

# Synthesis and characterization of a novel epoxy resin based on cyclotriphosphazene and its thermal degradation and flammability performance



Guang-Rui Xu, Miao-Jun Xu, Bin Li\*

Heilongjiang Key Laboratory of Molecular Design and Preparation of Flame Retarded Materials, College of Science, Northeast Forestry University, Harbin 150040, PR China

## ARTICLE INFO

### Article history:

Received 29 December 2013

Received in revised form

9 July 2014

Accepted 23 July 2014

Available online 2 August 2014

### Keywords:

Epoxy resin

Synthesis

Cyclotriphosphazene

Flame retardancy

Thermal degradation

## ABSTRACT

The cyclotriphosphazene-based epoxy resin hexa-[4-(glycidyloxycarbonyl) phenoxy]cyclotriphosphazene defined as CTP-EP was successfully synthesized from hexachlorocyclotriphosphazene, *p*-hydroxybenzaldehyde and epichlorohydrin. Its chemical structure was characterized by Fourier transform infrared (FTIR) spectroscopy, <sup>1</sup>H NMR, <sup>13</sup>C NMR and <sup>31</sup>P NMR spectroscopy. The prepared compound was cured with diamino diphenyl methane (DDM), diamino diphenyl sulfone (DDS) and *m*-phenylenediamine (mPDA), respectively. The flame retardant properties, thermal degradation behavior and flame retardant mechanism of the cured CTP-EP were investigated. The LOI values of all cured CTP-EP samples increased from 19.9% for cured diglycidyl ether of bisphenol-A (DGEBA) to above 30% and successfully passed UL-94 V-0 rating, which demonstrated that the prepared CTP-EP thermoset exhibited excellent flame retardancy. The dynamic mechanical thermal analysis (DMA) test demonstrated that the glass transition temperature (*T*<sub>g</sub>) enhanced from 155 °C for the cured DGEBA to 167 °C for CTP-EP thermoset. The results of thermogravimetric analysis/infrared spectrometry (TG-IR) tests suggested that the phosphazene group and high aromatic content in CTP-EP thermoset stimulated the dehydration of the matrix at earlier degradation process and the formation of char layer, which retarded the release of pyrolysis gas and enhanced the thermal stability of the cured CTP-EP at high temperature. The cone calorimeter tests (cone) test revealed that heat release rate (HRR), total heat release (THR), smoke production rate (SPR) and total heat production (TSP) of the cured CTP-EP decreased significantly compared with the cured DGEBA. The scanning electron microscopy (SEM) results showed that the phosphazene groups in CTP-EP obviously stimulated the formation of the intumescent, compact and stable char layer, which enhanced the flame retardancy of the matrix during combustion. Consequently, the underlying materials were protected from further degradation and combustion during a fire and result in the efficient flame retardancy of CTP-EP thermoset.

© 2014 Elsevier Ltd. All rights reserved.

## 1. Introduction

Epoxy resins are important thermosetting materials and have been widely used as advanced composite matrices in various areas from surface coatings, adhesives, automobiles to space vehicles, shipping and electronic/electrical industries for their outstanding properties, such as good mechanical properties, chemical resistance, excellent electric insulating property and low manufacturing cost [1–3]. However, the flammability of epoxy resins leads to fire

disaster inevitably, which severely limits their functional applications. Therefore, the epoxy resins are subjected to various mandatory controls for safety reasons [4,5].

Traditionally, brominated reactive compounds are used as comonomers with epoxy resins to obtain fire-retarded materials. However, flame-retarded 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 [6–8]. Recently, in consideration of environmental problems, researches for halogen-free flame retardant epoxy resins have attracted a great deal of attentions. Organophosphorus molecules are efficient radical scavengers and flame quenching materials. Combustion processes

\* Corresponding author. Tel./fax: +86 451 82192699.

E-mail address: [libinzh62@163.com](mailto:libinzh62@163.com) (B. Li).

are essentially exothermic free radical reactions, so the existence of radical stabilizers impedes combustion by the quenching mechanism. On the other hand, the nitrogen-containing compounds can release the inert gaseous by-products to form a highly porous char that provides thermal insulation and prevents the combustion from spreading [9–12]. There are lots of works reported about the molecular design and synthesis of flame retardant epoxy resins as well as a reactive flame-retardant additives by incorporating phosphorus-containing flame retarding units such as phosphine oxide, phosphates, and other phosphorylated and phosphonylated derivatives [13–19]. Today [18,19] developed a series of phosphorus-containing amines (TEDAP, TMPDAP and TOPDAP) which acted as flame retardant crosslinking agents in epoxy resins. The tests results showed that the epoxy resins with more than 2 wt % phosphorus content could reach excellent flame retardancy. However, these phosphorus-containing epoxy resins have some disadvantages, such as poor resistance to acid and base, low weight fraction of phosphorus, which is resulting in a low degree of flame retardancy [20,21]. Currently, a great interest is focusing on the design of both the backbone and the side groups of epoxy resins with more highly flame retarding moieties like phosphazenes, particularly cyclotriphosphazenes [22–26]. Many researchers have reported the phosphazene-based family of materials because they not only possess a wide range of thermal and chemical stabilities, but also can improve the thermal and flame retardant properties to polymers and their composites [27–34]. El Gouri M [27,28], synthesized a novel epoxy resin (HGCP) which was used as a reactive flame retardant and then blended with pure DGEBA to prepare flame retardant epoxy resins. The results showed that the addition of HGCP could effectively improve the thermal stability of DGEBA and exhibited self-extinguishing characteristics. Wang XD [29] synthesized a novel cyclotriphosphazene-based epoxy compound (PN-EPC) as a halogen-free reactive flame retardant. The tests revealed that the incorporation of PN-EPC could impart excellent flame retardancy to the epoxy thermoset, increased the glass transition temperature and thermal stability of the thermoset and the cyclotriphosphazene rings acted in both condensed and gaseous phases. Hexachlorocyclotriphosphazene is a versatile starting oligomer for the synthesis of phosphazene-based polymers because there are two chlorine groups attaching to each phosphorus atom in cyclotriphosphazenes which are active to be substituted by different nucleophiles. Multiple functions can be realized by replacing the chlorine groups with various functional substituents [35–39]. Once the cyclotriphosphazene is incorporated into the network of thermoset polymers, they exhibit unusual properties such as flame retardancy and self-extinguishing ability due to phosphorous and nitrogen flame retardant synergistic effect. The phosphazene-based polymers present more effective flame retardancy than other flame-retardants, which make them a new research focus [40–43]. Previous reports [30,40,42] show that epoxy thermoset containing cyclotriphosphazene units exhibit a potential application in the modern electric industry for their superior flame retardancy and thermal stability. So it is desirable to obtain novel cyclotriphosphazene-based epoxy materials with excellent comprehensive performance. However, the phosphazene used as primary component for synthesizing the flame retardant epoxy resins was seldom reported [24,27,29,30] and the flame retardant mechanism needs to be further investigated.

In this work, the cyclotriphosphazene-based flame retardant epoxy resin hexa-[4-(glycidyloxycarbonyl)phenoxy] cyclotriphosphazene (CTP-EP) was synthesized. Its chemical structure was characterized by FTIR,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and  $^{31}\text{P}$  NMR. The thermal stability, flame retardancy, thermal decomposition behaviors and flame retardant mechanism of the synthesized CTP-EP thermoset were investigated by limiting oxygen index (LOI),

vertical burning test (UL-94), thermogravimetric analysis (TGA), thermogravimetric analysis/infrared spectrometry (TG-IR), cone calorimeter tests (cone) and scanning electron microscopy (SEM).

## 2. Experimental

### 2.1. Materials

Hexachlorocyclotriphosphazene (HCCP) and 4-hydroxybenzaldehyde were purchased from Wuhan Yuancheng Chemical Co. Ltd., China. Tetrahydrofuran (THF), triethylamine (TEA), ethyl acetate (EA), sodium hydroxide (NaOH), potassium permanganate ( $\text{KMnO}_4$ ), sodium sulfate ( $\text{Na}_2\text{SO}_4$ ) and sulfuric acid ( $\text{H}_2\text{SO}_4$ ) were purchased from Tianjin Kemiou Chemical Reagent Co. Ltd., China. Diamino diphenyl methane (DDM), diamino diphenyl sulfone (DDS), m-phenylenediamine (mPDA), epichlorohydrin (ECH) and benzyltriethylammonium chloride (TEBA) were purchased from Aladdin reagent (Shanghai) Co. Ltd., China. Diglycidyl ether of bisphenol-A (DGEBA) (E-44, epoxide equivalent weights = 213 g/epoxide) of technical grade was supplied by Guangzhou Fude Chemicals Industry Co. Ltd., China.

### 2.2. Synthesis of CTP-EP

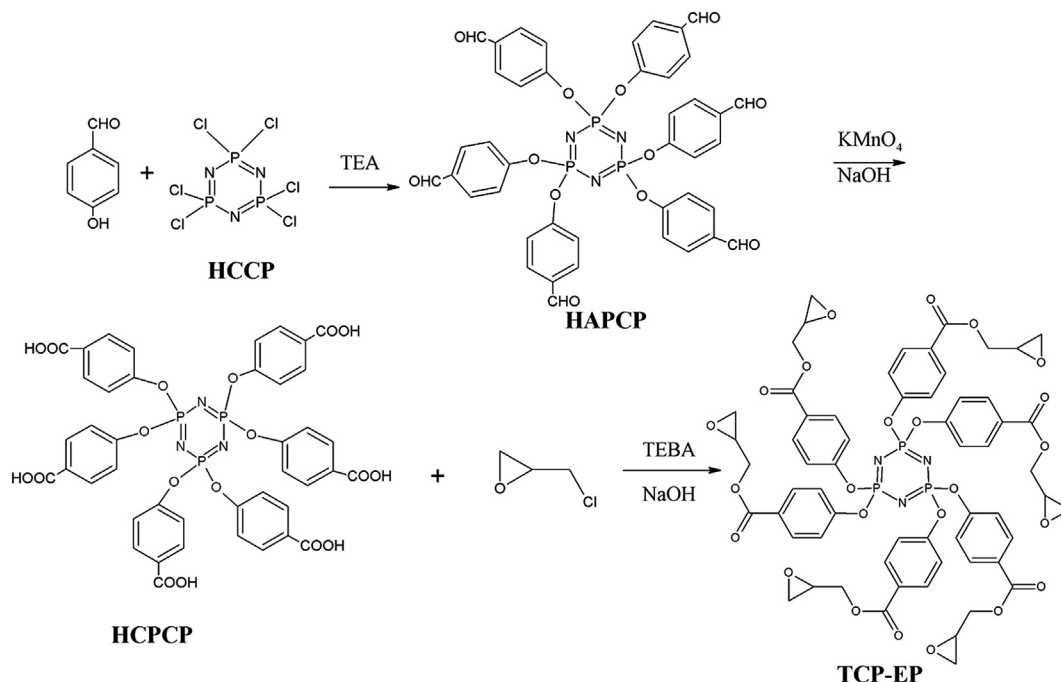
The final compound, hexa-[4-(glycidyloxycarbonyl)phenoxy] cyclotriphosphazene (CTP-EP), was prepared according to the following three steps and the synthesis routes are shown in Scheme 1.

#### 2.2.1. Synthesis of hexa-(4-aldehyde-phenoxy)-cyclotriphosphazene (HAPCP)

35 g (0.28 mol) 4-hydroxybenzaldehyde dissolved in 150 mL THF and 28 g (0.28 mol) triethylamine as the acid scavenger agent was added into a four-necked-flask equipped with a mechanical stirrer, a reflux condenser and a nitrogen inlet. 14 g (0.04 mol) hexachlorocyclotriphosphazene (HCCP) dissolved in 50 mL THF was added dropwise into the flask continuously and slowly under nitrogen atmosphere at room temperature. The reaction mixture was heated slowly to the reflux temperature and then allowed to stir strongly for 24 h. After that, the mixture was filtered twice to remove triethylamine hydrochloride. The solution was concentrated on a rotary evaporator and then poured into a large amount of water to precipitate the crude product. The compound HAPCP was recrystallized and purified by ethyl acetates following the procedure according to the reported literature [37] and the yield was 31.6 g (92%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 9.9 (6H, -CHO) and 7.13–7.75 ppm (24H,  $-\text{C}_6\text{H}_4$ ).

#### 2.2.2. Synthesis of hexa-(4-carboxyl-phenoxy)-cyclotriphosphazene (HCPCP)

According to our previous work [36], hexa-(4-carboxyl-phenoxy)-cyclotriphosphazene (HCPCP) was obtained from oxidizing hexa-(4-aldehyde-phenoxy)-cyclotriphosphazene (HAPCP) by potassium permanganate. 33.3 g potassium permanganate (0.21 mol), 6.3 g sodium hydroxide (0.16 mol) and 320 mL  $\text{H}_2\text{O}$  was added to the solution of 21 g HAPCP (0.024 mol) in 400 mL THF in a three-neck-flask equipped with a mechanical stirrer and refluxing condenser, then the reaction mixture was stirred for 30 h at refluxing temperature. After removing THF in the mixture on a rotary evaporator, the crude product deposited from adding sulfuric acid. The white precipitate was collected by filtration and washed with a great deal of water, then dried in vacuum at 60 °C and the yield was 22.7 g (97%).  $^1\text{H}$  NMR ( $\text{DMSO}-d_6$ ):  $\delta$  = 12.95 (6H, -COOH) and 7.85, 6.90 (24H,  $-\text{C}_6\text{H}_4$ ).



Scheme 1. Schematic procedures of synthesis for CTP-EP.

### 2.2.3. Synthesis of hexa-[4-(glycidyloxycarbonyl)phenoxy]cyclotriphosphazene (CTP-EP)

9.57 g HPCP (0.01 mol), 0.1 g TEBA and 50 g ECH were added and mixed together in a three-neck-flask equipped with a mechanical stirrer and refluxing condenser, and then stirred at 120 °C until homogeneous. After that, the mixture was cooled down to 50 °C and 6 g NaOH aqueous solution (50%) was added dropwise into the reaction system. After stirring at 50 °C for an additional 5 h, the mixture was cooled down to room temperature and the precipitant was filtered out, then the obtained filtrate was washed thoroughly with water until neutral and dried over  $\text{Na}_2\text{SO}_4$ . A light yellow viscous product was finally obtained after removal of solvent under vacuum and the yield was 11.2 g (86%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 2.72–2.92(12H,  $-\text{CH}_2-$ ), 3.38(6H, epoxy ring), 4.13, 4.69(12H, epoxy ring) and 7.02–7.92 ppm (24H,  $-\text{C}_6\text{H}_4$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 44.70 ( $-\text{CH}_2$  of epoxy ring), 49.42 ( $-\text{CH}$  of epoxy ring), 165.13 ( $-\text{CH}_2$ ) and 120.95–131.56 ppm ( $-\text{C}_6\text{H}_4$ ).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 7.44 ppm.

### 2.3. Preparation of the cured epoxy resins

The synthesized CTP-EP and DGEBA as a control were cured with the curing agents of DDM, DDS and mPDA, respectively. The epoxy resins and curing agents were heated to melt until the mixture became homogeneous in an epoxide/amino equivalent ratio of 1/1. The mixtures were then poured into prepared moulds and cured in a convection oven at 150 °C for 2 h followed by 180 °C for 2 h. Thereafter, all samples were cooled slowly to room temperature in order to avoid cracking.

### 2.4. Characterization

Fourier transform infrared (FTIR) spectra were characterized on potassium bromide discs and Perkin Elmer 400 spectrometer (USA). Nuclear magnetic resonance (NMR) spectra were obtained using 10–25% solutions in deuteriochloroform ( $\text{CDCl}_3$ ) or

deuteron dimethyl sulfoxide ( $\text{DMSO}-d_6$ ) and Bruker ADVANCE III 400 NMR spectrometer (Germany) ( $^1\text{H}$  NMR at 400 Hz,  $^{31}\text{P}$  and  $^{13}\text{C}$  NMR at 100 Hz). Proton and carbon chemical shifts were reported with respect to tetramethylsilane (TMS) as internal reference. Phosphorus chemical shifts were reported with respect to 85% aqueous phosphoric acid solution as external reference.

The LOI values were measured on a JF-3 oxygen index instrument (Jiangning, China) with sheet dimensions of 130 mm  $\times$  6.5 mm  $\times$  3 mm according to ISO 4589-2:1996. The vertical burning ratings were measured on a CZF-2-type instrument (Jiangning, China) with sheet dimensions of 125 mm  $\times$  12.5 mm  $\times$  1.6 mm and 125 mm  $\times$  12.5 mm  $\times$  3 mm according to the American National Standard ANSI/UL 94–2010.

Dynamic mechanical thermal analysis (DMA) was carried out using Perkin–Elmer 7 series thermal analysis system in air at a heating rate of 10 K/min at a frequency of 10 Hz.

TGA was carried out on the TGA Q5000 IR thermogravimetric analyzer. The samples (usually from 4 to 5 mg) were heated from 50 °C to 700 °C under the pure nitrogen atmosphere at a rate of 10 °C  $\text{min}^{-1}$ .

Thermogravimetric analysis/infrared spectrometry (TG/FTIR) of the samples was performed on the TGA Q5000 IR thermogravimetric analyzer interfaced to the Nicolet 6700 FTIR spectrophotometer. FTIR was directly connected to TG and measured the gaseous decomposition products from TG by real time. About 5.0 mg sample was put in an alumina crucible and heated from 50 to 700 °C at a heating rate of 10 °C  $\text{min}^{-1}$  under nitrogen atmosphere with a flow rate of 20 mL  $\text{min}^{-1}$ .

Cone data were acquired with a dual cone calorimeter (manufactured by FTT) at an incident heat flux of 50 kW  $\text{m}^{-2}$  according to ISO 5660-1 standard. All samples were laid on a horizontal holder.

SEM images were observed by using a Quanta 200 scanning electron microscope. The morphological structures of the char residue from CONE tests were obtained. The specimens were previously coated with a conductive layer of gold.

### 3. Results and discussion

#### 3.1. Characterization of CTP-EP

As indicated above, CTP-EP was synthesized and its chemical structure was characterized by FTIR,  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR spectroscopy. The FTIR spectra of HCCP, HAPCP, HCPCP and CTP-EP are shown in Fig. 1. As shown in curve (a) for the original material of HCCP, the strong absorption peak around  $1208\text{ cm}^{-1}$  attributed to  $\text{P}=\text{N}$  stretching and the absorption peaks at  $608$  and  $526\text{ cm}^{-1}$  corresponded to the  $\text{P}-\text{Cl}$  bond can be observed. In the spectra of HAPCP (curve (b)), HCPCP (curve (c)) and CTP-EP (curve (d)), the peaks around  $1208\text{ cm}^{-1}$  for  $\text{P}=\text{N}$  stretching are still existing, the peaks at  $608$  and  $526\text{ cm}^{-1}$  corresponded to  $\text{P}-\text{Cl}$  bond disappear and the strong absorption peaks around  $1600$  and  $1500\text{ cm}^{-1}$  appear attributed to the aromatic ring, moreover, the characteristic absorption peaks at  $2823$  and  $1706\text{ cm}^{-1}$  illustrating the presence of the carbonyl group in the spectra of HAPCP (curve (b)), which demonstrate the  $\text{P}-\text{Cl}$  bonds disappear and the chloride atoms are absolutely substituted by p-aldehyde phenoxy group. In addition, a strong absorption peak at  $3081\text{ cm}^{-1}$  in the spectrum of HCPCP (curve (c)) contributed to the carboxyl stretching ( $-\text{COOH}$ ) appears, which confirms the aldehyde groups are completely oxidized. In the spectrum of CTP-EP (curve (d)), the characteristic absorption peaks appear at  $1270$ ,  $950$  and  $860\text{ cm}^{-1}$  indicate the presence of the epoxy groups.

The characterization results of FTIR and NMR (summarized in Section 2.2) confirm the chemical structure of CTP-EP. Although the compound has been reported [30,31], the synthesis method presented in this paper is different comparing with the report and the flame retardant mechanism of the compound need to be further investigated.

#### 3.2. Flame retardancy of the cured epoxy resins

The flame retardant properties of the cured CTP-EP specimens have been measured by LOI and UL-94 vertical burning test, and the data are summarized in Table 1. The DGEBA is highly combustible and its LOI value is only around 20%. It can be seen that the LOI values of CTP-EP systems dramatically increased from 21.1, 21.7 and 19.9% for DGEBA to 33.5, 34.3 and 31.8% cured with DDM, DDS and mPDA, respectively. Moreover, all samples with the thickness of 1.6 mm of CTP-EP cured with different curing agents can successfully pass UL-94 V-0 rating, while there is no rating for cured DGEBA. The results indicate that the prepared CTP-EP possesses excellent flame retardant properties.

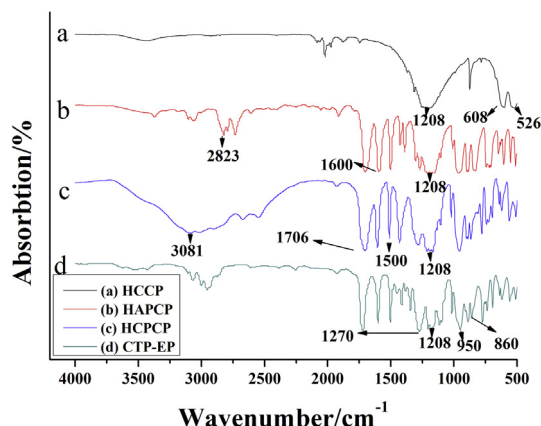


Fig. 1. FTIR spectra of HCCP, HAPCP, HCPCP and CTP-EP.

Table 1

The LOI and UL-94 data of the cured epoxy resins.

Curing system	Phosphorus content (wt%)	LOI/%	UL-94 rating			
			3.0 mm	Dripping	1.6 mm	Dripping
DGEBA/DDM	0	21.1	Burning	NO	Burning	NO
DGEBA/DDS	0	21.7	Burning	NO	Burning	NO
DGEBA/mPDA	0	19.9	Burning	NO	Burning	NO
CTP-EP/DDM	5.8	33.5	V-0	NO	V-0	NO
CTP-EP/DDS	5.6	34.3	V-0	NO	V-0	NO
CTP-EP/mPDA	6.4	31.8	V-0	NO	V-0	NO

#### 3.3. Thermal analysis of the cured epoxy resins

The loss tangent spectrum ( $\tan \delta$ ) of cured samples was determined using a dynamic mechanical thermal analyzer. The main data extracted from these runs is the glass transition temperature ( $T_g$ ) corresponding to the temperature location of the maximum value of  $\tan \delta$ .  $T_g$  is an important parameter for application of epoxy resin thermoset. The  $T_g$ ,  $\tan \delta$  of the cured DGEBA/DDM and CTP-EP/DDM are presented in Fig. 2. The  $T_g$  for the DGEBA/DDM and CTP-EP/DDM composites are  $155^\circ\text{C}$  and  $167^\circ\text{C}$ , respectively. The increased  $T_g$  value of CTP-EP thermoset is due to the incorporation of cyclotriphosphazene structure with six-fold functional groups which are bulky and rigid. These groups confirm the formation of intercross linking network and would increase the rotational barrier of epoxy, consequently enhance the  $T_g$  of the prepared CTP-EP thermoset.

TGA is widely used to evaluate the thermal stability and thermal degradation behavior of polymers. TGA and DTG curves of CTP-EP and DGEBA thermoset cured with DDM under nitrogen atmosphere are shown in Fig. 3, and the detailed data are summarized in Table 2. The initial decomposition temperature can be considered as the temperature at which the weight loss is about 5 wt%. The DGEBA thermoset begins to decompose at  $364^\circ\text{C}$  and the thermal degradation behavior is classified into two steps, as revealed in Table 2 and Fig. 3. The peak of step one at  $386^\circ\text{C}$  is corresponded to the degradation and carbonization of the backbone of the cured DGEBA and the maximum weight loss rate is  $15.3\text{ wt}\% \cdot \text{min}^{-1}$ . The second degradation stage appears at  $397^\circ\text{C}$  attributed to the degradation of the previously formed char layer with the weight loss rate of  $13.9\text{ wt}\% \cdot \text{min}^{-1}$  due to the relatively instability of the char layer at high temperature, which results in the char residue of 14.1 wt% at  $700^\circ\text{C}$ . Compared to the cured DGEBA, the degradation

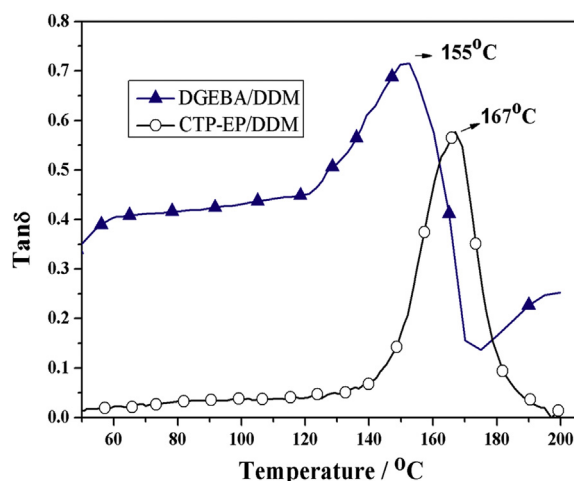


Fig. 2. DMA curves of the CTP-EP/DDM and DGEBA/DDM system.



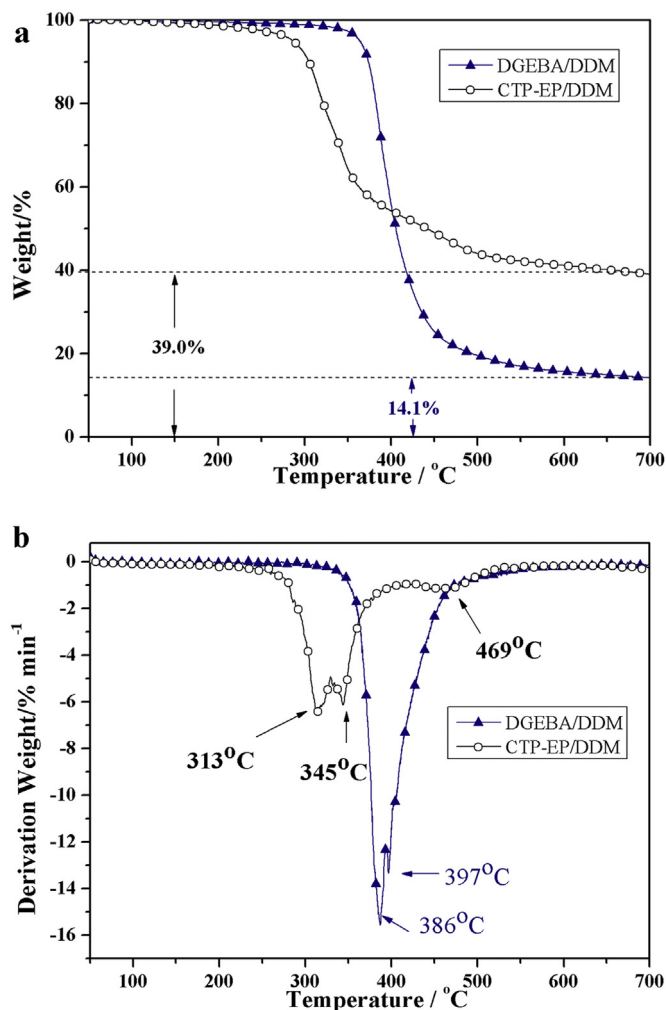


Fig. 3. TGA (a) and DTG (b) curves of the CTP-EP/DDM and DGEBA/DDM system.

of the CTP-EP thermoset occurs early and the initial decomposition temperature decreases from 364 to 290 °C, which is attributed to the instability of the P–O–C and C–O–C bonds of phosphazene-containing epoxy resin when heated. Moreover, the thermal degradation behavior of cured CTP-EP is much different and can be classified into three stages, as revealed in Fig. 3(b). The peak of first stage appears at 313 °C with a maximum weight loss rate of 6.4% min<sup>-1</sup> corresponded to the degradation of the P–O–C and C–O–C bonds of phosphazene-containing epoxy resin due to its instability when heated. The second peak appears at 345 °C and the maximum weight loss rate is 6.1% min<sup>-1</sup>, which could be attributed to the preliminary decomposition and char-forming of phosphazene groups. The third thermal decomposition peak appears at 464 °C is assigned to the further decomposition of the formed char residue, however, the peak is not clear and almost disappears, the decomposition intensity is dramatically decreased from 13.9% min<sup>-1</sup> for cured DGEBA to 1.2% min<sup>-1</sup>, and the char residue of

the cured CTP-EP is significantly increased from 14.1 wt% for DGEBA to 39.0 wt% at 700 °C. The results indicate that phosphazene groups degrade at relative low temperature and form a phosphorous-rich char layer which prevents further decomposition of the underlying matrix, decreases the degradation rates, enhances the thermal stability of the cured CTP-EP at high temperature and results in a higher char residue. Furthermore, the phosphazene groups greatly promote the carbonization of epoxy resins to produce sufficient and compact char layer with high strength and high thermal stability, which helps to prevent heat and O<sub>2</sub> transfer from the flame zone to the underlying materials and restrains the diffusion of the volatile small molecules into the combustion zone. It can deduce that the formed char layer protects CTP-EP thermoset from further decomposition, prolongs the thermal decomposition temperature and enhances its flame retardancy.

TG-IR is usually used to analyze the gas products during the thermal degradation process. In order to gain a deeper understanding of the flame retardant effect, the TG-IR spectra of DGEBA and CTP-EP thermoset were detected and their FTIR spectra of pyrolysis products at different degradation times are shown in Fig. 4. It can be observed that both in the curves of the cured DGEBA and CTP-EP, there are characteristic bands of water (3644 cm<sup>-1</sup>), carbon dioxide (2352 cm<sup>-1</sup>) and compounds containing aromatic ring (1606, 1504 cm<sup>-1</sup>), and the characteristic bands are almost similar between the two samples. Moreover, it is also can be observed that CTP-EP thermoset begins to release gas products at 28 min with the temperature of 330 °C, while the cured DGEBA starts to produce gas products at 33 min with the temperature of 380 °C, which is consistent with the results of the thermogravimetric analysis discussed above. It can be deduced that phosphazene-based epoxy resin of CTP-EP thermoset begins to decompose at early time and low temperature compared with the cured DGEBA.

In order to further explore the degradation behavior and flame retardant mechanism of DGEBA and CTP-EP system, the cured DGEBA, CTP-EP thermoset and their residues after TGA testing at 450 °C were measured by FTIR, and the spectra are presented in Fig. 5. For the cured DGEBA, peaks at 3400, 1603, 1510, 1363 and 1240 cm<sup>-1</sup> are corresponded to the characteristic absorptions of DGEBA, as revealed in curve (a). The spectra curve of the decomposition residue for DGEBA thermoset (curve (b)) approaches to a straight line which means most of cured DGEBA has decomposed. Meanwhile, the peaks of cured CTP-EP appear at 750, 899, 1438 and 1601 cm<sup>-1</sup>, which are the characteristic absorptions of the aromatic rings, and the peaks at 1222 cm<sup>-1</sup> corresponded to the phosphazene group, as shown in curve (c). However, for the residue of the cured CTP-EP, the absorption peaks at 1220 cm<sup>-1</sup> which can give direct evidence of P=N bonds for the phosphazene structure and the peaks at 1438 and 1601 cm<sup>-1</sup> assigned to aromatic rings still remain after degradation, as revealed in curve (d). The results demonstrate that the most of DGEBA thermoset decomposed, on the contrary, the most of the CTP-EP structures of the cured CTP-EP still remained at high temperature.

#### 3.4. Cone calorimetry of the cured epoxy resins

The cone calorimeter (cone) has been widely used to evaluate the combustion performance of polymeric materials based on the oxygen consumption principle, and the results have good correlation with real fire disaster. The parameters including time to ignition (TTI), the heat release rate (HRR), the peak heat release rate (PHRR), the total heat release (THR), time of peak heat release rate (*t*<sub>PHRR</sub>), smoke production rate (SPR), total smoke production (TSP), CO production (COP), CO<sub>2</sub> production (CO<sub>2</sub>P) and effective heat combustion (EHC) are determined and used to predict the

Table 2  
TGA and DTG data of the cured epoxy resins.

Samples	T-5 wt%/°C	R <sub>1peak</sub> /T <sub>1peak</sub> (%·min <sup>-1</sup> /°C)	R <sub>2peak</sub> /T <sub>2peak</sub> (%·min <sup>-1</sup> /°C)	R <sub>3peak</sub> /T <sub>3peak</sub> (%·min <sup>-1</sup> /°C)	Char residues (wt%) 700 °C
DGEBA/DDM	364	15.3/386	13.9/397	—	14.1
CTP-EP/DDM	290	6.4/315	6.1/345	1.2/464	39.0

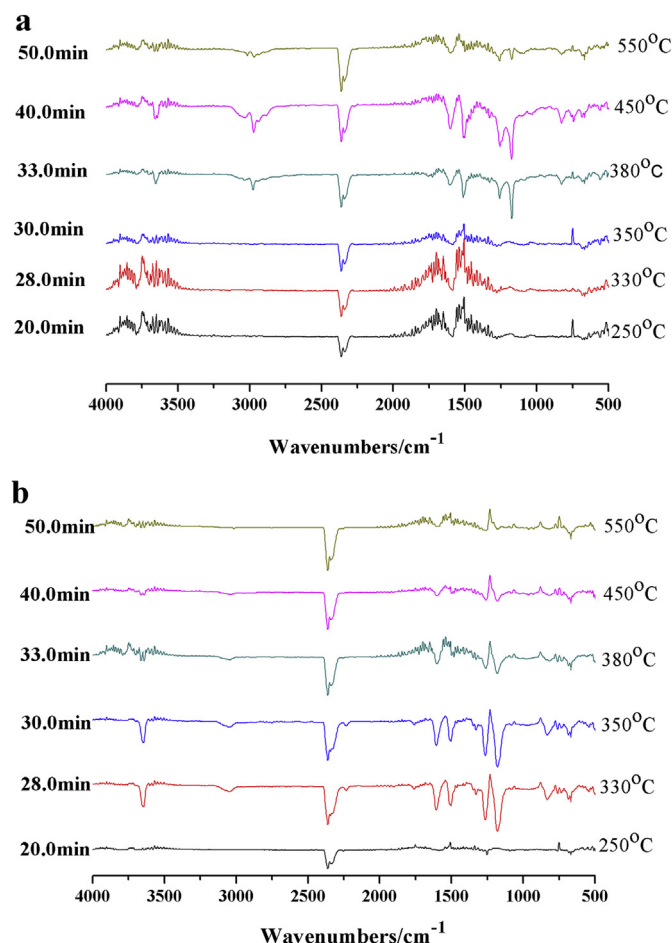


Fig. 4. TG-IR spectra of pyrolysis products for cured DGEBA (a) and CTP-EP (b) at different decomposition times.

combustion behavior of materials in real fires. Figs. 6 and 7 and Table 3 present the plots and the detailed information of combustion behavior of for cured DGEBA and CTP-EP/DDM systems obtained from the cone calorimeter test at a heat flux of  $50 \text{ kW m}^{-2}$ .

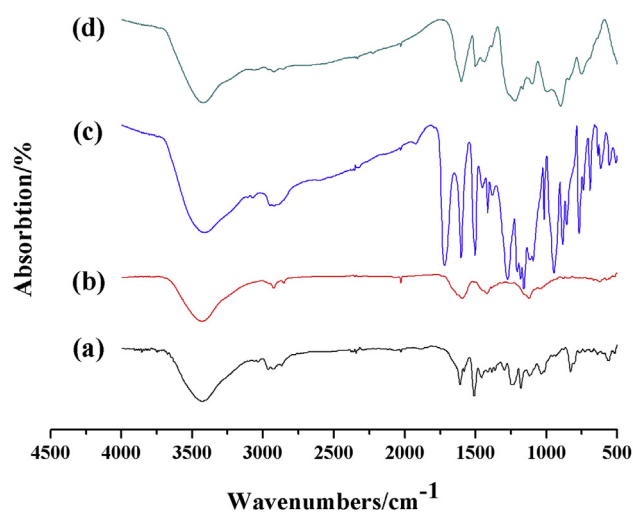


Fig. 5. The FTIR spectra of cured epoxy resins and their pyrolysis residues at  $450^\circ\text{C}$ : (a) DGEBA/DDM thermoset; (b) the residue of DGEBA/DDM thermoset; (c) CTP-EP/DDM thermoset; (d) the residue of CTP-EP/DDM thermoset.

The HRR is recognized to be the most important parameter to quantify the size of fire, and an effective flame retardant system normally shows a lower HRR value. Fig. 6 gives the HRR and THR curves of DGEBA and CTP-EP thermoset and the results reveal that the cured DGEBA burns rapidly after ignition and only one sharp HRR peak appears with a peak value of  $732 \text{ kW m}^{-2}$  at 185 s, the total combusting time is 486 s. In contrast, the curve of the cured CTP-EP shows much lower peaks and prolonged combusting time from 486 to 947 s. There are two peaks in the HRR curve of CTP-EP, the first peak appears at 50 s with the peak value of  $187 \text{ kW m}^{-2}$  corresponded to the fast surface combustion of CTP-EP thermoset and the char layer formation at the initial stage of heating. At 322 s after ignition, the second peak attributed to the further decomposition of the previously formed char layer appears. However, the second peak is not obvious and the peak value dramatically decreases from  $732 \text{ kW m}^{-2}$  of DGEBA to  $132 \text{ kW m}^{-2}$ . Similar to the HRR curves, the THR curve of CTP-EP thermoset is much lower than that of cured DGEBA, and the THR value greatly decreases from 103 to  $63 \text{ MJ m}^{-2}$ . The results may be contributed to the decomposition of the phosphazene groups incorporated into the CTP-EP thermoset at relative low temperature promotes the formation of the phosphorus-rich char shield with high strength and thermal stability, which prevent the char layer from cracking, resists the heat and oxygen transferring into the interior matrix and flammable volatiles into flame zone, and results in suppressing the further degradation of CTP-EP thermoset. The decomposition behavior is in agreement with the TGA results discussed above.

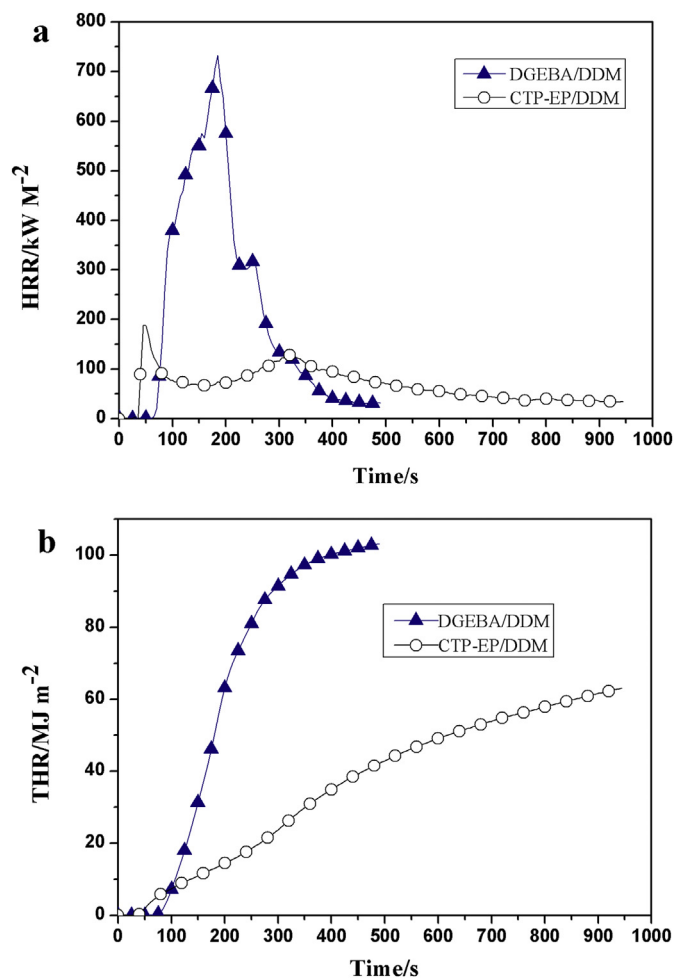


Fig. 6. HRR (a) and THR (b) curves of DGEBA/DDM and CTP-EP/DDM composites.

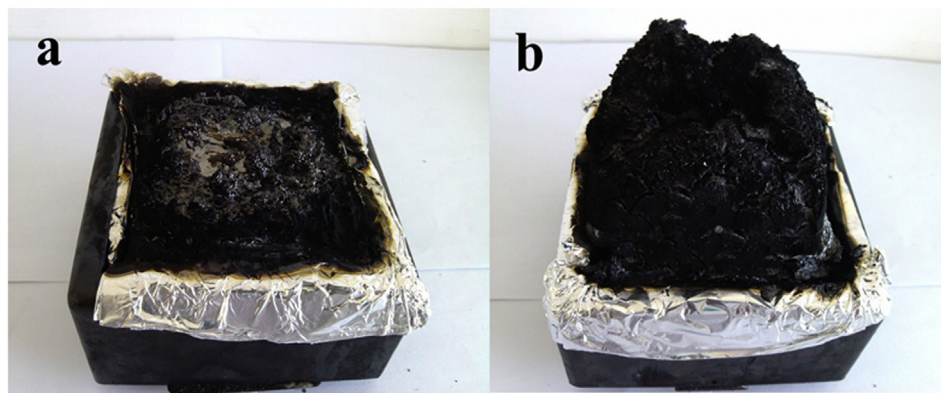


Fig. 7. Digital photographs of the char residues after cone tests: (a) DGEBA/DDM; (b) CTP-EP/DDM.

The emission of smoke and toxic gas is considered as another important parameter for the flame retarded materials. The SPR peak of cured DGEBA appears with the value of  $0.31 \text{ m}^2 \text{ s}^{-1}$ . The SPR curve of CTP-EP thermoset presents two peaks and its values are far lower than that of DGEBA, which is similar to the HRR curves. The first peak appears at early stage and the second peak is not clear with an extremely lower SPR value. Moreover, the TSP value also significantly decreases from  $47.59 \text{ m}^2 \text{ kg}^{-1}$  for cured DGEBA to  $18.57 \text{ m}^2 \text{ kg}^{-1}$ . The COP and  $\text{CO}_2\text{P}$  curves are also similar to the HRR curves, and the values of the cured CTP-EP are much lower than that of cured DGEBA. The reason is that the incorporation of phosphazene group into the CTP-EP makes the thermoset decompose at initial stage of combustions and stimulates the formation of the phosphorus-rich and compact char as a protective layer on the thermoset surface, which prevent the transfer of heat and restrict the production of combustible gases, thus suppress the intensity of combustion pyrolysis reactions and decrease the release of the quantity of smoke to interfere the combustion of the thermoset.

The EHC is heat released from combustion of the volatile portion of the material. The lower EHC value indicated that noncombustible gas exist in gas phase. As revealed in Table 3, the averaged value of EHC (av-EHC) for cured CTP-EP/DDM system decreases from  $22.73 \text{ MJ kg}^{-1}$  for cured DGEBA/DDM system to  $16.65 \text{ MJ kg}^{-1}$ . The reason is that the CTP-EP thermoset containing phosphazene group released noncombustible gases, such as volatile phosphide,  $\text{N}_2$ ,  $\text{NH}_3$  and  $\text{CO}_2$  during the combustion process [24,27,42], which could dilute flammable gases and reduce the oxygen concentration around the material. Although the chemical mechanism of action, such as scavenging free radicals in the flame, can not be characterized precisely in this paper, the nonflammable gases could play a role in the gas phase.

Table 3  
Cone results of the cured epoxy resins.

Sample	DGEBA/DDM	CTP-EP/DDM
TTI (s)	63	30
Peak1HRR ( $\text{kW m}^{-2}$ )	732	187
$t_{\text{Peak1-HRR}}$ (s)	185	50
Peak2HRR ( $\text{kW m}^{-2}$ )	—	132
$t_{\text{Peak2-HRR}}$ (s)	—	322
THR ( $\text{MJ m}^{-2}$ )	103	63
Peak1SPR ( $\text{m}^2 \text{ s}^{-1}$ )	0.31	0.16
Peak2SPR ( $\text{m}^2 \text{ s}^{-1}$ )	—	0.05
TSP ( $\text{m}^2 \text{ kg}^{-1}$ )	47.59	18.57
Peak1COP ( $\text{g s}^{-1}$ )	0.017	0.013
Peak2COP ( $\text{g s}^{-1}$ )	—	0.006
Peak1 $\text{CO}_2\text{P}$ ( $\text{g s}^{-12}$ )	0.40	0.10
Peak2 $\text{CO}_2\text{P}$ ( $\text{g s}^{-1}$ )	—	0.09
av-EHC ( $\text{MJ kg}^{-1}$ )	22.73	16.65

### 3.5. Morphology of the residue

In order to further investigate the relationship between the morphology of the char layers and flame retardant properties of the cured CTP-EP, the char residues of cured DGEBA and CTP-EP after cone tests were measured by digital camera and SEM magnified by 3000 times, as shown in Figs. 7 and 8, respectively. There is no efficient intumescent char formed because DGEBA almost decomposes completely, while CTP-EP can form good and coherent intumescent char, as revealed in Fig. 7. Moreover, it can see that the surface morphology of the char layer for cured DGEBA presents a relatively loose structure including some small crevasses and holes on the surface due to insufficient char formation during combustion, therefore, heat and flammable volatiles could penetrate the char layer into the flame zone. On the contrary, the char layer for cured CTP-EP appears more homogenous and compact than that of cured DGEBA, as revealed in Fig. 8. The results suggest that the introduction of phosphazene group promote to produce the crosslink network on the char layer surface, result in a more compact char layer and consequently the char layer possesses higher thermal stability, which may effectively stops the transfer of heat and flammable volatiles leading to excellent flame retardancy.

Based on the above discussions, it can be deduced that the incorporation of phosphazene group stimulate the cured thermoset decompose at earlier degradation process which promote to release noncombustible gases and form sufficient and compact char layer with high thermal stability. At the same time, the large amounts of aromatic content in CTP-EP molecular will turn into thick rings as part of char. The char layer acting in condensed phase can suppress the production of combustible carbon-containing volatiles and reduce the exothermicity caused by the pyrolysis reactions and the thermal conductivity of the surface burning material. Meanwhile, the released noncombustible gases can dilute flammable gases and reduce the oxygen concentration around the material, thus play an important role in gas phase. As a result, the CTP-EP thermoset obtain excellent flame retardant efficiency.

## 4. Conclusions

The phosphazene-based flame retardant epoxy resin hexa-[4-(glycidylloxycarbonyl)phenoxy]cyclotriphosphazene (CTP-EP) has been successfully synthesized and confirmed. The cured CTP-EP successfully passed UL-94 V-0 rating with the LOI value of above 30%, exhibiting excellent flame retardant performance. The CTP-EP thermoset possessed high glass transition temperature of  $167^\circ\text{C}$  compared with the cured DGEBA and decomposed at earlier



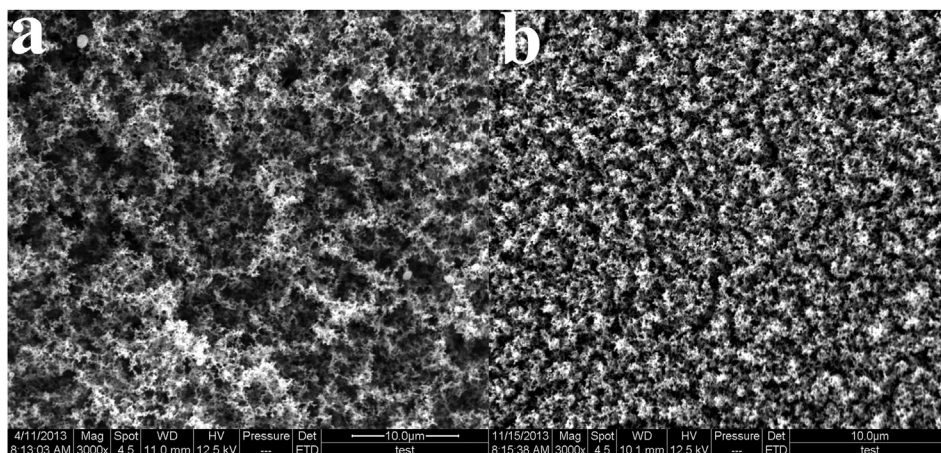


Fig. 8. SEM images of the char residues after cone tests: (a) DGEBA/DDM; (b) CTP-EP/DDM.

degradation process of heating, which promoted the release of noncombustible gases and the formation of the sealing, thermal stable and phosphorus-rich char layer, dramatically increased the char residue and thermal stability of the CTP-EP thermoset at high temperature due to the incorporation of phosphazene group. The formed char layer and the released noncombustible gases prevented underlying materials from further combustion during combustion and enhanced the fire retardant performance, consequently resulting in a great reduction of HRR, THR, SPR, TSP and EHC of the cured CTP-EP. As a result, the phosphazene group in the CTP-EP led to excellent flame retardant efficiency and thermal stability at high temperature.

## Acknowledgments

The authors acknowledge the support by National Nature Science Foundation of China (Grant NO. 21174025), Heilongjiang Major Research Projects (GA12A102), China Postdoctoral Science Foundation (2012 M510907 and 2013 T60339), Heilongjiang Postdoctoral grant (LBH-Z11252) and Youth Science Fund of Heilongjiang Province (QC2011C102).

## References

- [1] Wang X, Hu Y, Song L, Xing W, Lu H. Thermal degradation mechanism of flame retarded epoxy resins with a DOPO-substituted organophosphorus oligomer by TG-FTIR and DP-MS. *J Anal Appl Pyrol* 2011;92(1):164–70.
- [2] Wan J, Li C, Bu ZY, Xu CJ, Li BG, Fan H. A comparative study of epoxy resin cured with a linear diamine and a branched polyamine. *Chem Eng J* 2012;188:160–72.
- [3] Nakamura Y, Yamaguchi M, Okubo M, Matsumoto T. Effects of particle size on mechanical and impact properties of epoxy resin filled with spherical silica. *J App Polym Sci* 1992;45(7):1281–9.
- [4] Kandola BK, Biswas B, Price D, Horrocks AR. Studies on the effect of different levels of toughener and flame retardants on thermal stability of epoxy resin. *Polym Degrad Stab* 2010;95(2):144–52.
- [5] Leu TS. Structure and characterization for continuously linked polymer of short-chain epoxy resin with triallyl isocyanurate and bismaleimide. *J App Polym Sci* 2006;102(3):2470–80.
- [6] Luda MP, Balabanovich AI, Zanetti M. Pyrolysis of fire retardant anhydride-cured epoxy resins. *J Anal Appl Pyrol* 2010;88(1):39–52.
- [7] Uddin MA, Bhaskar T, Kusaba T, Hamano K, Muto A, Sakata Y. Dehalogenation of flame retardant high impact polystyrene (HIPS-Br) by hydrothermal treatment and recovery of bromine free plastics. *Green Chem* 2003;5(2):260–3.
- [8] Lu SY, Hamerton I. Recent developments in the chemistry of halogen-free flame retardant polymers. *Prog Polym Sci* 2002;27(8):1661–712.
- [9] Wang X, Song L, Xing W, Lu H, Hu Y. A effective flame retardant for epoxy resins based on poly(DOPO substituted dihydroxyl phenyl pentaerythritol diphosphonate). *Mater Chem Phys* 2011;125(3):536–41.
- [10] Sun S, He Y, Wang X, Wu D. Flammability characteristics and performance of halogen-free flame-retarded polyoxymethylene based on phosphorus-nitrogen synergistic effects. *J App Polym Sci* 2010;118(1):611–22.
- [11] Gao F, Tong L, Fang Z. Effect of a novel phosphorous-nitrogen containing intumescent flame retardant on the fire retardancy and the thermal behaviour of poly(butylene terephthalate). *Polym Degrad Stab* 2006;91(6):1295–9.
- [12] Gao M, Yang S. A novel intumescent flame-retardant epoxy resins system. *J App Polym Sci* 2010;115(4):2346–51.
- [13] Levchik SV, Weil ED. Thermal decomposition, combustion and flame-retardancy of epoxy resins—a review of the recent literature. *Polym Int* 2004;53(12):1901–29.
- [14] Wu K, Song L, Hu Y, Lu H, Kandola BK, Kandare E. Synthesis and characterization of a functional polyhedral oligomeric silsesquioxane and its flame retardancy in epoxy resin. *Prog Org Coat* 2009;65(4):490–7.
- [15] Liu YL, Hsiue GH, Lee RH, Chiu YS. Phosphorus-containing epoxy for flame retardant. III: using phosphorylated diamines as curing agents. *J App Polym Sci* 1997;63(7):895–901.
- [16] Gao LP, Wang DY, Wang YZ, Wang JS, Yang B. A flame-retardant epoxy resin based on a reactive phosphorus-containing monomer of DODPP and its thermal and flame-retardant properties. *Polym Degrad Stab* 2008;93(7):1308–15.
- [17] Ren H, Sun J, Wu B, Zhou Q. Synthesis and properties of a phosphorus-containing flame retardant epoxy resin based on bis-phenoxy (3-hydroxy) phenyl phosphine oxide. *Polym Degrad Stab* 2007;92(6):956–61.
- [18] Toldy A, Anna P, Csontos I, Szabó A, Marosi Gy. Intrinsically flame retardant epoxy resin—Fire performance and background—Part I. *Polym Degrad Stab* 2007;92(12):2223–30.
- [19] Toldy A, Szolnoki B, Csontos I, Marosi G. Green chemistry approach for synthesizing phosphorus flame retardant crosslinking agents for epoxy resins. *J App Polym Sci* 2014;131:40105.
- [20] Wang CS, Shieh JY. Synthesis and properties of epoxy resins containing bis(3-hydroxyphenyl) phenyl phosphite. *Eur Polym J* 2000;36(3):443–52.
- [21] Liu H, Xu K, Ai H, Zhang L, Chen M. Preparation and characterization of phosphorus-containing Mannich-type bases as curing agents for epoxy resin. *Polym Advan Technol* 2009;20(9):753–8.
- [22] Diefenbach U, Allcock HR. Synthesis of cyclo- and polyphosphazenes with pyridine side groups. *Inorg Chem* 1994;33(20):4562–5.
- [23] Zhu L, Zhu Y, Pan Y, Huang Y, Huang X, Tang X. Fully crosslinked poly[cyclotriphosphazene-co-(4, 4'-sulfonyldiphenol)] microspheres via precipitation polymerization and their superior thermal properties. *Macromol React Eng* 2007;1(1):45–52.
- [24] Liu R, Wang X. Synthesis, characterization, thermal properties and flame retardancy of a novel nonflammable phosphazene-based epoxy resin. *Polym Degrad Stab* 2009;94(4):617–24.
- [25] Chen-Yang YW, Yuan CY, Li CH, Yang HC. Preparation and characterization of novel flame retardant (aliphatic phosphate) cyclotriphosphazene-containing polyurethanes. *J App Polym Sci* 2003;90(5):1357–64.
- [26] Allcock HR, Austin PE. Schiff base coupling of cyclic and high-polymeric phosphazenes to aldehydes and amines: chemotherapeutic models. *Macromolecules* 1981;14(6):1616–22.
- [27] El Gouri M, El Bachiri A, Hegazi SE, Rafik M, El Harfi A. Thermal degradation of a reactive flame retardant based on cyclotriphosphazene and its blend with DGEBA epoxy resin. *Polym Degrad Stab* 2009;94(11):2101–6.
- [28] El Gouri M, El Bachiri A, Hegazi SE, Rafik M, El Harfi A. A phosphazene compound multipurpose application-Composite material precursor and reactive flame retardant for epoxy resin materials. *J Mater Environ Sci* 2011;2(4):319–34.
- [29] Bai Y, Wang XD, Wu D. Novel cycloliner cyclotriphosphazene-linked epoxy resin for halogen-free fire resistance: synthesis, characterization, and flammability characteristics. *Ind Eng Chem Res* 2012;51(46):15064–74.



- [30] You GY, Cai Z, Peng H, Tan XS, He HW. A well-defined cyclotriphosphazene-based epoxy monomer and its application as a novel epoxy resin: synthesis, curing behaviors, and flame retardancy. *Phosphorus Sulfur Silicon Relat Elem* 2014;189(4):541–50.
- [31] You GY, He HW, Huang Y, Cai Z. Phosphonitrilic chloride trimer epoxy compound with flame-retardant property and preparation and application thereof. CN 102503982A; 2012-6–20.
- [32] Ding J, Shi W. Thermal degradation and flame retardancy of hexaacrylated/hexaethoxyl cyclophosphazene and their blends with epoxy acrylate. *Polym Degrad Stab* 2004;84(1):159–65.
- [33] Kumar D, Fohlen GM, Parker JA. Fire-and heat-resistant laminating resins based on maleimido-substituted aromatic cyclotriphosphazenes. *Macromolecules* 1983;16(8):1250–7.
- [34] Orme CJ, Klaehn JR, Harrup MK, Lash RP, Stewart FF. Characterization of 2-(2-methoxyethoxy) ethanol-substituted phosphazene polymers using pervaporation, solubility parameters, and sorption studies. *J App Polym Sci* 2005;97(3):939–45.
- [35] Kumar D, Khullar M, Gupta AD. Synthesis and characterization of novel cyclotriphosphazene-containing poly (etherimide)s. *Polymer* 1993;34(14):3025–9.
- [36] Bing BC, Li B. Synthesis, thermal property and hydrolytic degradation of star-shaped hexa[p-(carbonyl glycinomethyl ester) phenoxy] cyclotriphosphazene. *Sci China Ser B* 2009;52(12):2186–94.
- [37] Yuan WZ, Tang XZ, Huang XB, Zheng SX. Synthesis, characterization and thermal properties of hexaarmed star-shaped poly( $\epsilon$ -caprolactone)-b-poly(D,L-lactide-co-glycolide) initiated with hydroxyl-terminated cyclotriphosphazene. *Polymer* 2005;46(5):1701–7.
- [38] Allen CW. Regio- and stereochemical control in substitution reactions of cyclophosphazenes. *Chem Rev* 1991;91(2):119–35.
- [39] Chang JY, Rhee SB, Cheong S, Yoon M. Synthesis and thermal reaction of acetylenic group substituted poly (organophosphazenes) and cyclotriphosphazene. *Macromolecules* 1992;25(10):2666–70.
- [40] Chen S, Zheng Q, Ye G, Zheng G. Fire-retardant properties of the viscose rayon containing alkoxycyclotriphosphazene. *J App Polym Sci* 2006;102(1):698–702.
- [41] Yuan CY, Chen SY, Tsai CH, Chiu YS, Chen-Yang YW. Thermally stable and flame-retardant aromatic phosphate and cyclotriphosphazene-containing polyurethanes: synthesis and properties. *Polym Advan Technol* 2005;16(5):393–9.
- [42] Qian LJ, Ye L, Qiu Y, Qu S. Thermal degradation behavior of the compound containing phosphaphenanthrene and phosphazene groups and its flame retardant mechanism on epoxy resin. *Polymer* 2011;52(24):5486–93.
- [43] Conner DA, Welna DT, Chang Y, Allcock HR. Influence of terminal phenyl groups on the side chains of phosphazene polymers: structure-property relationships and polymer electrolyte behavior. *Macromolecules* 2007;40(2):322–8.