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Synthesis of a novel flame retardant based on cyclotriphosphazene and DOPO groups and its application in epoxy resins

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ABSTRACT

A novel flame retardant additive with phosphazene and phosphaphenanthrene groups hexa-[4-(*p*-hydroxyanilino-phosphaphenanthrene-methyl)-phenoxyl]-cyclotriphosphazene defined as CTP-DOPO was successfully synthesized from hexachlorocyclotriphosphazene, *p*-hydroxybenzaldehyde, 4-aminophenol and 9,10-dihydro-9-oxa-10-phosphaphenanthrene 10-oxide (DOPO). Its chemical structure was well characterized by Fourier transform infrared (FTIR) spectroscopy, ^{1}H nuclear magnetic resonance (^{1}H NMR) and ^{31}P nuclear magnetic resonance (^{31}P NMR). The prepared flame retardant additive CTP-DOPO was incorporated into diglycidyl ether of bisphenol-A (DGEBA) to prepare flame retardant epoxy resins thermosets. The flame retardant properties, thermal degradation behavior and combustion behavior of the DGEBA thermosets cured by 4, 4′ -Diamino-diphenyl sulfone (DDS) were investigated by limiting oxygen index (LOI), vertical burning test (UL-94), thermogravimetric analysis/infrared spectrometry (TG-IR) and cone calorimeter tests. The structure and surface morphology of the char residues after cone calorimeter tests was measured by FTIR and scanning electron microscopy (SEM). The results revealed that DGEBA/CTP-DOPO thermosets successfully passed UL-94 V-0 flammability rating and its LOI value dramatically increased from 21.7% for cured pure DGEBA to 36.6% when the loading amount of CTP-DOPO was 10.6 wt % and the phosphorus content was only 1.1 wt % in thermosets, which indicated that the prepared CTP-DOPO possessed excellent flame retardancy for DGEBA thermoset. The TG-IR results indicated that the introduction of CTP-DOPO stimulated epoxy resins matrix decomposed and char forming ahead of time, which led to a higher residual char and thermal stability for epoxy resins thermosets at high temperature. The cone calorimeter tests revealed that the incorporation of CTP-DOPO effectively reduced the combustion parameters of DGEBA thermosets, such as heat release rate (HRR), total heat release (THR), smoke production rate (SPR) and total heat production (TSP), and so on. The SEM results showed that the phosphazene and phosphaphenanthrene groups in CTP-DOPO obviously stimulated the formation of the intumescent, compact and strong char layer, which enhanced the flame retardany of the DGEBA matrix during combustion. Therefore, the underlying materials were protected from further degradation and combustion and resulted in the efficient flame retardancy for EDGEBA thermoset.

1. Introduction

Epoxy resins are important thermosetting materials in modern industry and have been widely used as advanced composite matrices in various areas for its outstanding properties of good mechanical properties, chemical resistance, high intensity, excellent electric insulating property and low manufacturing cost [1,2]. However, the flammability of epoxy resins lead to fire disaster inevitably, which severely limits their functional applications. Therefore, the epoxy resins are subjected to various mandatory controls for safety reasons [3].

Traditionally, bromine containing reactive compounds are used as co-monomers for epoxy resins to obtain fire-retardant materials. However, the flame retardant epoxy resins materials containing bromine may release super-toxic halogenated dibenzodioxins and dibenzofurans with deleterious effects on the environment and human health [4]. Recently, in consideration of environmental

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problems, researches for halogen-free fire retardant epoxy resins have attracted a great deal of attention. Organo-phosphorus molecules are efficient radical scavengers and flame quenching materials, and combustion processes are essentially exothermic free radical reactions, so the existence of radical stabilizers impedes combustion by the quenching mechanism [5]. 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 [6,7]. 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 the other phosphorylated and phosphonylated derivatives [8–10]. However, these phosphorus-containing epoxy resins have some disadvantages, such as low weight fraction of phosphorus, which resulting in a low degree of flame retardancy [11,12]. 9, 10-dihydro-9-oxa-10- phosphaphenanthrene-10-oxide (DOPO) and its derivatives have been widely used for their high reactivity, applicability and flame retardancy on epoxy resins [13–17]. But the mechanical properties of the flame retardant epoxy resins prepared by above methods is obviously decreased and the flame retardant epoxy resins based on DOPO reach UL-94 V-0 flammability rating still need a higher adding ratio of DOPO or its derivatives for their low phosphorus content [18,19].

Currently, 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 provide improved thermal and flame retardant properties to polymers and their composites [20–22]. Hexachlorocyclotriphosphazene is a versatile starting oligomer for the synthesis of phosphazene-based polymers as 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 [23–25]. When cyclotriphosphazenes are incorporated into the network of thermoset polymers, they exhibit unusual properties such as flame retardancy and self-extinguishability 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 focus [26–30]. So we attempt to construct a novel molecule with multifunctional groups of amino, phenolic hydroxyl, phosphazene and DOPO groups for preparing the DGEBA thermosets with excellent comprehensive properties as well as the efficient flame retardancy.

In this work, the compound with phosphazene and DOPO groups hexa-[4-(*p*-hydroxyanilino-phosphaphenanthrene-methyl)-phenoxyl]-cyclotriphosphazene defined as CTP-DOPO was successfully synthesized and used as flame retardant additive for epoxy resins. Its chemical structure was well characterized by FTIR, ^{1}H NMR and ^{31}P NMR. The obtained flame retardant CTP-DOPO was blended with DGEBA and then cured with 4, 4′ -Diamino-diphenyl sulfone (DDS) to prepare the flame retardant DGEBA thermosets. The flame retardancy, thermal decomposition and combustion behaviors for the prepared DGEBA thermosets were characterized and disclosed.

2. Experimental

2.1. Materials

Hexachlorocyclotriphosphazene (HCCP), 4-hydroxybenzaldehyde and 4-aminophenol and 9,10-Dihydro-9-oxa-10-phosphaphenanthrene 10-oxide (DOPO) were purchased from Wuhan Yuancheng Chemical Co. Ltd., China. Tetrahydrofuran (THF), alcohol, 1,4-dioxane, triethylamine (TEA) and ethyl acetates (EA) were purchased from Tianjin Kemiou Chemical Reagent Co. Ltd., China. Diamino diphenyl sulfone (DDS) and 4-aminophenol 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-DOPO

The hexa-[4-(*p*-hydroxyanilino-phosphaphenanthrene-methyl)-phenoxyl]-cyclotriphosphazene defined as CTP-DOPO was synthesized according to the following steps and the synthetic routes are shown in Scheme 1. Firstly, according to the previously reported works of our laboratory [31], in a 200 mL four necked flask equipped with a mechanical stirrer, a reflux condenser and a nitrogen inlet, 14 g (0.04 mol) hexachlorocyclotriphosphazene (HCCP), 35 g (0.28 mol) 4-hydroxybenzaldehyde and 50 mL dry THF was added at room temperature. The reaction mixture was heated to reflux temperature with stirring and maintained for 24 h at that temperature under nitrogen atmosphere. 28 g (0.28 mol) TEA used as deacid reagent was added dropwise into the mixture. After reaction, the mixture was concentrated by rotary evaporator to remove part of the solvent and then poured into a large amount of water to precipitate the crude product. The compound HAPCP was recrystallized and purified by ethyl acetates and 31.6 g HAPCP was obtained with the yield of 92%.

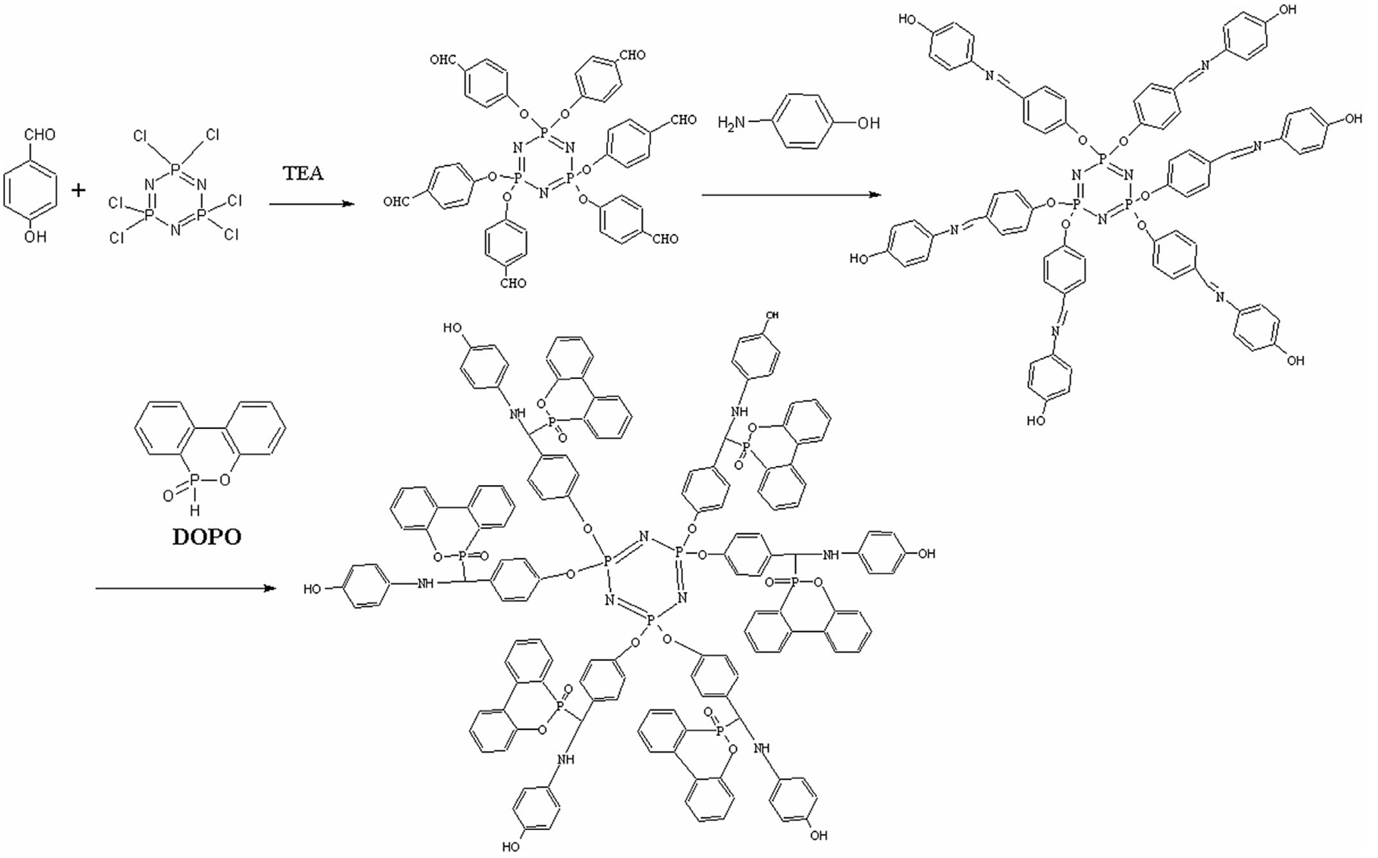
The obtained intermediate product HAPCP (17.2 g, 0.02 mol) and 100 mL 1,4-dioxane was added in a four-necked-flask equipped with a mechanical stirrer, a reflux condenser and a nitrogen inlet. After the HAPCP was completely dissolved in 1,4-dioxane with stirring, 4-aminophenol (15 g, 0.14 mol) was added in the reaction mixture and then the mixture was heated to reflux temperature and maintained for 12 h. After that, DOPO (30 g, 0.14 mol) was added into the reaction system and reacted for another 12 h at refluxed temperature. After reaction, most of the solvent was removed by rotary evaporator and the concentrated reaction mixture was poured into the cold alcohol, a great deal of precipitates appeared in alcohol solution. Finally, the light yellow solids was obtained by filtrated and respectively washed three times with hot water and cold alcohol, and then dried at 105 °C in a drying oven to constant weight. Finally, 52.4 g light yellow product was obtained with the yield of 97%.

2.3. Preparation of the cured epoxy resins

In order to prepare the flame retardant epoxy resins thermosets with various content of CTP-DOPO, the flame retardant additive, epoxy resins and the curing agent of DDS were mixed homogeneously in an epoxide/N–H equivalent ration of 1/1 by mechanical stirrer at 120 °C. The prepared CTP-DOPO containing secondary amines can not be acted as a hardener for epoxy resins due to the large steric hindrance existed in the surrounding of N–H bonds. Then the liquid mixture was poured into the 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, and then carried out the performance testing.

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



Scheme 1. Schematic procedures of the synthesis for CTP-DOPO.

using 10–25% solutions in deuteron dimethyl sulfoxide (DMSO-d_6) and Bruker ADVANCE III 400 NMR spectrometer (Germany) (^1H NMR at 400 Hz and ^{31}P NMR at 100 Hz). Proton 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 limiting oxygen index (LOI) values were measured at room temperature by a JF-3 oxygen index meter (Jiangning Analysis Instrument Company, China) according to ISO 4589-2: 2006 standard with specimen dimension of 130 × 6.5 × 3 mm^3. Vertical burning (UL-94) tests were performed on a CZF-2-type instrument (Jiangning Analysis Instrument Company, China) according to ANSI/UL 94-2013 test standard with specimen dimension of 130 × 13 × 3.2 mm^3. UL-94 testing results were carried out for burning ratings V-0, V-1, or V-2. V-0 rating corresponds to the best flame retardancy of polymeric materials.

Thermogravimetric analysis/infrared spectrometry (TG-IR) 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. The weight of the samples was kept within 4–5 mg and the sample was put in an alumina crucible and heated from 50 to 700 °C at a heating rate of 10 °C min^{-1} under nitrogen atmosphere with a flow rate of 20 ml min^{-1}.

The combustion behavior under ventilated conditions was measured using a Fire Testing Technology cone calorimeter (West Sussex, UK), in conformance with ISO 5660-1 standard. Samples with size of 100 × 100 × 3 mm^3 were exposed to cone at a heat flux of 50 kW m^{-2} and three specimens were tested for every sample.

SEM was used to examine the morphology of the char residue obtained from cone calorimeter tests using a FEI QuanTa-200 (Eindhoven, Netherlands) SEM. The accelerating voltage was set to 15 kV. The surface of char residues was sputter-coated with gold layer before examination.

3. Results and discussion

3.1. Characterization of CTP-DOPO

The chemical structure of the synthesized CTP-DOPO is characterized by FTIR, ^1H and ^{31}P NMR, respectively. The FTIR spectrum of CTP-DOPO is shown in Fig. 1. The strong absorption peak around 1200 cm^{-1} is attributed to P=N stretching vibration of the phosphazene groups. The absorption peak at 3300 cm^{-1} is assigned to the presence of the N–H bonds and the strong absorption peak at 1044 cm^{-1} is contributed to the P–O–C bonds. The characteristic absorption peaks at 1476 and 1595 cm^{-1} is corresponded to the P-Ph of the DOPO groups, which indicate the DOPO groups are successfully incorporated into the product.

The ^1H NMR spectrum of the synthesized CTP-DOPO is presented in Fig. 2 and the assignment of each peak is also marked. The peaks at 8.44 and 8.42 ppm are attributed to hydroxy protons (H^a and $H^{a'}$). The peaks between 6.86 and 8.11 ppm are corresponded to the protons of DOPO groups. The peaks at 6.33–6.49 ppm are assigned to the protons of aromatic rings. The two peaks at 5.52and 5.98 ppm are contributed to secondary amines (NH and NH′) and the two peaks at 5.63 and 6.02 ppm are assigned to the aliphatic hydrogen (H5 and H5′). It is can be deduced that there are two diastereomers in the synthesized CTP-DOPO compound.

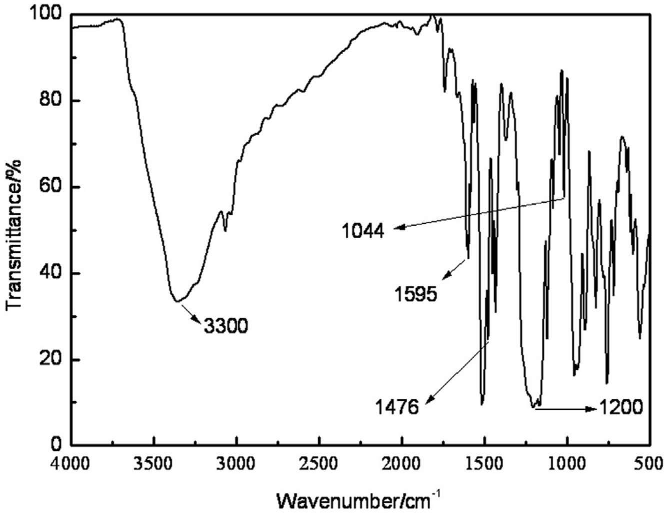


Fig. 1. FTIR spectrum of the synthesized CTP-DOPO.

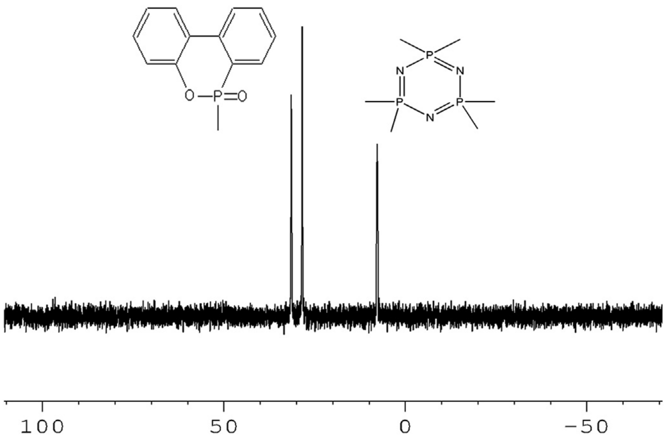


Fig. 3. ^{31}P NMR spectrum of CTP-DOPO.

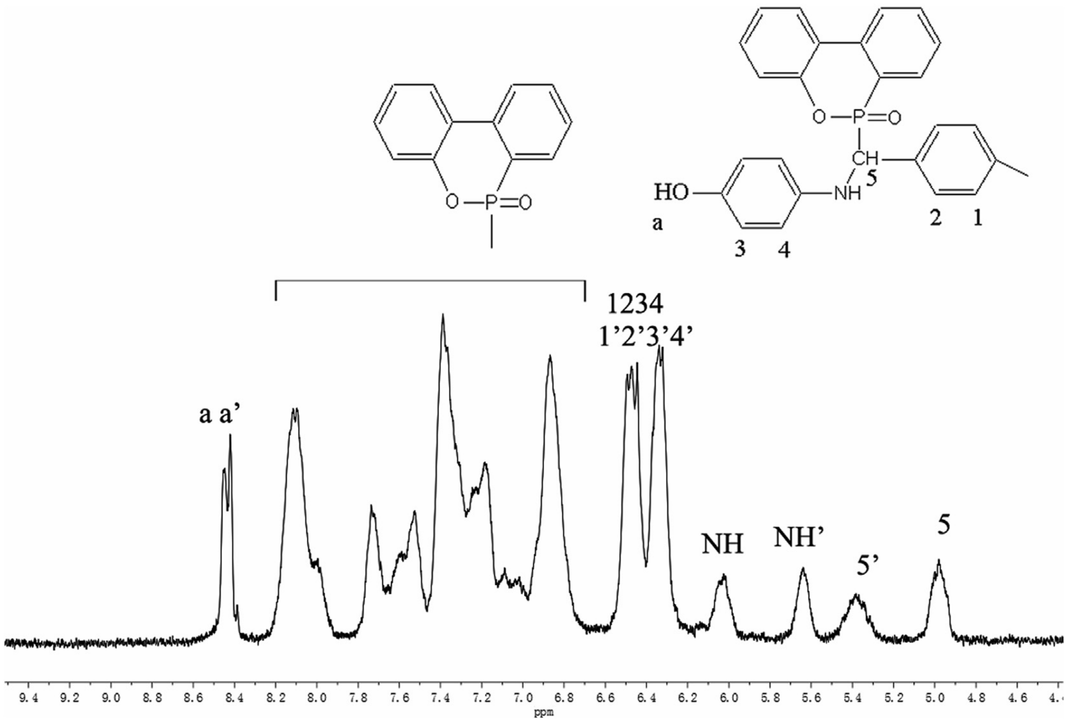


Fig. 2. ^{1}H NMR spectrum of CTP-DOPO.

^{31}P NMR spectrum of CTP-DOPO is shown in Fig. 3. The peaks at 31.43 and 28.47 ppm are assigned to phosphorus atoms of the DOPO groups, which indicate the existence of the two diastereomers. The peak at 7.44 ppm is attributed to the phosphorus atoms in phosphazene group. All above characterization results confirm the chemical structure of the prepared CTP-DOPO.

3.2. Flame retardancy of the cured epoxy resins

To evaluate the effects of CTP-DOPO on the flame retardancy for epoxy resins thermosets, LOI and vertical burning (UL-94) tests are conducted and the concerned data are summarized in Table 1. It can be seen that the pure DGEBA thermosets is highly combustible with the LOI value of 21.7%. The LOI value of the cured DGEBA/CTP-DOPO composites are dramatically increased from 21.7% for pure DGEBA thermosets to 34.3% when the loading amount of CTP-DOPO is only 9.7 wt % with the phosphorus content of 1.0 wt % in thermosets. The flame retardancy of the DGEBA/CTP-DOPO thermosets is gradually increased with the improvement of the CTP-DOPO content in DGEBA thermosets. The sample of S3 can successfully pass UL-94 V-0 flammability rating and the LOI value is as high as 36.6% when the CTP-DOPO content is only 10.6 wt % and the phosphorus content is 1.1 wt % in the DGEBA thermosets, which indicates that the prepared CTP-DOPO additive exhibiting high efficiency in enhancing flame retardancy for epoxy resins. The fact can be attributed that the prepared CTP-DOPO flame retardant additive containing phosphazene and phosphaphenanthrene groups in epoxy resins thermosets can act as acid precursors and decompose to

Table 1
Formulations and flame retardancy for epoxy resins thermosets.

Sample	DGEBA(g)	DDS (g)	CTP-DOPO (g)	CTP-DOPO (wt%)	P (wt%)	LOI (%)	UL-94 rating (3.0 mm)
S1	100	31	0	0	0	21.7	Fail
S2	100	31	14.1	9.7	1.0	34.3	V-1
S3	100	31	15.6	10.6	1.1	36.6	V-0
S4	100	31	17.3	11.7	1.2	38.5	V-0
S5	100	31	18.9	12.6	1.3	39.8	V-0

phosphoric and polyphosphoric acid during combustion which promotes the formation of char layer in the condensed phase [32]. The formed char layer can stop the propagation of heat and oxygen to underlying polymer matrix during combustion and protect the underlying materials from further burning. On the other hand, the action of the CTP-DOPO compound can take place in the vapor phase, in which PO, P and P2 species could be produced and likely to react with H and OH radicals to form HPO during combustion [4]. The reaction can interrupt the exothermic processes and suppress combustion by a radical mechanism. Comparing the reported work about the phosphorus containing flame retardants for epoxy resins [9,33], the CTP-DOPO possess higher flame retardant efficiency for epoxy resins because there are cyclotriphosphazene structure with high phosphorus content in the molecular structure of CTP-DOPO.

3.3. Thermal analysis of CTP-DOPO and the cured epoxy resins

A sample loses mass with increasing temperature can be measured by thermogravimetric analysis (TGA), which provides direct information about the thermal stability, char formation and the degradation behavior of samples. The initial decompose temperature defined as the temperature at which 5 wt % weight losses occurs and T_{max} defined as the temperature at maximum weight loss rate. TGA and DTG curves of CTP-DOPO, DGEBA and DGEBA/10.6 wt % CTP-DOPO thermosets cured with DDS under nitrogen atmosphere are shown in Fig. 4, and the detailed data are summarized in Table 2. The synthesized CTP-DOPO flame retardant additive begins to decompose at 314.6 °C and the char yield is 42.8 wt % at 700 °C, as shown in Fig. 4(a), which indicates the synthesized CTP-DOPO possess excellent charring ability at high temperature due to the presence of abundant aromatic structure, cyclotriphosphazene and phosphaphenanthrene in CTP-DOPO structure. From the DTG curves revealed in Fig. 4(b), it can be observed that the whole degradation process of CTP-DOPO can be divided into two stages, and the peak of step one appears at 324.9 °C, which can be attributed to the degradation of P—O—C bonds in CTP-DOPO due to its relative instability. The second stage of decomposition occurs from 400 to 550 °C and the peak appears at 461.7 °C, which can be attributed to the decomposition and char-forming of CTP-DOPO. The pure DGEBA thermosets starts to decompose at 380.7 °C and the char yield is 14.1 wt % at 700 °C, as revealed in Fig. 4(a) and Table 2. The thermal degradation course of DGEBA thermosets present only one stages, as reveals in Fig. 4(b) and Table 2, the peak of maximum thermal decomposition rate appears at 421.8 °C with the loss weight rate of 20.46% min^{-1} due to the decomposition and char-forming of epoxy resins thermosets. However, the initial thermal decomposition temperature of the DGEBA/10.6 wt % CTP-DOPO thermosets decreases from 380.7 °C for pure DGEBA thermosets to 345.3 °C due to the incorporation of CTP-DOPO into DGEBA composites, as revealed in Fig. 4(a) and Table 2. The phenomenon may be attributed that the cured epoxy resins including CTP-DOPO with phosphazene and phosphaphenanthrene groups could undergo degradation and produce phosphoric, polyphosphoric acid at a relative low temperature, and then the produced acid accelerated the decomposition of the epoxy resins [32]. The reaction stimulates the epoxy resins degrade at earlier stage on heat to form sufficient char. As a result, the char yield of DGEBA/10.6 wt % CTP-DOPO thermosets is enhanced from 14.1 wt % for pure DGEBA thermosets to 29.2 wt %, and the T_{max} is decreased from 421.8 °C for the cured pure epoxy resins to 387.8 °C. Meanwhile, the maximum weight loss rate of DGEBA/10.6 wt % CTP-DOPO thermosets greatly decrease from 20.46% min^{-1} for pure DGEBA thermosets to 10.09% min^{-1} and decrease by 50.7%. The fact possibly attributes that the previously formed char layer with high thermal stability protect the underlying epoxy resins matrix from further degradation, which leads to the incompletely decomposition of epoxy resins thermosets and increases the char residue at high temperature. The increased char yield limits the combustible carbon-containing gases, decrease the exothermic effect due to pyrolysis reactions, as well as decrease the thermal conductivity at

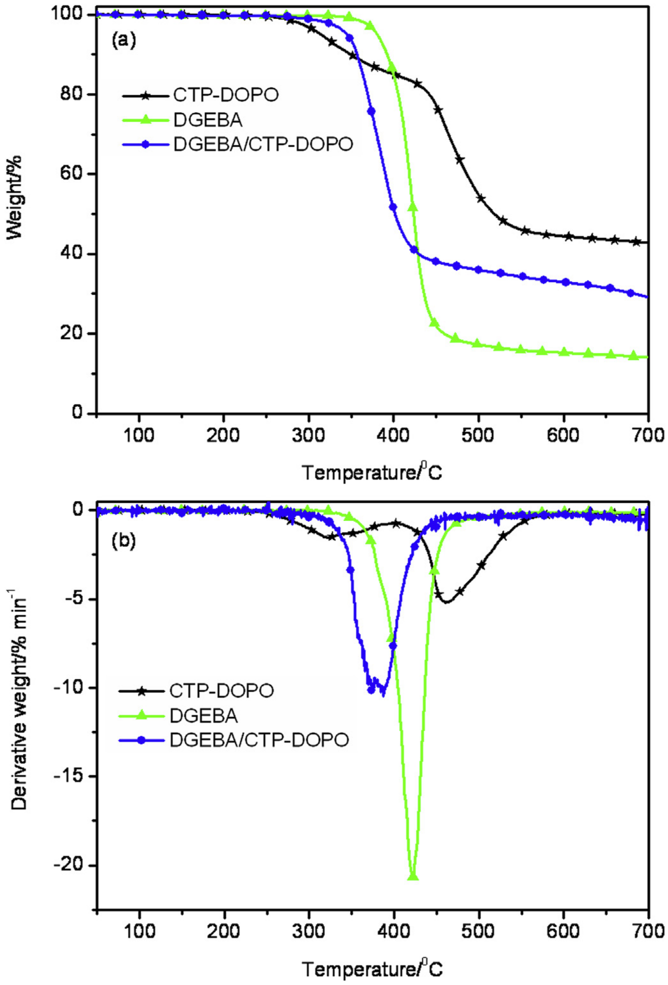


Fig. 4. TGA (a) and DTG (b) curves of CTP-DOPO and cured epoxy resins composites.

Table 2
Thermal degradation data of CTP-DOPO and the cured epoxy resins composites.

Sample	$T_{initial}$ (°C)	R_{1peak}/T_{1peak} (% min^{-1}/°C)	R_{2peak}/T_{2peak} (% min^{-1}/°C)	Char residue (wt%) 700 °C
CTP-DOPO	314.6	1.65/324.9	5.23/461.7	42.8
DGEBA	380.7	20.46/421.8	–	14.1
DGEBA/CTP-DOPO	345.3	10.09/387.8	–	29.2

the surface of the epoxy resins materials. The higher char yield will enhance the flame retardancy of the DGEBA thermosets. The thermal degradation results coincide with the flame retardancy tests discussed above.

TG-IR is usually used to analyze the gaseous products during the thermal degradation process. In order to obtain a deeper understanding of the flame retardant effect of CTP-DOPO for epoxy resins, the TG-IR spectra of DGEBA and DGEBA/10.6 wt % CTP-DOPO thermosets are detected and their FTIR spectra of pyrolysis products at different degradation temperature are shown in Fig. 5. It can be observed that both in the curves of the cured DGEBA (Fig. 5(a)) and DGEBA/10.6 wt % CTP-DOPO composite (Fig. 5(b)), there are characteristic bands of water (3648 cm^{-1}), carbon dioxide (2349 cm^{-1}) and compounds containing aromatic ring (1610, 1502 cm^{-1}), and the characteristic bands are almost similar between the two samples. Moreover, it is also can be observed that the cured DGEBA starts to produce gas products at 35 min with the temperature of 400 °C, as reveals in Fig. 5(a). While the DGEBA/10.6 wt % CTP-DOPO thermoset begins to release gas products at 31 min with the temperature of 360 °C, as reveals in Fig. 5(b). The fact is consistent with the results of the thermogravimetric analysis discussed above. It can be deduced that the incorporation of CTP-DOPO flame retardant additive based phosphazene-DOPO groups can serve as the dehydration agent and stimulate the epoxy resin thermosets begin to decompose at early stage on heating and low temperature compared with the cured DGEBA.

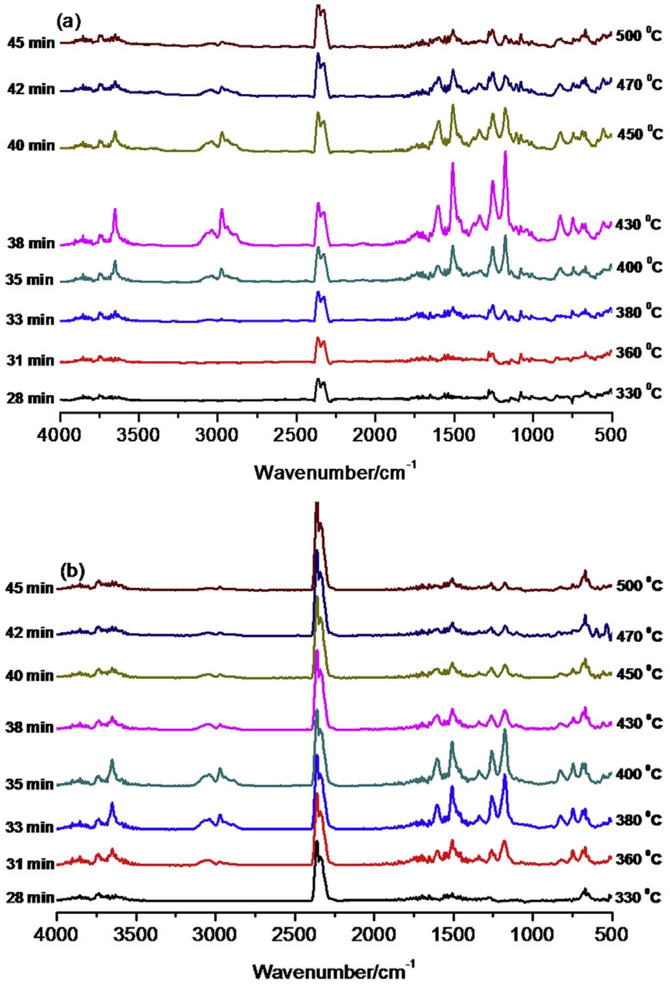


Fig. 5. TG-IR spectra of pyrolysis products for cured DGEBA (a) and DGEBA/10.6 wt % CTP-DOPO (b) at different decomposition temperature.

3.4. *Cone calorimeter of the cured epoxy resins*

The cone calorimeter has been widely used to evaluate the flammability and potential fire safety of polymer materials under well-ventilated conditions, which remains one of the most effective bench-scale tests that is used to predict the combustion behaviors of materials in a real fire. 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_{PHRR}), smoke production rate (SPR), total smoke production (TSP), residual weight and average effective heat combustion (av-EHC) are determined and used to predict the combustion behavior of materials in real fires. Figs. 6–8 and Table 3 present the plots and the detailed information of combustion behavior of for cured DGEBA and DGEBA/10.6 wt % CTP-DOPO composites obtained from the cone calorimeter tests at a heat flux of 50 kW m^{-2}.

TTI is used to determine the influence of a flame retardant on ignitability, which can be measured from the onset on an HRR curve. As revealed in Table 3, TTI of the DGEBA/10.6 wt % CTP-DOPO thermosets decreases from 63 s for cured pure DGEBA to 52 s. The fact may be attributed that the flame retardant additive of CTP-DOPO not only decompose ahead of time itself but also promote the epoxy resins matrix to degrade at lower temperature. In certain conditions, the degradation behaviors ahead of time contribute to charring earlier during combustion and benefit to the better flame retardancy for epoxy resins thermosets.

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 DGEBA/10.6 wt % CTP-DOPO thermosets and the results reveal that the cured pure DGEBA burns rapidly after ignition and only one sharp HRR peak appears at 147.8 s with a peak heat release rate (PHRR) of 619.9 kW m^{-2}, which corresponding to the combustion of epoxy resins thermosets. In contrast, the HRR curve of the DGEBA/10.6 wt % CTP-DOPO thermosets appear two peaks, but the peaks appear earlier and lower than that of the cured pure DGEBA. The first HRR peak of DGEBA/10.6 wt % CTP-DOPO thermosets appears at 69.6 s with a PHRR of 282.6 kW m^{-2}, which may be attributed to the CTP-DOPO additive decomposes itself at the initial stage on heating and stimulates the epoxy resins matrix to degrade and charring at early stage. The insulation of char layer formed on the materials surface, that is, the heat insulating char causes a rapid rise in the surface temperature and accelerates the decomposition of epoxy resins matrix on the surface of DGEBA thermosets. The second HRR peak of DGEBA/10.6 wt % CTP-DOPO thermosets corresponding to the combustion of the epoxy resins

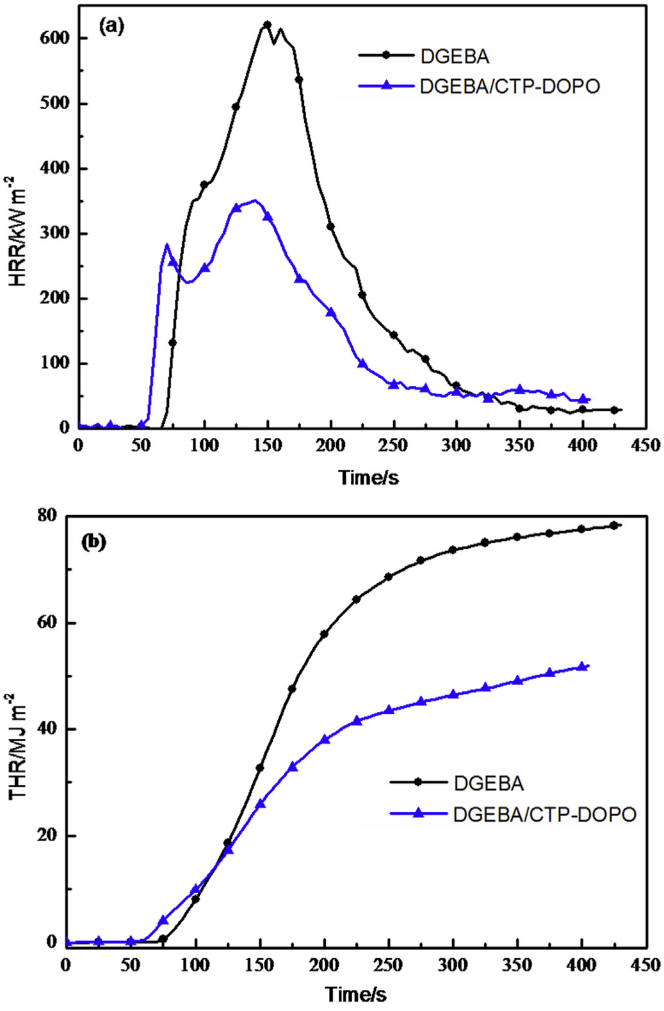


Fig. 6. HRR (a) and THR (b) curves of the cured pure DGEBA and DGEBA/10.6 wt% CTP-DOPO composites.

thermosets can be observed at 139.1 s and the peak heat release rate is obviously decreased from 619.9 kW m^{-2} for pure DGEBA thermosets to 349.9 kW m^{-2}, as revealed in Fig 6(a) and Table 3. Similar to the HRR curves, the THR curve of DGEBA/10.6 wt % CTP-DOPO thermosets is much lower than that of cured DGEBA, and the THR value is decreased from 77.6 MJ m^{-2} for pure DGEBA thermosets to 51.7 MJ m^{-2}, as revealed in Fig. 6(b) and Table 3. The results may be contributed to the decomposition of the phosphazene and phosphaphenanthrene groups of CTP-DOPO at relative low temperature promote the formation of the phosphorus-rich char shield with high strength and thermal stability. The formed char shield inhibit the heat and oxygen transferring into the interior matrix and flammable volatiles into flame zone during the combustion process, thus degrading the intensity of combustion pyrolysis reactions and decreasing the release of the quantity of heat. The lower THR value indicates that a part of DGEBA/10.6 wt % CTP-DOPO thermosets has not completely combusted and possibly undergoing a char-forming process. It can be deduced that the lower HRR and THR relate to condensed phase and contributed to better flame retardancy for epoxy resins thermosets.

The smoke production along with the HRR is also considered as another critical parameter in fire. The SPR and TSP curves of pure DGEBA and DGEBA/10.6 wt % CTP-DOPO thermosets are presented in Fig. 7. It can be observed that the tendency of SPR curves similar

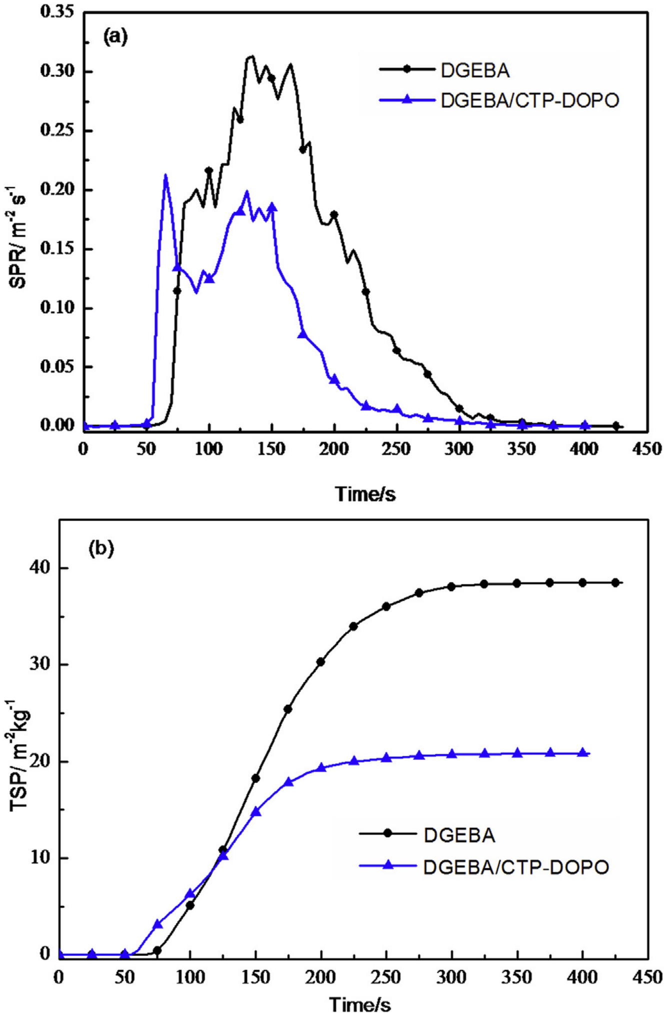


Fig. 7. SPR (a) and TSP (b) curves of the cured pure DGEBA and DGEBA/10.6 wt% CTP-DOPO composites.

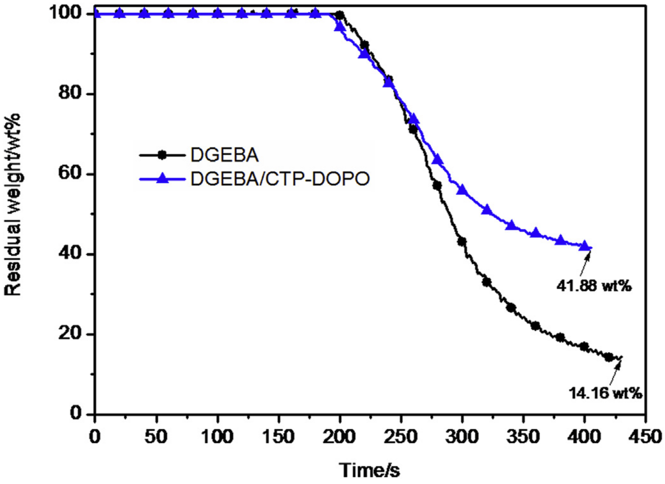


Fig. 8. Residual weight curves of the cured pure DGEBA and DGEBA/10.6 wt% CTP-DOPO composites.

with the HRR curves, as reveals in Fig. 7(a). The SPR curve of DGEBA thermosets present only one peaks occurs at 132.3 s with a peak

Table 3
Cone calorimeter data for the cured epoxy resins.

Sample	DGEBA	DGEBA/10.6 wt% CTP-DOPO
TTI (s)	63	52
Peak$_1$-HRR (kW m^{-2})	619.9	282.6
$t_{\text{Peak1-HRR}}$ (s)	147.8	69.6
Peak$_2$-HRR (kW m^{-2})	–	349.9
$t_{\text{Peak2-HRR}}$ (s)	–	139.1
THR (MJ m^{-2})	77.6	51.7
Peak$_1$-SPR (m^2 s^{-1})	0.31	0.21
$t_{\text{Peak1-SPR}}$ (s)	132.3	64.7
Peak$_2$-SPR (m^2 s^{-1})	–	0.19
$t_{\text{Peak2-SPR}}$ (s)	–	129.2
TSP (m^2 kg^{-1})	38.44	20.77
av-EHC (MJ kg^{-1})	21.16	18.95

value of 0.31 m^2 s^{-1} due to the combustion of DGEBA thermosets. Similar to the HRR curve, the SPR curve of DGEBA/10.6 wt % CTP-DOPO thermosets present two peaks which occurs ahead of time than that of pure DGEBA thermosets. The first SPR peak appears at 64.7 s with a peak value of 0.21 m^2 s^{-1}, which corresponding to the rapid decomposition of CTP-DOPO on the sample surface at the initial stage on heating and produce phosphoric and polyphosphoric acid. The produced acid can stimulate the degradation of epoxy resins matrix and char forming, which result in the smoke emission ahead of time. The second SPR peak appears at 129.2 s and the peak value of DGEBA/10.6 wt % CTP-DOPO thermosets dramatically decrease from 0.31 m^2 s^{-1} for pure DGEBA thermosets to 0.19 m^2 s^{-1}, as reveal in Fig. 7(a) and Table 3. The phenomenon is contributed to the formation of compact and continuous char laye with high strength and thermal stability on the surface of the materials, 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. Consequently, the TSP value of DGEBA/10.6 wt % CTP-DOPO thermosets evidently decreases from 38.44 m^2 kg^{-1} for cured pure DGEBA to 20.77 m^2 kg^{-1} and decrease by 45.9%, as reveal in Fig. 7(b) and Table 3.

The reduction of HRR and SPR for DGEBA/10.6 wt % CTP-DOPO thermosets indicates that a cohesive char layer is formed during combustion which acts as an insulating barrier between fire and epoxy resins matrix. The curves of the residual mass obtained from cone calorimeter tests also further confirm that the thermal decomposition behavior of epoxy resins is obviously influenced by the CTP-DOPO flame retardant additive, as shown in Fig. 8. For cured DGEBA, the char residue is 14.16 wt % at the end of the test, which is consistent with the TGA results. However, with the incorporation of CTP-DOPO into epoxy resins, the amount of the char residue for the cured DGEBA/10.6 wt % CTP-DOPO composite is enhanced to 41.88 wt %. This indicates that the introduction of CTP-DOPO effectively prevents epoxy resins matrix from decomposition and probably stimulates epoxy resins to form much more char residue. The char formation during burning is desirable, which can retard the combustion of the epoxy resins materials effectively.

The EHC represents the total heat evolved per total mass loss on combustion for analysis of the flame retardancy mechanism in the gas phase during forced-flaming combustion. The lower EHC value indicates that noncombustible gas exist in gas phase. As reveal in Table 3, the average value of EHC for DGEBA/10.6 wt % CTP-DOPO thermosets decreases from 21.16 MJ kg^{-1} for cured pure DGEBA to 18.95 MJ kg^{-1}. The reason is that the thermoset containing phosphazene and DOPO groups release noncombustible gases, such as volatile phosphide, N_2, NH_3 and CO_2 during the combustion process [18,21], which could dilute flammable gases and reduce the oxygen concentration around the material. On the other hand, the flame retardants containing DOPO groups can act in the gas phase through flame inhibition and in the condensed phase through charring [16]. 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.

3.5. Morphologis of the char residue

In order to further investigate the relationship between the morphology of the char layers and flame retardant properties of the CTP-DOPO, the char residues of cured DGEBA and DGEBA/CTP-DOPO after cone calorimeter tests were taken photographs with a digital camera and measured by SEM magnified by 3000 times, as shown in Figs. 9 and 10, respectively. As for pure DGEBA thermosets (see Fig. 9(a)), there is no efficient intumescent char formed because DGEBA thermosets almost decomposes completely. However, the DGEBA/10.6 wt % CTP-DOPO thermosets can form good, coherent intumescent and thick char layer, as reveals in Fig. 9(b).

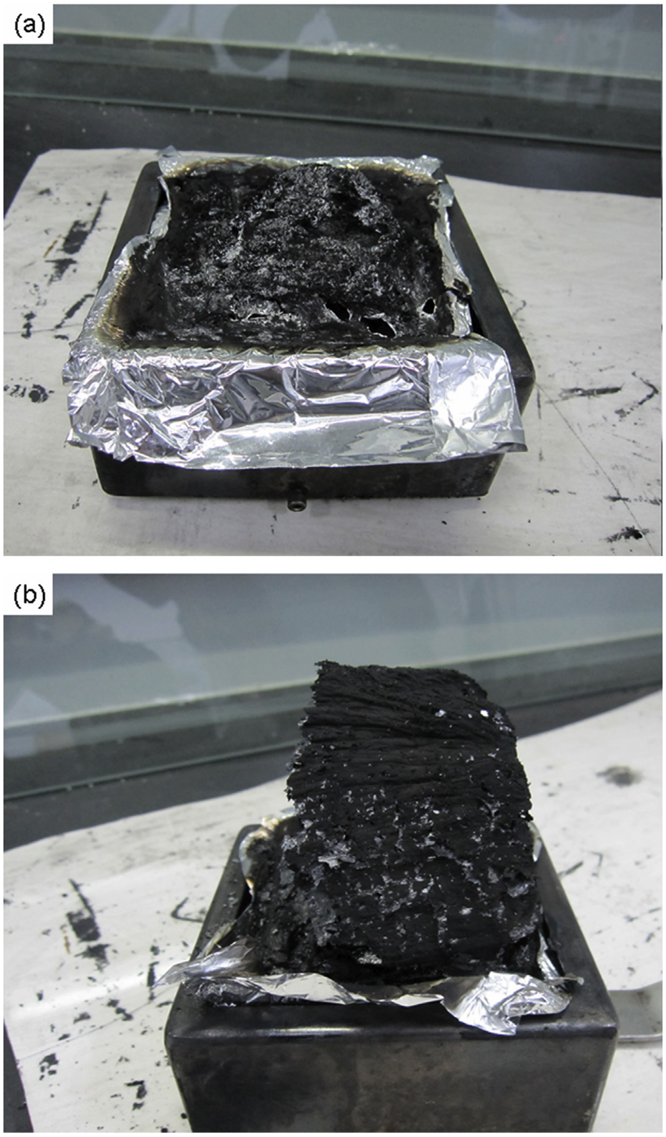


Fig. 9. Digital photos of residual char for pure DGEBA (a) and DGEBA/10.6 wt % CTP-DOPO thermosets (b).

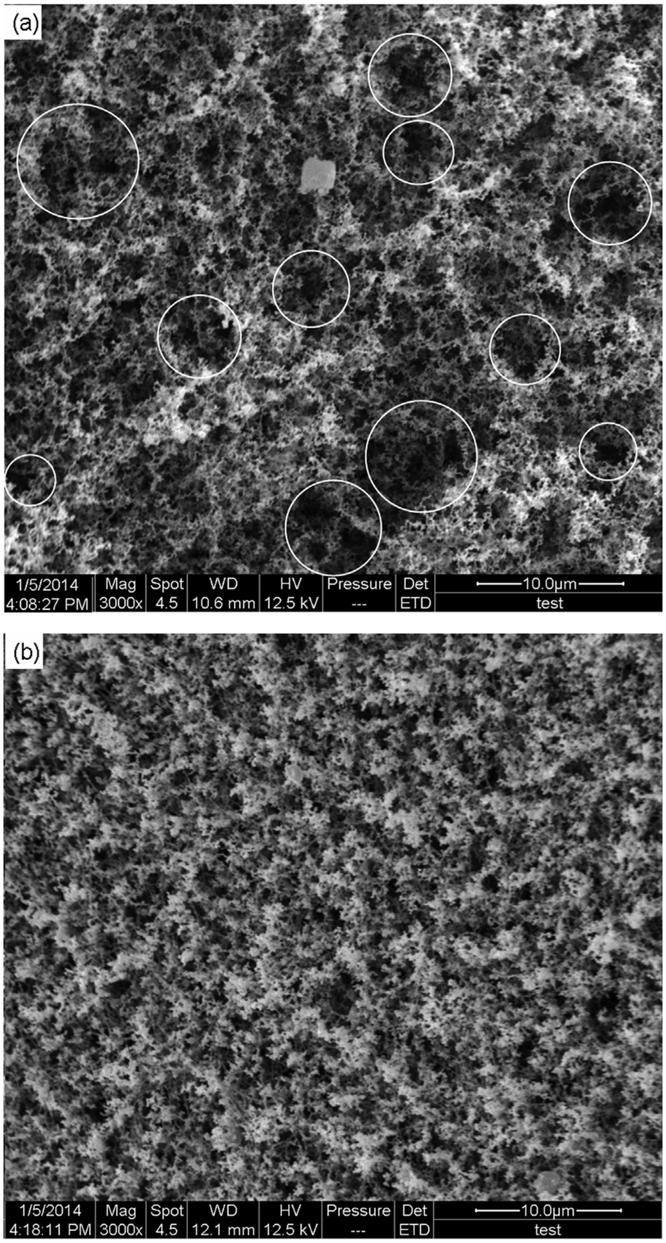


Fig. 10. SEM images of the char residue of the cured epoxy resins after cone calorimeter tests. (a) pure DGEBA, 3000 ×; (b) DGEBA/10.6 wt% CTP-DOPO thermosets, 3000 ×.

Moreover, it can be observed 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 (see Fig. 10(a)) 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 DGEBA/10.6 wt % CTP-DOPO composite appears more homogenous and compact than that of cured DGEBA, as reveals in Fig. 10(b). The results indicate that the incorporation of CTP-DOPO containing phosphazene and phosphaphenanthrene groups promote to form more sufficient and compact char layer with higher thermal stability, which can restrict the transfer of heat and flammable volatiles and leading to excellent flame retardancy. As a result, the flame retardancy of the cured DGEBA/CTP-DOPO composites is obviously enhanced.

In order to further elucidate the formation of intumescent char layer, the structure of the residual char for DGEBA/10.6 wt % CTP-DOPO thermosets after cone calorimeter tests is examined by FTIR spectra, as reveals in Fig. 11. The peak around 3429 cm^{-1} is due to the N—H and O—H stretching vibration, the peaks at 1416 and 1589 cm^{-1} assigned to the remained aromatic rings after combustion. The absorption peak around 1196 cm^{-1} is attributed to the stretching vibration for P═N bonds in phosphazene group, which gives the direct evidence for the phosphazene structure with excellent thermal stability existed in the residual char. The peak at 1110 cm^{-1} can be ascribed to the stretching vibration of PO_2/PO_3 in phosphate carbon complexes, and the peak at 912 cm^{-1} belong to the stretching vibration of P—O—P bond [34], which indicates that some phosphate groups link each other and form polyphosphoric acid during thermal degradation of CTP-DOPO. The formed acid can serve as the dehydration agent and promote the formation of the carbonaceous char by carbonization. The formed char layer combined with the phosphazene structure remained in condense phase could well protect the epoxy resins matrix.

4. Conclusions

A novel flame retardant additive CTP-DOPO with phosphazene and phosphaphenanthrene groups has been successfully synthesized and characterized. The cured DGEBA/10.6 wt % CTP-DOPO composites with only 1.1 wt % phosphorus content in thermosets successfully passed UL-94 V-0 flammability rating and the LOI value reached 36.6%. The incorporation of CTP-DOPO stimulated DGEBA matrix decompose and char forming ahead of time, enhanced the char yield and thermal stability of DGEBA thermosets at high temperature. The CTP-DOPO in thermoset promoted the formation of the uniform, sealing, intumescent and continuous char layer with high thermal stability due to the existing of abundant aromatic structure, phosphazene and phosphaphenanthrene groups in CTP-DOPO additive. The formed char layer prevented the heat transmission and diffusion, limited the production of combustible gases, inhibited the emission of smoke and then led to the reduction of the heat release rate and smoke produce rate. As a result, the introduction of the prepared CTP-DOPO flame retardant additive into DGEBA thermosets led to higher flame retardant efficiency and thermal stability at a high temperature.

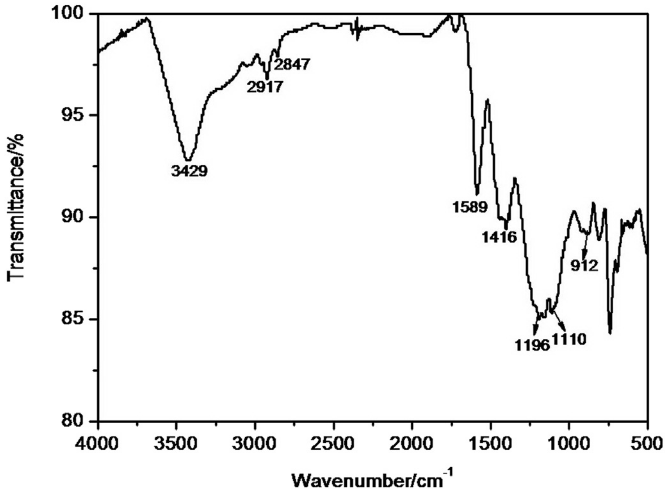


Fig. 11. FTIR spectrum of the residual char of DGEBA/10.6 wt % CTP-DOPO thermosets obtained after cone calorimeter test.

Acknowledgments

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