

Novel Flame Retardant Thermosets from Nitrogen-Containing and Phosphorus-Containing Epoxy Resins Cured with Dicyandiamide

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ABSTRACT: A novel phosphorus-containing epoxy resin (EPN-D) was prepared by addition reaction of 9,10-dihydro-9-oxa-10-phosphaphenanthrene 10-oxide (DOPO) and epoxy phenol-formaldehyde novolac resin (EPN). The reaction was monitored by epoxide equivalent weight (EEW) titration, and its structure was confirmed by FTIR and NMR spectra. Halogen-free epoxy resins containing EPN-D resin and a nitrogen-containing epoxy resin (XT resin) were cured with dicyandiamide (DICY) to give new halogen-free epoxy thermosets. Thermal properties of these thermosets were studied by differential scanning calorimeter (DSC), dynamic mechanical analysis (DMA), thermal mechanical analyzer (TMA) and thermal-gravimetric analysis (TGA). They exhibited very high glass transition tem-

peratures (T_g s, 139–175°C from DSC, 138–155°C from TMA and 159–193°C from DMA), high thermal stability with $T_{d,5}$ wt % over 300°C when the weight ratio of XT/EPN-D is ≥ 1 . The flame-retardancy of these thermosets was evaluated by limiting oxygen index (LOI) and UL-94 vertical test. The thermosets containing isocyanurate and DOPO moieties showed high LOI (32.7–43.7) and could achieve UL-94 V-0/V-1 grade. Isocyanurate and DOPO moieties had an obvious synergistic effect on the improvement of the flame retardancy. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 2391–2397, 2007

Key words: halogen-free epoxy resin; flame-retardancy; thermal property

INTRODUCTION

Epoxy resins are widely used as functional materials for their superior thermo-mechanical properties and excellent processability. However, their flammability limited the usage in the field of electrical/electronic substrate. Halogen-containing epoxy resins were developed to improve the nonflammability, but most of them have some shortcomings such as low T_g , low thermal stability and especially a series of environmental issues during decomposition or incineration^{1,2}; thus they cannot be used as advanced electrical/electronic substrates. In recent years, many halogen-free flame-retardant epoxy resins/curing agents^{3–30} have been developed to meet the environmental protection requirements. Generally, covalent incorporation of nitrogen,^{8,19,23–27} phosphorous^{3–17,20–22} into the backbone of the epoxy thermosets could provide excellent flame retardancy without environmental issues. For example, DOPO (9,10-dihydro-9-oxa-10-phosphaphenanthrene 10-oxide) derivative epoxy resins^{4,9} which were investigated intensively for their high flame

retardancy. Recently, in order to make “lead-free” electrical/electronic products, nitrogen-containing epoxy resins are paid more attention, not only for their excellent flame retardancy, but also for their superior heat resistance. Phosphorous- and nitrogen-containing epoxy systems^{9,28} were designed and prepared for that P-N synergistic effect can improve the flame retardancy dramatically.

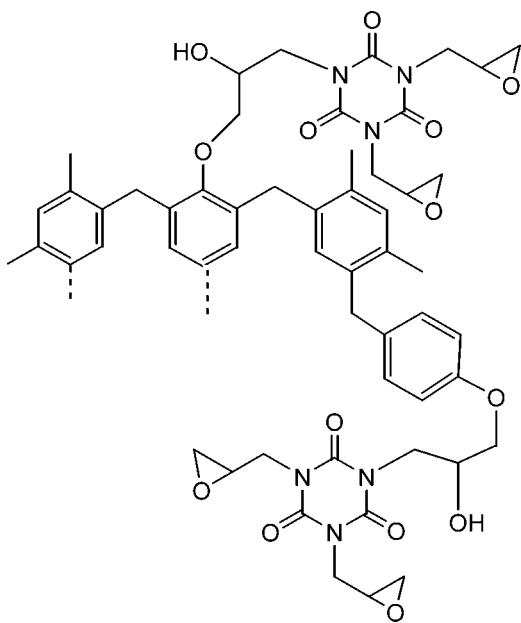
In our previous work, a novel nitrogen-containing epoxy resin (XT resin) was synthesized by chain extension reaction between xylenephormaldehyde (XPF resin) and triglycidyl isocyanurate (TGIC).²⁴ In this work, a novel phosphorus-containing epoxy resin was synthesized by addition reaction of DOPO and epoxy phenol-formaldehyde novolac resin (EPN), and then combined with XT resin to give a new halogen-free flame-retardant epoxy system. The thermal properties and flame retardancy of the resultant thermosets were investigated in detail.

EXPERIMENTAL

Materials

Xylenephormaldehyde resin (XF2602, from Suzhou Special Chemicals Co., China; acid value < 0.3 mg KOH/g, $M_w = 300$ –500, oxygen content is 11 wt %),

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Scheme 1 Structure of nitrogen-containing resin (XT).

triglycidyl isocyanurate (TGIC, purchased from Jiangsu Niutang Chemical Co.) was reprecipitated in CH_3OH before use, and phenol (purchased from Hangzhou Chemical Reagent Co.) was used as received. *p*-Toluenesulfonic acid (*p*-TSA), triphenyl phosphate (Ph_3P) and lithium hydroxide were purchased from Sinopharm Chemical Reagent Co. (Shanghai, China) and used as catalysts. Epoxy phenolformaldehyde novolac resin (EPN, functionality = 4–6) with EEW 182 g/eq was purchased from Shanghai Resin Company in China. 9,10-Dihydro-9-oxa-10-phosphaphenanthrene 10-oxide (DOPO) was supplied kindly by Hangzhou JLS Flame Retardant Co. (Hangzhou, China); dimethylformamide (DMF) was purchased from Hangzhou Shuanglin Chemical Reagent Co. (Hangzhou, China) and used as received.

Synthesis of nitrogen-containing epoxy resin (XT)

A general synthetic route of XT resin was described as the published procedures²⁴ (Scheme 1). The epoxy

equivalent weight (EEW) of XT resin was 357 g/eq determined by HClO_4 / potentiometric titration method.

Synthesis of phosphorous-containing epoxy resin (EPN-D)

General example of synthesis of EPN-D resin (shown in Scheme 2) is as follows: 100 g EPN and 40 g DOPO were added to a four-necked round bottom flask equipped with a heating mantle, mechanical stirrer, thermocouple and condenser. The mixture was gradually heated to 100°C under vacuum till DOPO was dissolved completely and the solution became clear and no any bubbles produced, and then added the catalytic amounts of Ph_3P . The mixture was heated to 160°C under vacuum and maintained about 150–170 min to obtain yellow viscous liquid resin, which is a transparent solid in the room temperature.

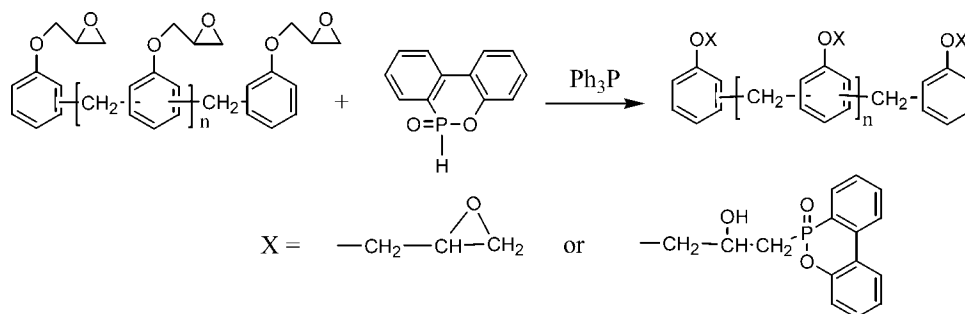
Preparation of the cured epoxy resins

XT and EPN-D were dissolved into acetone and mixed well by stirring at weight ratios of 3, 1, and 0.33 respectively. XT resin, EPN-D resin and the mixed XT/EPN-D (3, 1, and 0.33) resin were mixed with equal stoichiometric DICY. Samples for DSC and TGA test were cured at 160°C for 60 min and 180°C for 120 min.

Characterization

Infrared spectra were recorded by using a VECTOR 22 FT-IR spectra photometer ($400\text{--}4000\text{ cm}^{-1}$). $^1\text{H-NMR}$ spectrum was obtained with an Advance DMX 500 NMR spectrometer at 35°C using CDCl_3 as a solvent.

Three to five milligrams of above samples were placed in aluminum DSC pans and run on a Perkin-Elmer DSC 7 thermal analyzer at a heating rate of $20^\circ\text{C}/\text{min}$ and nitrogen was used as carries gas at a



Scheme 2 Schematic outline of the synthesis of phosphorus-containing epoxy resin (EPN-D).

flow of 40 mL/min for determining T_g . Thermogravimetric analyses (TGA) were carried out on a Perkin-Elmer Pyris 1 under N_2 atmosphere at a heating rate of $10^\circ\text{C}/\text{min}$ from 50°C to 850°C .

Specimens for DMA and LOI test were obtained from the prepreg which needs pre-curing process (about $160^\circ\text{C}/10\text{min}$), and then heat curing in a heat-press with the procedure of $130\text{--}160^\circ\text{C}/15\text{ min}$ (heating rate of $2^\circ\text{C}/\text{min}$) and $180^\circ\text{C}/90\text{ min}$ for complete cure of the samples. A specimen with 60 mm in length, 12.6 mm in width, and approximately 1.6 mm in thickness was used for DMA test, and performed with a Perkin Elmer 7 DMA. The storage modulus G' and $\tan \delta$ were determined while the sample was subjected to temperature scan mode at a programmed heating rate of $3^\circ\text{C}/\text{min}$ from the room temperature to about 250°C at a frequency of 1 Hz. T_g data were obtained from the measurement of the $\tan \delta$ peak. LOI values were measured on a HC-2 LOI tester according to ASTM D-2863-77. The percentage in the $O_2\text{-}N_2$ mixture deemed sufficient to sustain the flame was taken as the LOI.

The UL-94 vertical test was performed according to the testing method proposed by Underwriter Laboratory,³¹ with the test specimen bars of 130 mm in length, 13 mm in width, and 1.6 mm in thickness. During the test, five sample bars suspended vertically over surgical cotton were ignited by a Bunsen burner. A flame was applied twice to the lower end of the bar for 10 s. The ratings of V-0, V-1 were achieved if burning stops within 10 s, 30 s after two applications of 10 s each of a flame to a test bar, and no flaming drips allowed. The class of V-2 was achieved if burning stops within 30 s after ignited, but the surgical cotton below the specimen was ignited with the flaming drippings.

The Z-axis coefficient of thermal expansion (Z-CTE) was measured with a DuPont 943 thermal mechanical analyzer (TMA) in accordance with ASTM E83-186. A specimen of 4 mm in length, 4 mm in width, and 1.6 mm in thick was used at a heating rate of $5^\circ\text{C}/\text{min}$. Normally, the thermal expansion increases with increasing of the temperature and the CTEs were calculated from the slope. An abrupt change in slope of the expansion curve indicates a transition of the material from one state to another. α_1 and α_2 are the CTE values below and above T_g respectively.

RESULTS AND DISCUSSION

Syntheses and characterizations

The synthesis of XT resin and corresponding synthetic kinetics were investigated intensively in our previous work.²⁴ Herein, we investigated mainly on the synthesis of a new phosphorous-containing

epoxy resin (EPN-D) via the addition reaction of DOPO and EPN. Compared with epoxy cresol-formaldehyde novolac resin (ECN),⁹ EPN was chosen for its lower viscosity and more reactivity of oxirane ring. Figure 1 shows a typical DSC exothermal curve of the reaction of DOPO and EPN in a heating rate of $20^\circ\text{C}/\text{min}$ under N_2 . The endothermic peak starts from 60°C to 128°C and is wide, which is attributed to the melting process of the mixture of EPN, DOPO and DOPO-OH (formed by the reaction of DOPO and moisture in air for DOPO's strong hydrophilicity) and dehydration of DOPO-OH.⁹ The first and second exothermal peaks in Fig. 1 are at 184°C and 271°C respectively, which are attributed to the addition reaction of P-H and oxirane ring and the etherification reaction of resulting aliphatic OH group and oxirane ring respectively, and lower than exothermal peak values reported⁹ for more reactivity of EPN and the addition of catalyst Ph_3P .

In order to avoid the side reaction of DOPO-OH and epoxide, we kept the reaction mixture in the flask under vacuum at $100\text{--}110^\circ\text{C}$ to eliminate water and other volatiles, and then elevated the temperature to 160°C for complete reaction. The reaction kinetics of EPN and DOPO with or without vacuum were traced by EEW titration. Figure 2 shows the EEW of products at different reaction time with or without vacuum used (Curves 1 and 2 respectively). The EEWs of the product under vacuum in 150 min and 170 min are 392 g/mol, which is consistent with the calculated EEW of the product (391 g/mol when the conversion is 100%). When there is no vacuum, the EEWs of the product in 120, 150, and 170 min are 392, 397, and 400 g/mol respectively. Slight decrease of EEW is found, which indicates that side reaction occurred without vacuum. And so the

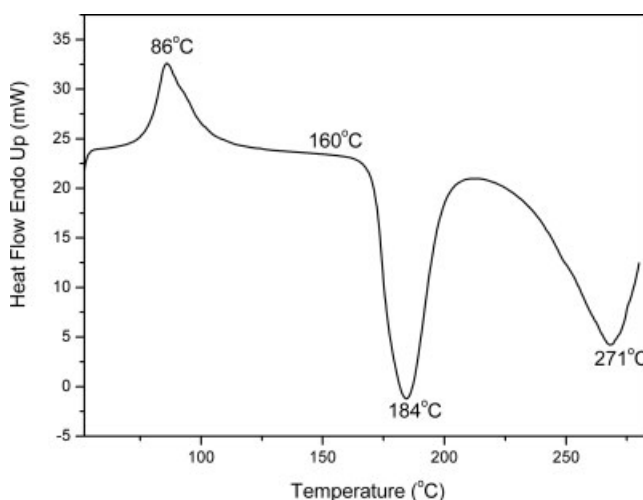


Figure 1 Typical DSC curve of reaction of DOPO and EPN (the weight ratio of DOPO/EPN is 0.4, Ph_3P (0.1 wt %) as a catalyst, $20^\circ\text{C}/\text{min}$, N_2 atmosphere).

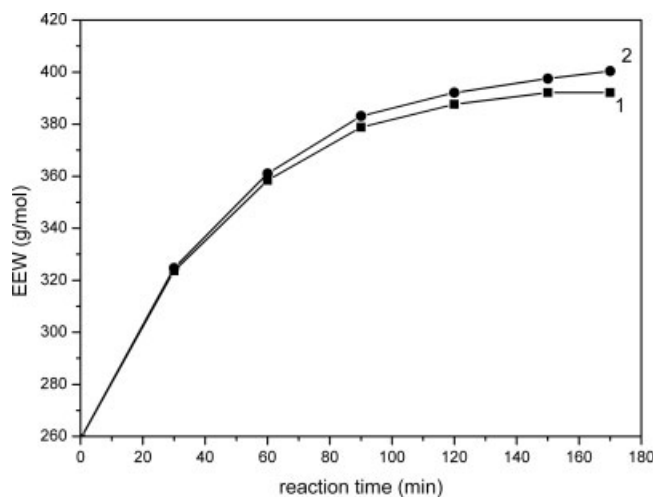


Figure 2 The EEW of the products of DOPO and EPN in different reaction time. Ph_3P (0.1 wt %) as a catalyst. Line 1, under vacuum; line 2, no vacuum.

optimum reaction condition for EPN and DOPO was obtained.

Figure 3 shows the IR spectra of DOPO, EPN, and EPN-D resin. The IR spectrum of DOPO was reported elsewhere.^{4,9,12,32} It shows the characteristic absorptions at 755 , 1117 cm^{-1} (P—O—Ph), 1590 , 1477 cm^{-1} (P—Ph), and 1198 , 1239 cm^{-1} (P=O). The absorption at 2430 cm^{-1} is attributed to the characteristic stretching vibration peak of P—H bond, which disappears completely in the IR spectrum of EPN-D resin. The IR peak of the generated secondary aliphatic hydroxyl is at 3396 cm^{-1} for ring opening reaction of oxirane ring of EPN. The characteristic asymmetrical vibration of oxirane ring of EPN is at 917 cm^{-1} and its intensity decreases when it reacts with DOPO, while characteristic IR peaks of

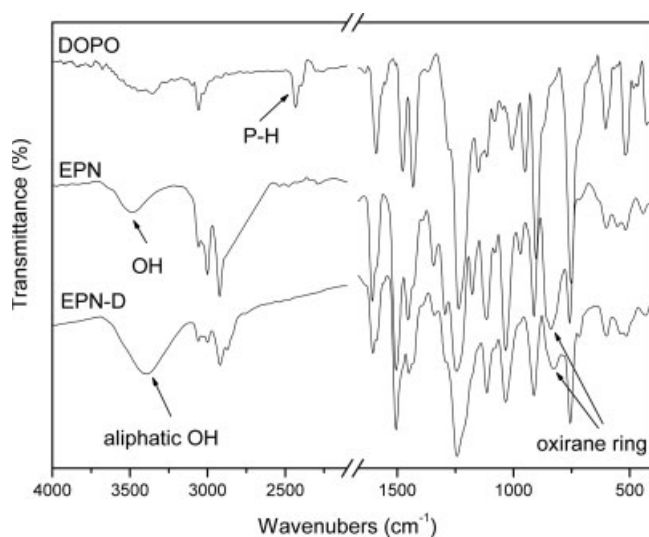


Figure 3 FTIR spectra of DOPO, EPN, and EPN-D.

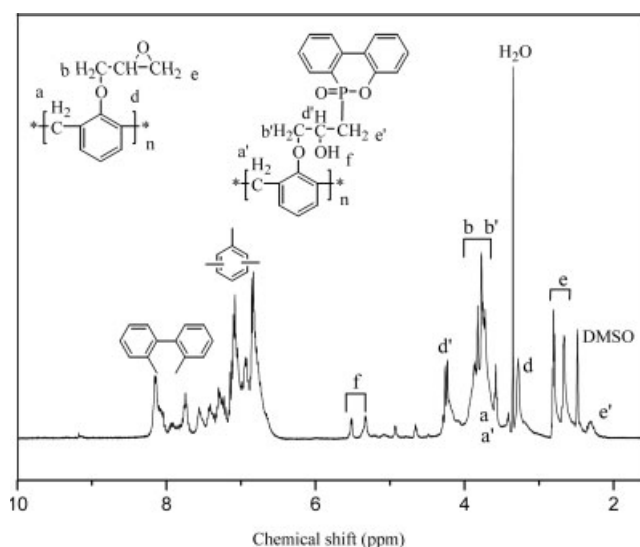


Figure 4 ^1H NMR spectrum of phosphorus-containing epoxy resin EPN-D.

P—O—Ph, P—Ph and P=O groups of DOPO remain in the IR spectrum of EPN-D resin. Figure 4 shows the ^1H -NMR spectrum of EPN-D resin. The chemical shifts of all protons are assigned in detail. Chemical shifts of the oxirane group (3.27, 2.81, and 2.67 ppm) of EPN-D resin indicate that partial oxirane group remained after the reaction, and chemical shift at 4.26 ppm is originated from the proton of >CH- of EPN-D structure which generated from the ring opening reaction of oxirane ring (shift from 3.27 to 4.26 ppm).

From above results of IR and ^1H -NMR spectra, we concluded that a phosphorus-containing epoxy resin (EPN-D) was synthesized.

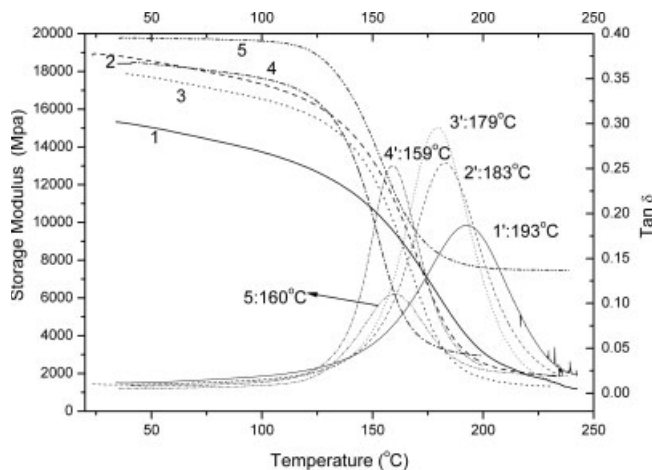


Figure 5 The relationship of storage modulus (G') Tan δ and temperature of the XT/EPN-D/DICY thermosets ($3^\circ\text{C}/\text{min}$, 1Hz). 1, 1': XT; 2, 2': XT/EPN-D=3; 3, 3': XT/EPN-D =1; 4, 4': XT/EPN-D = 0.33; 5, 5': EPN-D (weight ratio).

TABLE I
DMA Analysis of the Epoxy Thermosets

The cured epoxy resin	T_g ($^{\circ}\text{C}$, DMA)	Height of $\tan \delta$	Modulus 50°C (MPa)	Modulus $T_g + 40^{\circ}\text{C}$ (MPa)	Modulus (50°C)/modulus ($T_g + 40^{\circ}\text{C}$)
XT	193	0.187	15,043	1455	10.3
XT/EPN-D(=3)	183	0.256	18,570	2000	9.3
XT/EPN-D(=1)	179	0.296	17,660	1362	13.0
XT/EPN-D(=0.33)	159	0.253	18,387	2943	6.2
EPN-D	160	0.110	19,727	7625	2.8

DMA analysis

Dynamic mechanical analysis (DMA) can provide information about the microstructure and thermo mechanical properties of the epoxy thermosets. Figure 5 shows the dynamic mechanical behaviors of the XT/DICY, XT/EPN-D (= 3, 1, 0.33, weight ratio)/DICY and EPN-D/DICY thermosets with a heating rate of $3^{\circ}\text{C}/\text{min}$ from the room temperature to about 250°C at a frequency of 1 Hz. Their T_g s are 193, 183, 179, 159, and 160°C (those are peak temperatures of α relaxation transition) respectively and decrease with increasing content of EPN-D resin. According to the rubber elastic theory,³³ the crosslink density of a thermosetting resin is proportional to the G' in $T_g + 40^{\circ}\text{C}$, so the ratio of the crosslink density of the XT, XT/EPN-D (= 3, 1, 0.33, weight ratio) and EPN-D/DICY thermosets is about 1.5 : 2.0 : 1.4 : 2.9 : 7.6 (as shown in Table I) and all of them show an increasing trend, while T_g s of these epoxy thermosets decrease with increasing crosslink density. Compared with the influence of the crosslink density on T_g , rigid isocyanurate ring in main structure, which make the chain segment movement very difficult, and the plasticization of DOPO moiety¹⁰ are decisive structural factors for above T_g s change.

From Figure 5, the initial storage modulus (G') of the EPN-D/DICY thermoset is higher than those of the epoxy thermosets containing XT resin before T_g . Furthermore, G' of the EPN-D/DICY thermoset after T_g is still high and shows a typical DMA curve of a thermosetting resin, while the XT/DICY thermoset has lowest initial G' , although it has the highest T_g . Unsymmetrical xylene structure of XT resin would be responsible for low crosslink density of the thermosets. Actually, the unsymmetrical xylene, DOPO moiety, and isocyanurate ring have a combined associated effect on the G' of the XT/EPN-D/DICY thermosets, and a function related to the composition (content of XT or EPN-D) is not found.

TGA analysis

Figure 6 shows the TGA curves of the XT, XT/EPN-D (= 3, 1, 0.33, weight ratio) and EPN-D/DICY thermosets from the room temperature to 850°C at a

heating rate of $10^{\circ}\text{C}/\text{min}$ under N_2 atmosphere. 5 wt % decomposition temperatures ($T_{d,5 \text{ wt } \%}$; see Table II) increase with increasing the content of EPN-D resin for its phenolformaldehyde novolac structure. However, $T_{d,5 \text{ wt } \%}$ of the XT/DICY thermoset is only 253°C and lower than that of the EPN-D/DICY thermoset (358°C). It indicates that the XT resin has a low thermal-stable structure, which is regarded as xylene moiety. Moreover, unsymmetrical xylene and rigid isocyanurate structures can result in low curing conversion,²⁶ crosslink density and some defects in the structure, which decreased the thermo stability.

The char residue (Y_c , wt %) at 850°C of the XT/DICY thermoset is only 12.55, while that of the EPN-D/DICY thermoset is 30.93, and the char residue of these thermosets increases with increasing the content of the phosphorous. The decomposed products of the XT/DICY thermoset released are mainly in the form of the gas because isocyanurate structure favors to produce nitrogen-containing gases³⁴ which facilitate to flame resistance by a vapor phase flame-retardancy mechanism, while the EPN-D/DICY thermoset is helpful to form char residue for its multiple phenol formaldehyde structure and DOPO structure.

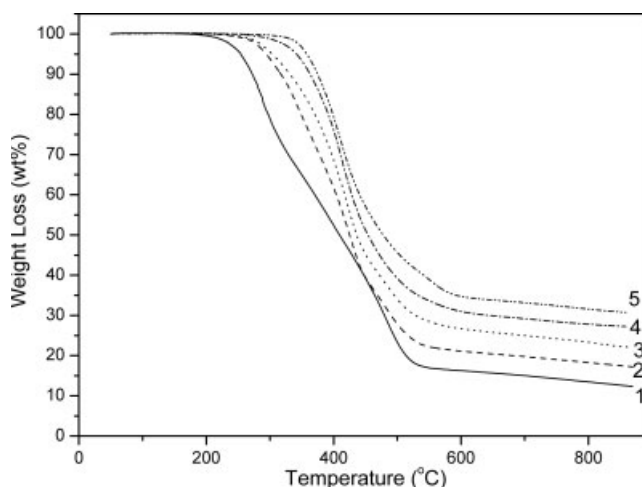


Figure 6 TGA curves of the XT/EPN-D/DICY thermosets ($10^{\circ}\text{C}/\text{min}$, N_2). 1. XT; 2. XT/EPN-D = 3; 3. XT/EPN-D = 1; 4. XT/EPN-D = 0.33; 5. EPN-D (weight ratio).

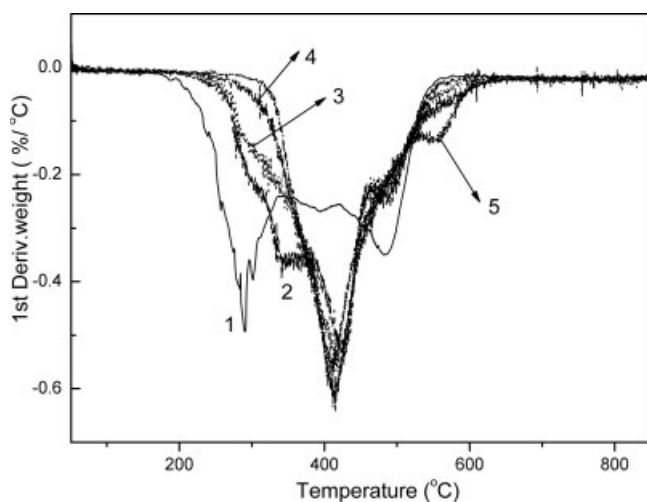


Figure 7 DTG curves of the XT/EPN-D/DICY thermosets (10°C/min, N₂). 1. XT; 2. XT/EPN-D =3; 3. XT/EPN-D=1; 4. XT/EPN-D =0.33; 5. EPN-D (weight ratio).

From the first differential thermogravimetric (DTG) thermograms of the above epoxy thermosets (Fig. 7), we can see that the DTG curve of the XT/DICY thermoset shows three decomposition peaks (290, 394, and 485°C), which mean three corresponding decomposition stages in its decomposition process. Multiple-stage decomposition behavior of the XT/DICY thermoset is mainly attributed to the combined effects of the decomposition of different groups in the thermoset, as well as the crosslink structure from the reaction of DICY and epoxy groups. Moreover, the first and third decomposition peaks of the XT/DICY thermoset decrease dramatically with increasing the weight percent of the EPN-D resin, while the second decomposition peak increases. When the weight ratio of XT/EPN-D is less than 0.33, there is one decomposition peak at about 415°C. The decomposition peak of a thermoset in high temperature means that it has good stability.

LOI and UL-94 results

Limited oxygen index (LOI) measures the minimum oxygen concentration (in a flowing mixture of

oxygen-nitrogen gas) required to support candle-like downward flame combustion.²⁰ A material with LOI of 26 or higher is rated as a flame-retardant material. It is strongly dependent on the char residue for halogen-free polymers³⁵ and is suitable as a semi-qualitative indicator of the effectiveness of the flame retardants in laboratory. UL-94 vertical test is another testing method for flame-retardancy evaluation of materials in industrial application and is similar to real scale fire process with strong heat input, and thus the results depend on the integrated effects of all flame-retardant elements the material contained.

LOI value of the XT/DICY thermoset is 24.5 and higher than that of the common epoxy thermoset (about 19.8), but it failed to pass UL-94 vertical test (Table III) although it has high nitrogen content (9.6 wt %). This indicates that only nitrogen element cannot ensure good flame retardancy. The LOI values of the thermosets containing EPN-D resin are from 32.7 to 43.7 and beyond 26, and increase with increasing the content of the phosphorous. From LOI evaluation, we know that these thermosets have good flame retardancy. The EPN-D/DICY thermoset has the highest LOI value (43.7), which may result from much more multiple phenol formaldehyde structure and high phosphorus content (2.5 wt %) that facilitate to form intumescent charred layers which were observed after ignition. However, the maximum burning time after 10 s ignition for the EPN-D/DICY thermoset is 15 s (UL-94 V-1 grade), which is longer than those of the XT/EPN-D (1 and 0.33) thermosets that were rated as V-0 and V-1 grade respectively (see Table III). The main reason is that the EPN-D/DICY thermoset was lack of gas source in combustion to form intumescent structure since it did not contain XT structure. Similar trend of the maximum burning times after 10-s ignition was found when another group of thermosets with various weight ratio of XT/EPN-D (4, 3/2, 2/3, and 1/4, only UL94 test results: 55, 13, 8, and 14 s respectively without any drippings) was carried out. So, incorporating about 1.25 wt % of phosphorus and 5.7 wt % nitrogen element into the thermoset for this system will make the thermoset as flame retardant polymers in industrial application.

TABLE II
Thermal Stability Parameters for the Epoxy Thermosets

The cured epoxy resin	T_g (°C, DSC)	$T_{d,5}$ wt % (°C)	T_{max1}	T_{max2}	T_{max3}	$Y_{c,wt}$ % (850°C)
XT	175	253	290	394	485	12.55
XT/EPN-D(=3)	160	293	299	425	489	17.57
XT/EPN-D(=1)	156	302	–	421	488	22.24
XT/EPN-D(=0.33)	139	340	–	414	–	27.26
EPN-D	143	358	–	411	–	30.93

TABLE III
 T_g (°C, TMA), CTE, and Flame Retardancy of the Epoxy Thermosets

The cured epoxy resin	N , wt %	P , wt %	T_g (°C, TMA)	CTE (α_1/α_2)	LOI	Burning time ^a	Classification
XT	9.6	0	145	59/212	24.5	62	Fail
XT/EPN-D(=3)	7.6	0.63	149	62/271	32.7	37	Fail
XT/EPN-D(=1)	5.7	1.25	138	24/163	37.4	10	V-0
XT/EPN-D(=0.33)	3.6	1.86	140	38/192	39.8	11	V-1
EPN-D	2.1	2.50	155	26/128	43.7	15	V-1

^a The maximum burning time after 10 s ignition for each test bar, no drippings.

Z-axis coefficient of thermal expansion (CTE)

The Z-axis coefficient of thermal expansion (CTE, α_1/α_2) of a polymer is a very important parameters for evaluating the usage stability and reliability of electrical/electronic substrate. It can be determined by TMA. The CTE values of aforementioned epoxy thermosets are shown in Table III. The less the α_1/α_2 is, the better the size stability of the thermoset is. The α_1/α_2 of the XT/DICY thermoset is 59/212 and bigger than that of the EPN-D/DICY thermoset (26/128). Unsymmetrical xylene structure might result in more free volume of the thermoset, which increases CTE values. But CTE values have no relation with the composition of the thermosets. Furthermore, T_g s (138–155°C) determined by TMA have also no relation with the composition of the thermosets, while T_g s from DSC (139–175°C; see Table II) and DMA (159–193°C) have the same trend related to the composition of the thermosets. Structural factor were regarded as the main factor for the change of T_g s determined from DSC and DMA methods, while T_g s from TMA not only depend on the structural factor, but also exterior factors (such as polishing, size of a sample) which can result in the volume change of a sample. Furthermore, different definition about T_g in different methods will result in different results.

CONCLUSION

A novel phosphorus-containing epoxy resin (EPN-D) was synthesized and characterized. Halogen-free epoxy system containing EPN-D resin and a nitrogen-containing epoxy resin (XT resin) were cured with dicyandiamide (DICY) to give new halogen-free epoxy thermosets. Due to the introduction of isocyanurate structure and DOPO moiety, the obtained thermosets had high T_g s and exhibited excellent thermal stability and improved flame retardant properties with the evaluation of LOI measurement and UL-94 vertical test. These halogen-free epoxy thermosets with balanced properties can be potentially applied in the electrical/electronic industries, especially can be used as the environment friendly “green” materials.

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