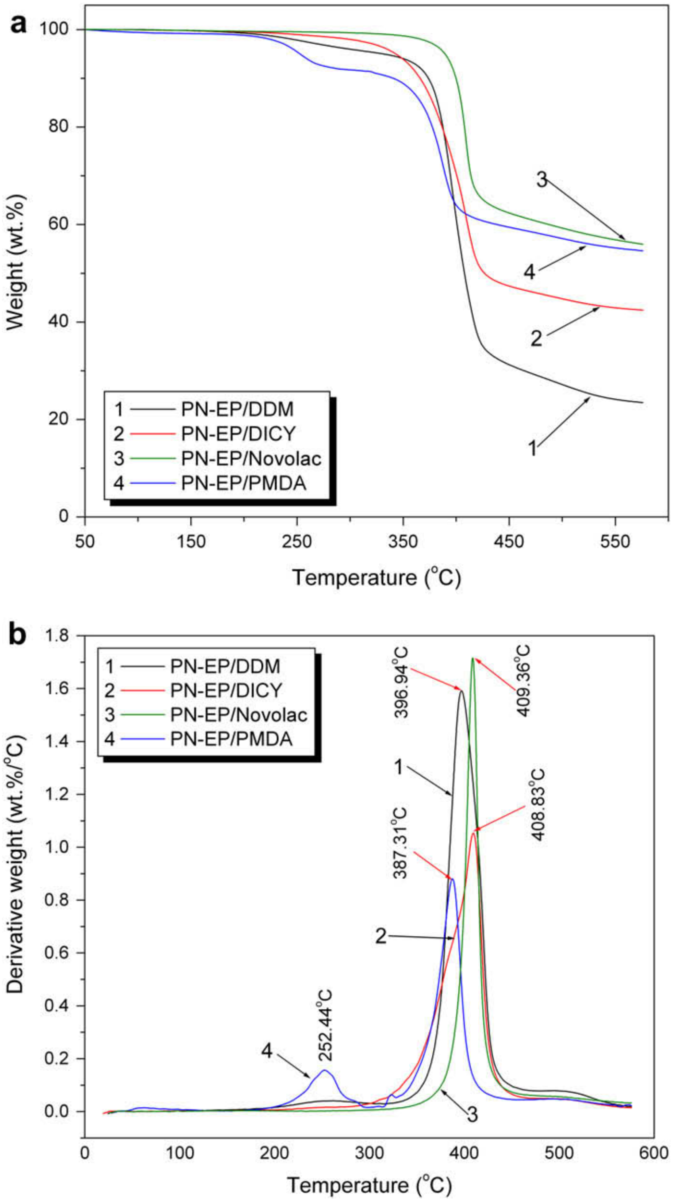

Fig. 8. TGA (a) and DTG (b) thermograms of the PN-EP thermosets with various curing agents.

3.5. Flame-retardant properties

Flame-retardant properties of the PN-EP thermosets with various curing agents were further evaluated by LOI measurement and UL94 horizontal/vertical flammability tests, and the results are

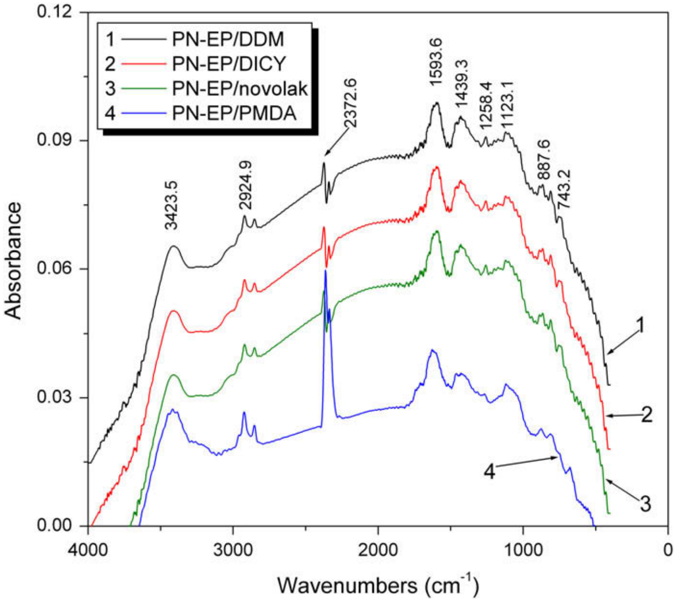

Fig. 9. FTIR spectra of the pyrolysis residues obtained from TGA measurements of the PN-EP thermosets with various curing agents.

listed in Table 3. It is clear that the PN-EP thermosets with these curing agents gain excellent flame retardancy in comparison with the flammable DGEBA curing systems reported in lots of literatures [36]. All the samples successfully achieved the flammability rating of UL94 HB. They also reached the UL94 V-0 rating and obtained the LOI values above 30 except for the PN-EP/DDM thermoset. These results indicate that incorporating cyclotriphosphazene moieties into DGEBA can provide excellent flame retardancy as well as improve their thermal stabilities. It is understandable that the degradation of the cyclotriphosphazene moieties forms a protective layer on the polymer surface and serves as a barrier against heat and oxygen diffusion to enhance both thermal stabilities and flame retardancy of materials. Nevertheless, the PN-EP/DDM thermoset only achieve an LOI value of 28.5 and the UL94 V-1 rating, which is consistent with the less char yield as discussed previously. It is concluded that DDM as a curing agent is distinctly not suitable for the flame-retardant curing system of PN-EP due to its low char yield.

It is also noteworthy that the flame retardancy of these PN-EP thermosets is independent of the nitrogen content in curing agents. Even if the nitrogen-free curing agents like novolak and PMDA were employed, the PN-EP thermosets also achieved excellent flame retardancy. On the contrary, the PN-EP cured with a nitrogen-containing curing agent, DDM, failed in reaching the flammability rating of UL94 V-0. It is clear that the significant improvement in flame-retardant properties of the epoxy resin results from the inherent flame retardancy of cyclotriphosphazene moieties as well as an effective synergism of phosphorus–nitrogen elements. However, the flame-retardant mechanism of phosphazene-based polymers is still not very clear, though they have considerable potential on the basis of their flame-retardant properties. There have been many proposals for the flame-retardant mechanisms of the phosphazene-based polymers, such as the gas phase mechanism [21], the condensed phase mechanism [22], and the phosphorus–nitrogen synergism mechanism [23]. On the basis of the investigation on the thermal decomposition and flame retardancy of phosphazene-based epoxy resin in this article, the flame retardancy of the phosphazene-based polymers results from not a sole mechanism but comprehensive effects including: (1) the cyclotriphosphazene moieties can produce phosphoric acid or metaphosphoric acid during pyrolysis, which acts in the condensed phase promoting char formation on the surface as a barrier to inhibit gaseous products from diffusing to the flame and to shield the polymer surface from heat and air; (2) the cyclotriphosphazene moieties can release the inflammable gases such as CO_2, NH_3 and N_2 during burning to dilute the hot atmosphere and cool the pyrolysis zone at the combustion surface; (3) these mentioned inflammable gases can cut off the supply of oxygen; (4) the cyclotriphosphazene moieties can also produce the phosphinylidyne free radicals (PO•), which can annihilate H• and OH• free radicals so as to terminate the combustion reaction [37]. However, the chemical transformations of the cyclotriphosphazene moieties and their participation in all stages of the combustion process for the phosphazene-based polymers are not yet fully understood, and a further intensive study is still necessary to clarify the flame-retardant mechanisms of the phosphazene-based polymers.

Table 3
Flame-retardant properties of PN-EP cured with various curing agents.

Curing system	UL94 rating		Dripping	LOI value (%)	*P*% (wt.%)	*N*% (wt.%)
	Horizontal burning test	Vertical burning test				
PN-EP/DDM	HB	V-1	None	28.5	2.40	3.47
PN-EP/DICY	HB	V-0	None	31.2	2.52	3.64
PN-EP/novolak	HB	V-0	None	33.5	2.18	0.98
PN-EP/PMDA	HB	V-0	None	32.9	2.38	1.07

4. Conclusion

A phosphazene-based oligomer PN–OH was synthesized through a two-step reaction, and was characterized by elemental analysis, ^{1}H NMR, ^{31}P NMR, and FTIR. And then, a new phosphazene-based epoxy resin for flame retardancy was synthesized by reaction between DGEBA and PN–OH using triphenylphosphine as a catalyst. The FTIR and GPC results confirm this successful synthesis. The PN-EP thermosets were obtained by curing with DDM, DICY, novolak and PMDA. The reactivity of the PN-EP thermosets with these curing agents presents an increase in the order of DDM, PMDA, novolak and DICY. The investigation on thermal properties shows that the PN-EP thermosets achieve higher T_gs and decomposition temperatures in comparison with the corresponding DGEBA ones while their char yields are improved significantly. It seems that the pyrolysis residues of these PN-EP thermosets consist of cross-linked phosphorous oxynitride and carbonized aromatic networks. These PN-EP thermosets also exhibit excellent flame retardancy. This result can be confirmed from the thermosets with novolak, DICY and PMDA that achieve the LOI values above 30 and the flammability rating of UL94 V-0, whereas the PN-EP/DDM system reaches the V-1 rating. The nonflammable halogen-free epoxy resin synthesized in this study has potential applications in electric and electronic fields in consideration of the environment and human health.

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