

Synthesis of a Novel Curing Agent Containing Organophosphorus and Its Application in Flame-Retarded Epoxy Resins

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ABSTRACT: A novel amine-terminated and organophosphorus-containing compound *m*-aminophenylene phenyl phosphine oxide oligomer (APPPPO) was synthesized and used as curing and flame-retarding agent for epoxy resins. Its chemical structure was characterized by Fourier transform infrared (FTIR) spectroscopy, ¹H nuclear magnetic resonance (¹H NMR), ¹³C nuclear magnetic resonance, and ³¹P nuclear magnetic resonance. The flame-retardant properties, combusting performances, and thermal degradation behaviors of the cured epoxy resins were investigated by limiting oxygen index (LOI), vertical burning test (UL-94), cone calorimeter test, and thermogravimetric analysis. The EPO/APPPPO thermosets passed V-1 rating with the thickness of 3.0 mm and the LOI value reached 34.8%. The thermosets could pass V-2 rating when the thickness of the samples was 1.6 mm. The cone calorimeter test demonstrated that the parameters of EPO/APPPPO thermosets including heat release rate and total heat release significantly decreased compared with EPO/PDA thermosets. Scanning electron microscopy revealed that the incorporation of APPPPO into epoxy resins obviously accelerated the formation of the compact and stronger char layer to improve flame-retardant properties of the cured epoxy resins during combustion. The mechanical properties and water resistance of the cured epoxy resins were also measured. After the water-resistance test, EPO/APPPPO thermosets still remained excellent flame retardant and the water uptake was only 0.4%.

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KEYWORDS: flame retardance; thermogravimetric analysis (TGA); thermosets

Received 5 February 2014; accepted 13 June 2014

DOI: 10.1002/app.41159

INTRODUCTION

In the modern polymer industry, epoxy resins are widely used as encapsulating materials in the electronic and electrical industries, transportation, and advanced composite matrices for structural laminates owing to their high tensile strength, good chemical resistance, and excellent dimensional stability.^{1,2} However, conventional epoxy resins are very flammable and they cannot satisfy some applications which require high flame-retardant grade. Therefore, the flame retardancy of epoxy resins is becoming an urgent problem and has attracted more and more attention.^{3,4} Traditionally, brominated and chlorinated compounds are used for preventing the epoxy resins' flammability. Although the halogenated compounds show good flame retardancy for epoxy resins and have been used widely for several decades, their use has been curtailed in many countries because of toxic and corrosive fumes released during combustion. Consequently, there is a trend toward using halogen-free flame retardants in epoxy resins.⁵⁻⁷

Phosphorus-containing compounds are mostly used as substitutes for the halogenated compounds in flame-retardant epoxy resins. Various phosphorus compounds, such as phosphine oxides, phosphonates, phosphates, phosphinates, and cyclotriphosphazenes, are used as additive or reactive flame retardants.⁸⁻¹³ Comparing the additive flame retardants, reactive organophosphorus compounds present excellent flame-retardant efficiency in the case of epoxy resins and can be incorporated into the backbone of the network either through being part of the curing agent or through the epoxy resins itself.¹⁴⁻¹⁶ At present, phosphonates, phosphites, and phosphate are widely used as curing agents for epoxy resins.¹⁷⁻¹⁹ However, these compounds have some inherent disadvantages,^{20,21} such as the poor thermal stability, which limit their application in electronic and electrical industries where there is a usual requirement of high operating temperatures. In addition, the compounds containing P—O—C bond hydrolyze easily and have poor resistance to acid and base, which limit their application range. A possible way to improve flame

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retardant and comprehensive performance for epoxy resins would be the incorporation of stable flame retardants.²²

Among the various phosphorus-containing compounds, phosphine oxides are preferred as curing agents to impart flame retardancy to epoxy resins.^{23,24} Based on the previously published reports,^{23–25} the phosphine oxides are more stable than the compounds containing P—O—C bonds. They possess good thermal stability and resistance to acid and base, and meanwhile, they can promote char formation and present high flame-retardant efficiency for epoxy resins at low phosphorus concentration. The action of the compounds can take place in the vapor phase by a radical mechanism to interrupt the exothermic processes and suppress combustion. In this case, PO, P, and P₂ species are likely to react with H and OH radicals to form HPO.²⁶ On the other hand, the compounds incorporated in polymer materials can act as acid precursors which participate in char formation in the condensed phase.^{27–29} Consequently, a protective char layer was formed to stop the propagation of heat and oxygen to underlying polymer matrix during combustion, which can prevent the polymer from further burning. Some phosphine oxides have been synthesized and used as curing agents to enhance the flame retardancy for epoxy resins, such as *bis*(4-hydroxyphenyl) phenylphosphine oxide, *bis*(3-aminophenyl)methyl phosphine oxide, *bis*(3-aminophenyl)phenylphosphine oxide, and *bis*(4-aminophenyl)phenylphosphine oxide.^{20,23,25,30} To date, aminophosphine oxide oligomer used as curing and flame-retarding agent to improve flame retardancy for epoxy resins has not been reported.

In this study, *m*-aminophenylene phenyl phosphine oxide oligomer (APPPPO) was synthesized and characterized. There is no P—O—C bond which existed in the traditional phosphate flame retardants and substituted by P—C bond in the APPPO structure. Our research aimed at using the P—C bond with excellent stability to replace the P—O—C bond in the compound structure and overcoming the shortcoming of hydrolyzing easily owing to the existing of P—O—C bond. The effects of APPPO on flame retardancy, thermal degradation, mechanical properties, and water resistance for epoxy resins were investigated.

EXPERIMENTAL

Materials

Absolute ethanol, carbon tetrachloride, chloroform, sulfuric acid (98%), fuming hydrochloric acid, and fuming nitric acid of analytical grade were purchased from Kermel Chemical Reagents Development Center (Tianjin, China). Sodium bicarbonate, tin(II) chloride dehydrate, sodium hydrate, and *m*-phenylenediamine (PDA) of analytical grade were obtained from Sinopharm Chemical Reagent (Shanghai, China). Epoxy resins (E-44, epoxide equivalent weights = 213 g/epoxide) of technical grade were supplied by Fude Chemicals Industry (Guangzhou, China). The compound of phenylene phenyl phosphine oxide oligomer (PPPO) was synthesized and reported in our previous study.³¹

Synthesis of PPPO

PPPO (0.1 mol, 18.4 g), 100 mL of absolute ethanol, and 200 mL of tetrachloromethane were mixed in a 500-mL glass

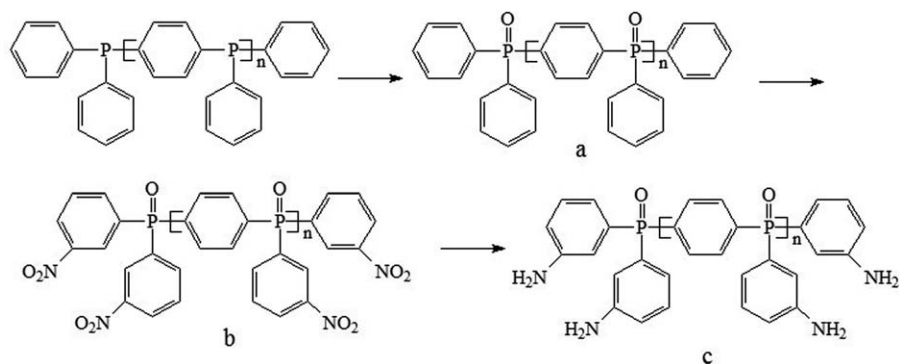
flask equipped with a condenser. The mixture was refluxed for 4 h, then the solvent was removed under reduced pressure, and the residue was added in 250 mL of cold water. White crystalline was formed, and then the precipitate was filtered off and dried under vacuum at 60°C for 12 h (19.0 g, yield: 94.8%). IR (KBr): 3052 cm⁻¹ (Ph—H), 1590 and 1484 cm⁻¹ (—Ph), 1439 cm⁻¹ (P—C), 1190 cm⁻¹ (P=O); ¹H nuclear magnetic resonance (¹H NMR) (CDCl₃): δ = 7.45–7.52 ppm (m, 3H, aromatic protons far from P=O), δ = 7.52–7.63 ppm (m, 4H, aromatic protons near P=O), δ = 7.65–7.70 ppm (m, 2H, H of the phenylene); ¹³C nuclear magnetic resonance (¹³C NMR) (CDCl₃): δ = 128.5 ppm (*m*-Ph), δ = 131.7 ppm (*p*-Ph), δ = 131.8–131.9 ppm (phenylene), δ = 132.0 ppm (*o*-Ph), δ = 133.1 ppm (P—Ph); ³¹P nuclear magnetic resonance (³¹P NMR) (CDCl₃): δ = 28.7 ppm.

Synthesis of *m*-Nitrophenylene Phenyl Phosphine Oxide Oligomer

PPPO (0.1 mol, 20.0 g) and 200 mL of sulfuric acid (98 wt %) were mixed in a 500-mL glass flask equipped with a condenser and a thermometer. The reactant was dissolved and the reaction mixture was cooled to -5°C with ice/salt bath. Then, a solution of 51.4 g of fuming nitric acid (0.8 mol) in 150 mL of sulfuric acid was added dropwise via an addition funnel for 2 h. After the addition, the temperature of reaction mixture was then increased to 40°C and kept for 24 h. After this process, the reaction solution was then hydrolyzed with 500 mL of ice. When the ice was completely melted, the mixture was filtered and washed with sodium bicarbonate aqueous solution and water, successively. A yellow solid powder was obtained and dried under vacuum at 80°C for 12 h (18.7g, yield: 81.5%). IR (KBr): 3082 cm⁻¹ (Ph—H), 1606 and 1572 cm⁻¹ (—Ph), 1522 and 1346 cm⁻¹ (N=O), 1422 cm⁻¹ (P—C), 1199 cm⁻¹ (P=O), 882 cm⁻¹ (C—NO₂); ¹H NMR (CDCl₃): δ = 7.51–7.59 ppm (d, 1H, *m*-H—Ph), δ = 7.79–7.85 ppm (t, 1H, aromatic protons near P=O), δ = 8.04–8.11 ppm (t, 2H, aromatic protons near P=O), δ = 8.51–8.55 ppm (s, 4H, H of the phenylene); ¹³C NMR (CDCl₃): δ = 126.5 and 126.7 ppm (near NO₂), δ = 130.7 ppm (*m*-Ph), δ = 130.8 ppm (phenylene), δ = 132.2 ppm (P—C), δ = 133.6 ppm (P—phenylene), δ = 137.3 ppm (near P=O), δ = 148.6 ppm (Ph—NO₂); ³¹P NMR (CDCl₃): δ = 23.1 ppm.

Synthesis of APPPO

m-Nitrophenylene phenyl phosphine oxide oligomer (NPPPO) (0.05 mol, 11.5 g), tin(II) chloride dehydrate (0.9 mol, 203.0 g), and 100 mL of absolute ethanol were mixed in a 500-mL glass flask equipped with a condenser and a thermometer. A solution of fuming hydrochloric acid (100 mL) in 150 mL of ethanol was added dropwise via an addition funnel. After the addition, the reaction mixture was stirred at room temperature for 24 h, and then the solution was concentrated and neutralized by a 25% sodium hydrate aqueous solution. The obtained solution was then extracted with chloroform and the organic layer was collected and concentrated under reduced pressure. A light yellow powder was obtained and dried under vacuum at 60°C for 12 h (7.3 g, yield: 72.7%). The synthesis reactions for PPPO, NPPPO, and APPPO are shown in Scheme 1.



Scheme 1. Synthesis of APPPOO: (a) PPPOO, (b) NPPPOO, and (c) APPPOO.

Characterization

Fourier transform infrared (FTIR) spectra were obtained using potassium bromide disks and PerkinElmer 400 spectrometer (USA). Nuclear magnetic resonance (NMR) spectra were obtained using 10–25% of solutions in deuteriochloroform (CDCl_3) or deuterio dimethyl sulfoxide ($\text{DMSO}-d_6$) and Bruker 300 NMR (300 MHz) spectrometer (Germany). Proton and carbon chemical shifts were reported with respect to tetramethylsilane as internal reference. Phosphorus chemical shifts were reported with respect to 85% of aqueous phosphoric acid solution as external reference.

Preparation of Samples

The curing agents, PDA and APPPOO, were combined in various equivalent ratios. Epoxy resins and amine compounds were mixed in stoichiometric amounts by dissolving the components in dichloromethane and subsequently evaporating the solvent at room temperature in vacuum. The weight ratios of PDA/APPPOO were 100/0, 80/20, 60/40, 40/60, 20/80, and 0/100, respectively. The mixture was placed in molds and cured at 120°C for 3 h and postcured at 170°C for 4 h. After curing, all samples were cooled to room temperature.

Flame Retardancy Tests

The LOI values were measured at room temperature on a JF-3 oxygen index meter (Jiangning Analysis Instrument, China) according to ISO4589-2:2006 standard. Dimensions of all samples were $130 \times 6.5 \times 3 \text{ mm}^3$ and 15 specimens were tested for each sample. Vertical burning (ANSI/UL 94–2010) tests were carried out on a CZF-2-type instrument (Jiangning Analysis Instrument, China) with the dimension of $130 \times 13 \times 3 \text{ mm}^3$ and $130 \times 13 \times 1.6 \text{ mm}^3$ according to UL-94 test standard and eight specimens were tested for each sample. 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.

Cone Calorimetry

The combustion behavior under ventilated conditions was measured using a Fire Testing Technology cone calorimeter (West Sussex, United Kingdom), in accordance with ISO 5660-1 standard. Samples with size of $100 \times 100 \times 3 \text{ mm}^3$ were exposed to cone at a heat flux of $50 \text{ kW}\cdot\text{m}^{-2}$ and one specimen was tested for every sample.

Scanning Electron Microscopy

Morphological studies on the residual chars were conducted using a FEI QUANTA-200 (Eindhoven, The Netherlands) scanning electron microscopy (SEM) at an acceleration voltage of 15 kV. The chars were adhered to a copper plate and then coated with gold for imaging.

Thermogravimetric Analysis

Thermogravimetric analysis (TGA) data were obtained using a PerkinElmer Pyris 1 Thermal Analyzer (MA, USA). A heating rate of $10^\circ\text{C}\cdot\text{min}^{-1}$ was used. The samples (2–4 mg) were placed in a standard platinum pan and heated from 50 to 800°C . The sample compartment was purged with N_2 and air at $20 \text{ mL}\cdot\text{min}^{-1}$ during analysis. All thermal degradation data were obtained from the TGA curves.

Mechanical Properties Test

Tests of tensile strength, flexural strength, and Izod impact of all samples were performed by Regeer computer-controlled mechanical instrument (Shenzhen, China) and Notched Izod impact instrument (Chengde, China), respectively, according to the ASTM standards. Dimensions of samples were $150 \times 10 \times 4 \text{ mm}^3$. At least five specimens were tested for each sample and the average values were reported.

Water-Resistance Test

The cured epoxy resin specimens were kept in water at 70°C and the time lasted 1–7 days. Then, water on the surface of the samples was absorbed by filter paper. The water resistance was monitored in terms of mass increase, flame retardancy, and mechanical properties. Mass increase of the sample was tested with the dimensions of $50 \times 50 \times 1 \text{ mm}^3$. Dimensions of samples for flame retardancy and mechanical properties tests were the same to that of the abovementioned tests. At every immersion time, the number of specimens for LOI, vertical burning, and mechanical properties tests were 15, 8, and 5, respectively.

RESULTS AND DISCUSSION

Synthesis and Structure Characterization

As indicated above, APPPOO was prepared in three steps with good yield. The technique of the synthesis of nitro and amino derivatives has been reported earlier.³⁰ To obtain a high yield, the amount of nitric acid is required under carefully controlled nitration step. The amino compound (APPPOO) was obtained

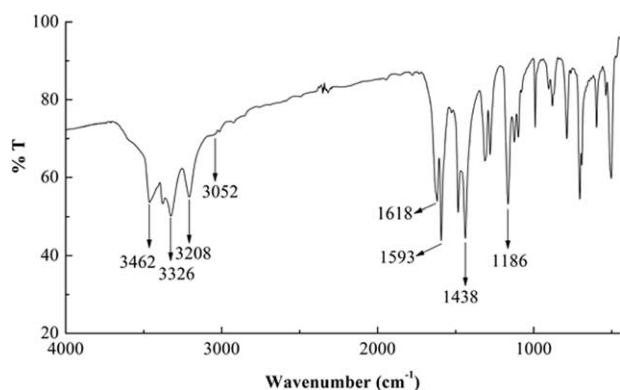


Figure 1. FTIR spectrum of APPPOO.

from subsequent hydrogenation. The chemical structure of the compound was characterized with FTIR and ^1H , ^{13}C NMR, and ^{31}P NMR.

As shown in Figure 1, the FTIR spectrum of APPPOO contains characteristic absorptions at 3462, 3326, and 3208 cm^{-1} corresponding to N—H stretching, 3052 cm^{-1} assigning to aromatic C—H stretching, 1618 and 1593 cm^{-1} for the phenyl nucleus, 1438 cm^{-1} for the P—C stretching and 1186 cm^{-1} attributing to the P—O stretching. The ^1H NMR spectrum of APPPOO is shown in Figure 2; the peak at 4.07 ppm is attributed to proton (a) of $-\text{NH}_2$ and the peaks between 6.69 and 6.72 ppm were corresponded to the protons (b) in the benzene ring. The signal from 6.83 to 6.87 ppm is attributed to protons (c) in the benzene ring. The signals from 7.01 to 7.14 ppm were attributed to protons (d) in the benzene ring. The peaks from 7.53 to 7.58 ppm were corresponded to the protons (e) of the phenylene ring. Figure 3 shows the ^{13}C NMR spectrum of APPPOO, the peaks at 116.9–117.1, 119.1–119.3, and 129.3 ppm were attributed to the carbon atoms (a–c) in the aromatic rings, respectively. The peaks at 133.6 and 134.9 ppm were corresponded to $-\text{CH}-$ carbon atoms (d) and (e) adjacent to $-\text{P}=\text{O}$ resonate. The signal at 149.2 ppm was attributed to $-\text{CH}-$ carbon atoms (f) from the benzene ring. As shown in Figure 4, the ^{31}P NMR

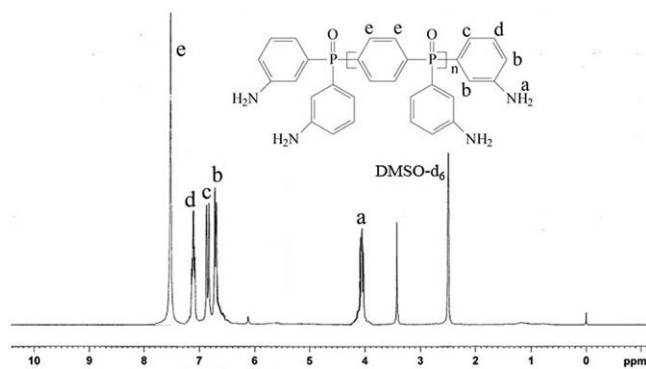


Figure 2. ^1H NMR spectrum of APPPOO.

spectrum of APPPOO appeared as a single resonance at 28.3 ppm, which suggests that there exists only unique phosphorus-containing compound.

Flame Retardancy

The results of the flame retardancy test for the cured epoxy resins containing various components are summarized in Table I. The LOI value of EPO/PDA thermosets was only 17.8% and it was no rating in vertical burning tests, which indicated that EPO/PDA thermosets were flammable. When APPPOO was incorporated into epoxy resins and the concentration of phosphorus was 1.4%, the LOI value significantly increased to 27.2%, EPO/40 wt % APPPOO/60 wt % PDA thermosets passed V-2 rating with the thickness of 3.0 mm. The flame retardancy of epoxy resins increased with the increase of the loading amount of APPPOO, the LOI value of EPO/80 wt % APPPOO/20 wt % PDA thermosets reached 31.7%, and the samples with 3.0 and 1.6 mm of thickness can successfully pass V-1 and V-2 rating, respectively. For the cured EPO/APPPOO system, the LOI value reached 34.8%, but there was no significant increase in vertical burning test although the phosphorus content increased to 3.3%. To date, numerous phosphorus compounds have been used to improve the flame retardancy for epoxy resins.^{20,23,32,33} For example, the LOI value of EPO/*bis*(4-aminophenoxy)phenylphosphine oxide thermosets was 33% when the phosphorus content reached

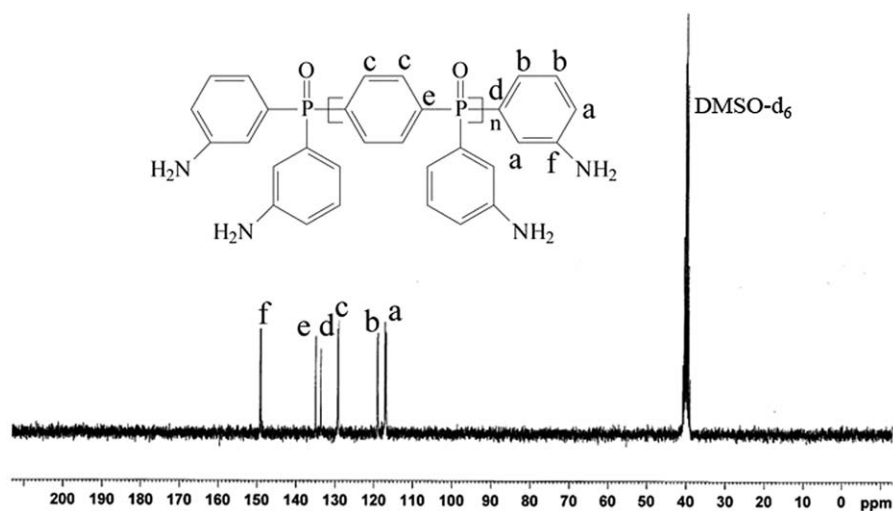


Figure 3. ^{13}C NMR spectrum of APPPOO.

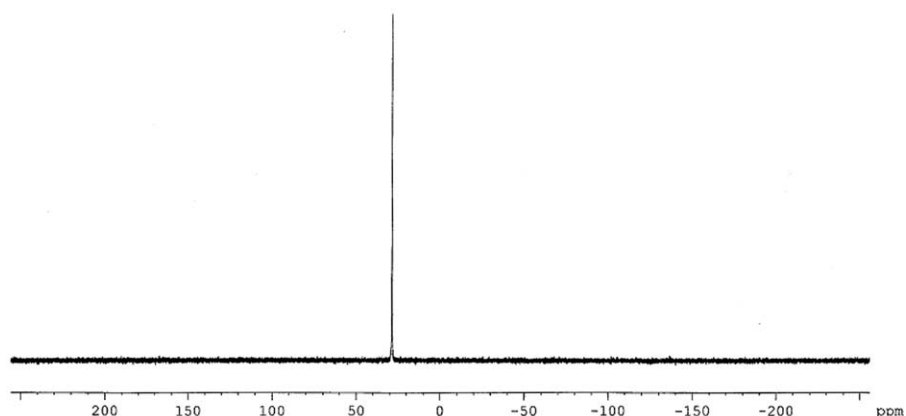


Figure 4. ^{31}P NMR spectrum of APPPOO.

Table I. Results of Flame Retardancy Test for Epoxy Resin Thermosets

Compositions			Curing agent compositions (APPPOO/PDA)	P %	LOI (%)	UL-94 rating			
EPO (wt %)	PDA (wt %)	APPPOO (wt %)				3.0 mm	Dripping	1.6 mm	Dripping
49.2	50.8	0	0/100	0	17.8	No rating	Yes	No rating	Yes
70.4	23.7	5.9	20/80	0.6	25.0	No rating	Yes	No rating	Yes
70.5	17.7	11.8	40/60	1.2	27.2	V-2	Yes	No rating	Yes
70.5	11.8	17.7	60/40	1.9	29.0	V-2	Yes	No rating	Yes
71.5	5.7	22.8	80/20	2.6	31.7	V-1	Yes	V-2	Yes
72.1	0	27.8	100/0	3.2	34.8	V-1	Yes	V-2	Yes

4.2%, but the composite has no rating in UL 94 test³²³²; EPO/3,3'-bis(maleimidophenyl)phenylphosphine oxide system material cannot pass the UL-94 V-0 rating with 3.0-mm sample and its LOI value was 28%³³³³; EPO/bis(3-hydroxyphenyl)phenyl phosphate thermosets pass only UL-94 V-2 rating with 3.0-mm sample and the LOI value reached 28%.²³ However, the previous research on flame-retarded epoxy resins cured with phosphorus-containing compounds showed low flame-retardant efficiency. Compared with the reported results, our synthesized APPPOO was a relatively high efficient flame retardant, the cured samples with 3.0 and 1.6 mm could, respectively, pass V-1 and V-2 rating and its LOI value reached 31.7% when the phosphorus content was 2.7%. After the addition of APPPOO, the cured epoxy resins could undergo

Table II. CONE Data of EPO/PDA and EPO/APPPOO Thermosets

Sample	EPO/PDA	EPO/APPPOO
TTI (s)	65	50
PHRR (kW·m ⁻²)	685	456
THR (MJ·m ⁻²)	95	67
t_{PHRR} (s)	150	125
ASEA (m ² ·kg ⁻¹)	1015	686
AMLR (g·s ⁻¹)	0.14	0.08
CO ₂ T(g·kg ⁻¹)	70.72	37.86
COT(g·kg ⁻¹)	3.02	2.97

degradation and produce phosphoric, polyphosphoric acid during the initial step of the thermal degradation, and then the produced acids accelerated the decomposition of the epoxy resins and formed an insulating protective char layer, which prevented the heat and oxygen from transferring to the surface of the materials and enhanced the flame retardancy of the resins.

Although the LOI and UL 94 tests are useful small-scale tests for flame-retarded polymer, the cone calorimeter provides a wealth of information on the combustion behavior under ventilation conditions. The cone calorimeter is one of the most effective bench-scale methods for studying the flame retardancy of materials. Some parameters provided by cone calorimeter such as time to ignition (TTI), heat release rate (HRR), total heat released (THR), peak heat release rate (PHRR), time of peak heat release rate (t_{PHRR}), average mass loss rate (AMLR), and average specific extinction area (ASEA, a measure of smoke) for EPO/PDA and EPO/APPPOO thermosets are summarized in Table II and shown in Figures 5 and 6.

TTI is used to determine the influence on ignitability, which can be measured from the onset on an HRR curve. TTI showed clear differences in the ignition behavior of the different samples (Table II); TTI of the cured EPO/APPPOO system was shorter than that of EPO/PDA thermosets, and this may be the reason that the flame-retarded epoxy resins decomposed in air and formed phosphoric and polyphosphoric acids, which may accelerate the thermal decomposition of the material.

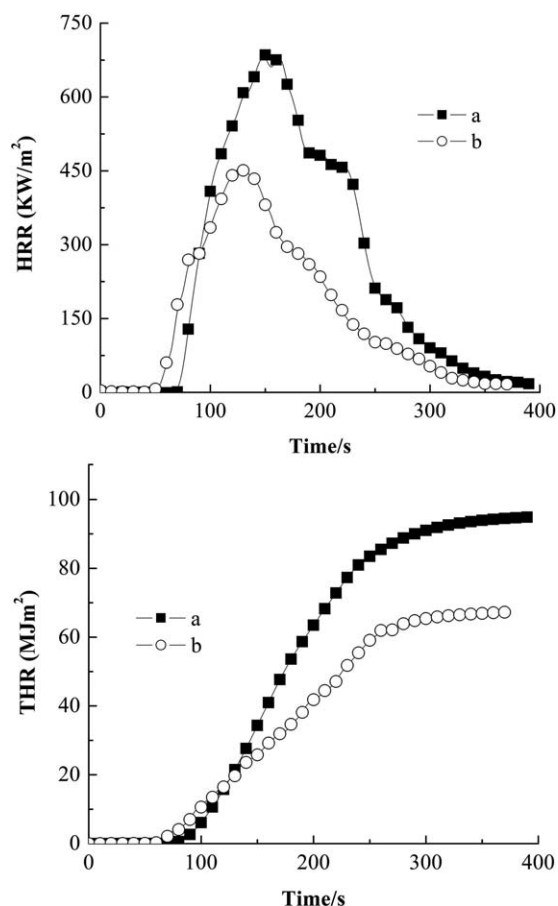


Figure 5. HRR and THR curves of EPO/PDA and EPO/APPPPO thermosets: (a) EPO/PDA and (b) EPO/APPPPO.

Figure 5 shows the HRR curves of cured EPO/PDA and EPO/APPPPO thermosets. The HRR of EPO/PDA system increased rapidly at the initial 100 s, and PHRR occurred at 150 s with the value of $685 \text{ kW}\cdot\text{m}^{-2}$. The HRR curve of EPO/APPPPO composite increased at a fast rate, PHRR occurred in a shorter time than did that of EPO/PDA system, and the PHRR and t_{PHRR} were $456 \text{ kW}\cdot\text{m}^{-2}$ and 125 s, respectively. The reduction of PHRR indicated that a cohesive char layer was formed during combustion which acted as an insulating barrier between the fire and the epoxy resins.²⁹ With the incorporation of APPPO into epoxy resins, the THR was decreased from $95 \text{ MJ}\cdot\text{m}^{-2}$ for EPO/PDA system to $67 \text{ MJ}\cdot\text{m}^{-2}$ as shown in Figure 5. The lower THR values indicated that a part of EPO/APPPPO had not completely combusted and possibly undergoing a char-forming process. It is believed that lower HRR and THR related to condensed phase and contributed to better flame retardancy for epoxy resin thermosets.

Apart from the heat release characteristics, the smoke, CO, and CO_2 releases are also important fire hazards. Smoke emission is caused by the evolution of the products of incomplete oxidation.²³ Owing to the aromatic structure, EPO/PDA and EPO/APPPPO systems evolved large amounts of smoke, the rate of smoke emission indicated by the ASEA decreased from $1015 \text{ m}^2\cdot\text{kg}^{-1}$ for the EPO/PAD system to $686 \text{ m}^2\cdot\text{kg}^{-1}$ for EPO/APPPPO system as summarized in Table II. Compared

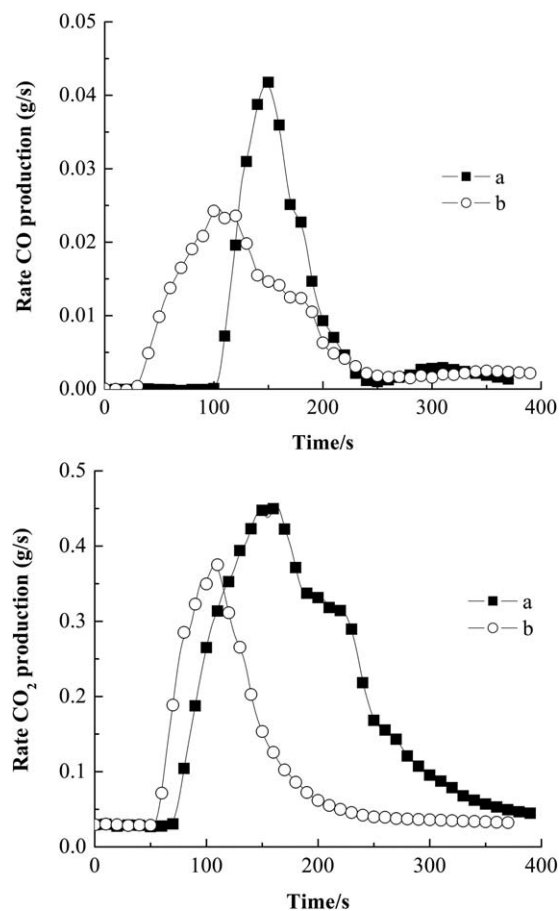


Figure 6. CO and CO_2 evolution for the epoxy resin system: (a) EPO/PDA and (b) EPO/APPPPO.

with the phosphorus-free system, the presence of phosphorus decreased the smoke production during combustion. Both CO and CO_2 production often indicate the flame-retardant mechanism.²³ Flame inhibition results in an increase in combustion products typically for incomplete combustion, in particular CO, whereas increased charring bears the potential decrease of the absolute CO production owing to an unchanged yield and a reduced mass loss. The temporal behavior of the CO and CO_2 evolution rate during the cone calorimetric experiments is shown in Figure 6. Compared with the EPO/PDA system, the phosphorus-containing sample of EPO/APPPPO system evolved less CO and CO_2 amount at a lower rate, which indicated that the chemical incorporation of phosphine oxide into the epoxy resins has a more effective flame-retardant effect in the condensed phase.

Figure 7 shows SEM images of the char layers of EPO/PDA and EPO/APPPPO systems after cone calorimeter test. A loose, porous structure was formed on the surface of EPO/PDA thermosets [Figure 7(a,b)]. The formed char layer with this structure failed to provide a good barrier to the transfer of heat and prevent the underlying epoxy resins from degradation and combustion. A very distinct difference in appearance was observed for the charred samples of EPO/APPPPO system and the surfaces of the material were covered by a continuous and compact

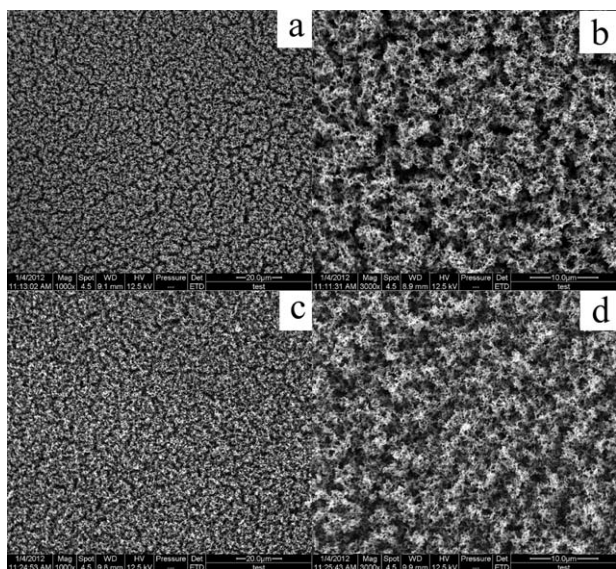


Figure 7. SEM of the char layer from combustion: (a) EPO/PDA thermosets magnified 1000 times; (b) EPO/PDA thermosets magnified 3000 times; (c) EPO/APPPPO thermosets magnified 1000 times; and (d) EPO/APPPPO thermosets magnified 3000 times.

char layer as shown in Figure 7(c,d). A high-quality char layer can effectively form a protective layer to stop the propagation of heat and oxygen to melt, and polymer matrix during combustion led to excellent flame retardancy of the epoxy resin thermosets.

Thermal Degradation Properties

The manner in which a sample loses mass with increasing temperature as measured using TGA provides direct information about the thermal stability and the degradation mechanism. Depending on the flame-retardant mechanism that is operating (in this case, largely related to the formation of a char layer), it also provides indirect information about the potential flame retardancy of the cured epoxy resins. The TGA curves of the cured epoxy resins performed under nitrogen and air

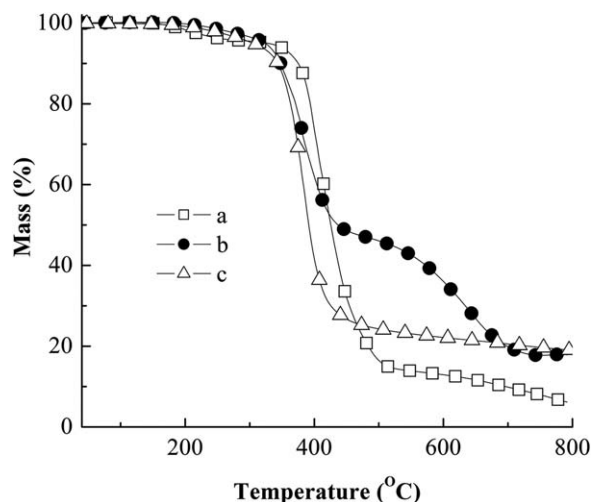


Figure 8. TGA curves of cured epoxy resins in N_2 : (a) EPO/PDA, (b) EPO/80 wt % APPPOO/20 wt % PDA, and (c) EPO/APPPPO.

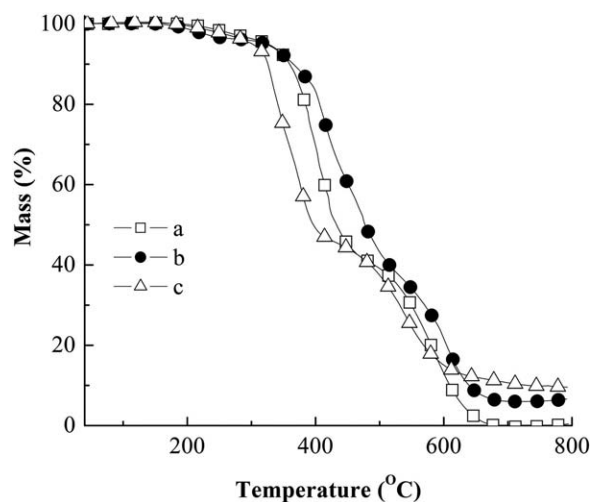


Figure 9. TGA curves of cured epoxy resins in air: (a) EPO/PDA, (b) EPO/80 wt % APPPOO/20 wt % PDA, and (c) EPO/APPPPO.

atmosphere are shown in Figures 8 and 9, and the data are summarized in Tables III and IV. $T_{initial}$ is defined as the temperature at which 5 wt % weight loss occurs and T_{max} is defined as the temperature at maximum weight loss rate.

The thermal decomposition of EPO/PDA and EPO/APPPPO thermosets occurred in one step in nitrogen atmosphere and EPO/80 wt % APPPOO/20 wt % PDA thermosets occurred in two steps as shown in Figure 8. $T_{initial}$ and T_{max} of EPO/PDA system were 328 and 397°C, respectively, and the char residue was 6.2% at 800°C. The initial decomposition temperature of EPO/80 wt % APPPOO/20 wt % PDA decreased from 328°C for EPO/PDA system to 310°C, the residual char enhanced from 6.2 to 17.2% at 800°C, and there were two mass loss peaks at

Table III. TGA Data of the Cured Epoxy Resins in Nitrogen

Samples	$T_{initial}$ (°C)	T_{max1} (°C)	T_{max2} (°C)	Char residues at 800°C (%)
EPO/PDA	328	397	-	6.2
EPO/80 wt % APPPOO/20 wt % PDA	310	374	621	17.2
EPO/APPPPO	305	380	-	19.3

Table IV. TGA Data of the Cured Epoxy Resins in Air

Samples	$T_{initial}$ (°C)	T_{max1} (°C)	T_{max2} (°C)	T_{max3} (°C)	Char residues at 800°C (%)
EPO/PDA	326	390	588	-	0.4
EPO/80 wt % APPPOO/20 wt % PDA	322	427	485	618	6.6
EPO/APPPPO	301	380	565	-	9.6

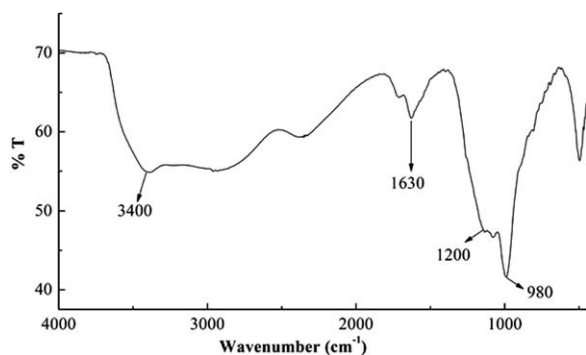


Figure 10. FTIR spectra of EPO/APPPPO thermosets during the thermal degradation in air at 600°C.

around 374 and 621°C which demonstrated two-step decomposition of the thermosets and the incorporation of APPPO changed the thermal degradation behaviors of epoxy resins. When the phosphorus content was increased in the cured epoxy resin system, the T_{initial} and T_{max} of EPO/APPPPO composite were 305 and 380°C, respectively, and the T_{initial} was lower than that of EPO/80 wt % APPPO/20 wt % PDA system, but the char residue was enhanced to 19.3% at 800°C. It was obvious that the char yields increased with the increase of phosphorus content in epoxy resins under nitrogen. The cured epoxy resins including APPPO could undergo degradation and produce phosphoric, polyphosphoric acid at a relative low temperature, and then the produced acids accelerated the decomposition of the epoxy resins and formed an insulating protective layer, which prevented the heat and oxygen from transferring to the surface of the materials and improved the fire performance.

The thermal decomposition curves of the cured epoxy resins in air atmosphere are shown in Figure 9 and the test data are summarized in Table IV. As summarized in Table IV, the T_{initial} of EPO/PDA thermosets in air is similar to those in nitrogen, which demonstrated that the thermal stability of phosphorus-containing epoxy resins did not decrease while they were being heated together with oxygen; furthermore, the following step of mass loss in air was not as rapid as that in nitrogen. However, two or three steps of mass loss appeared in the curves of the cured epoxy resins in air atmosphere, which was different from that of nitrogen. It was observed that the temperature of the first mass loss step of EPO/PDA and EPO/APPPPO was similar to those in nitrogen and the second step appeared at above 560°C, at which the thermal oxidative degradation occurred, the T_{initial} , T_{max1} , and T_{max2} of EPO/PDA thermosets were 326, 390 and 588°C, respectively, and the char residue was 0.4% at 800°C. For the epoxy resins containing phosphorus, the thermal decomposition behavior changed significantly and the T_{initial} of materials decreased with the increasing of phosphorus content in the epoxy resins (Figure 9 and Table IV) and the T_{initial} of EPO/80 wt % APPPO/20 wt % PDA and EPO/APPPPO thermosets were 322 and 301°C, respectively. Such a decrease of T_{initial} in decomposition temperature was characteristic for epoxy resins containing phosphorus, and the lower T_{initial} may be attributed to the fact that the P—C bond is less stable than the C—C bond. Typical bond energies of the P—C and C—C

bonds are 260 and 347 kJ·mol⁻¹, respectively. It can be deduced that P—C bond breaks first and then C—C bonds disconnect at a high temperature. The shift in degradation temperatures may be attributed to the fact that the cured epoxy resins could undergo oxidative degradation and form phosphoric and polyphosphoric acids at a relative lower temperature, and then the produced acids accelerated the decomposition of the epoxy resins. This phenomenon was reported earlier^{23,30,33} that *bis(m-aminophenyl)methylphosphine oxide* and *3,3'-bis(maleimido-phenyl)phenylphosphine oxide* were used as curing agents for epoxy resins and the thermosets thermal degradation in air atmosphere. T_{max1} , T_{max2} , and T_{max3} of EPO/80 wt % APPPO/20 wt % PDA system were 427, 485, and 618°C, respectively, but the residual char yield increased to 6.6% at 800°C. With the increasing of phosphorus content in epoxy resins, the T_{max1} and T_{max2} of EPO/APPPPO were 380 and 565°C, respectively, and the char residue enhanced to 9.6% at 800°C.

It can be seen that one additional mass loss peak was found at high temperature in air atmosphere owing to the oxidation of the formed char layer. Whether in air and nitrogen conditions, the char yields increased with the increase of phosphorus content in epoxy resins, which is in accordance with the mechanism of improved flame retardancy via phosphorus modification.²⁶ In this phenomenon, the phosphorus groups formed an insulating protective layer, which prevented the heat and oxygen from transferring to the surface of the materials and improved the flame retardancy of epoxy resin thermosets.

The FTIR spectrum of the residual char for EPO/APPPPO after thermal degradation in air at 600°C is shown in Figure 10. The absorption band at 1438 cm⁻¹ disappeared, which confirmed that P—C bond was broken and disappeared. Meanwhile, the broad peaks at 3400, 1200, and 980 cm⁻¹ appeared and the peaks at 3400 and 980 cm⁻¹ were attributed to the stretching vibration of P—OH groups and the peak at 1200 cm⁻¹ was attributed to P=O group^{34,34} because it was a process of thermal oxidative decomposition. The peak at 1630 cm⁻¹ presented polycyclic aromatic compounds in the char residues.³⁴ The FTIR spectra provided positive evidence that EPO/APPPPO produced phosphoric and polyphosphoric acids during thermal degradation in air, which acted as the dehydration agents and stimulated the formation of the char layer by carbonization. This result was in accordance with the mechanism mentioned above.

Mechanical Properties

Table V summarizes the mechanical properties of the cured epoxy resins. The tensile, flexural, and Izod impact strength of EPO/PDA were 52.2 MPa, 55.3 MPa, and 7.1 kJ·m², respectively. The incorporation of APPPO into epoxy resins showed a negative impact on the tensile, flexural, and Izod impact strength of the thermosets and the content of APPPO in the curing agent increased, the tensile, flexural, and Izod impact strength decreased. Based on the previous report,³⁵ although the intercrosslinking network formed, the incorporation of APPPO failed to increase the crosslink density and the mechanical properties of the cured resin decreased. The decrease of the tensile, flexural, and Izod impact strength was marginal when APPPO content increased from 20 to 60%. When the APPPO content

Table V. Mechanical Properties of the Cured Epoxy Resins

Curing agent compositions (APPPOO/PDA)	Mechanical properties		
	Tensile strength (MPa)	Flexural strength (MPa)	Izod impact Strength ($\text{kJ}\cdot\text{m}^{-2}$)
0/100	52.2 ± 0.1	55.3 ± 0.2	7.1 ± 0.1
20/80	50.0 ± 0.2	52.8 ± 0.3	6.2 ± 0.1
40/60	48.5 ± 0.3	51.2 ± 0.2	5.9 ± 0.2
60/40	46.7 ± 0.1	49.7 ± 0.2	5.5 ± 0.2
80/20	44.9 ± 0.4	48.3 ± 0.1	5.2 ± 0.1
100/0	43.3 ± 0.2	46.8 ± 0.2	4.8 ± 0.3

was increased to 80%, the tensile, flexural, and Izod impact strength of the cured epoxy resins decreased to 44.9 MPa, 48.3 MPa, and 5.2 $\text{kJ}\cdot\text{m}^{-2}$, respectively. For EPO/APPPOO system, the tensile, flexural, and Izod impact strength were 43.3 MPa, 46.8 MPa, and 4.8 $\text{kJ}\cdot\text{m}^{-2}$, respectively.

The previous research on the flame-retarded epoxy resins with phosphorus compounds showed deteriorative mechanical properties. For example, Liu et al.³⁵ reported that the

flexural strength of diglycidyl ether of bisphenol A/*bis*(4-aminophenoxy)phenyl phosphonate system decreased by 42.8% compared with bisphenol A/diethyltoluenediamine. However, the flexural strength of EPO/APPPOO decreased only by 15.4% in our study. It was demonstrated that the prepared curing agent of APPPOO caused slightly harmful effect on the mechanical properties of the cured epoxy resins.

Water Resistance

Water resistance of epoxy resins is of some concern because of the inherent hydrophilic nature of epoxy resins network. Water uptake most likely deteriorates its flame retardancy and mechanical properties because of greater exposure to the moisture condition.^{30,33}

Figure 11 shows the effect of the time on mass increase and flame retardancy of cured epoxy resins. After 3 days of the test, the increase of sample mass was marginal and their flame retardancy had not obviously change for all the samples. After 7 days, the mass increase of EPO/PDA thermosets was 1.6% and the LOI value dropped to 16.8%. However, the mass increase was lower than that of EPO/PDA system and water uptake decreased with increasing the content of APPPOO for the epoxy

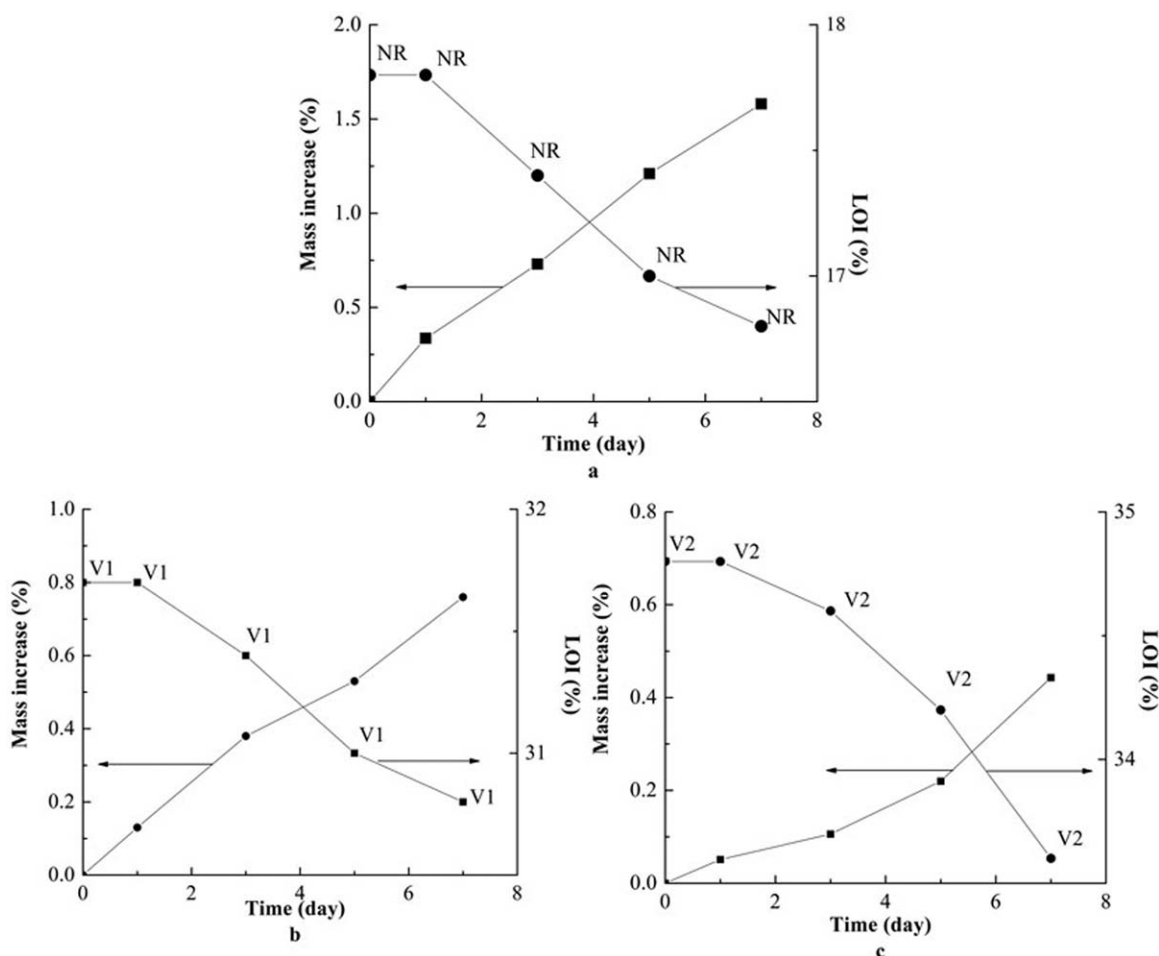


Figure 11. Effect of the time on mass increase and flame retardancy of cured epoxy resins during water-resistance test: (a) EPO/PDA, (b) EPO/80 wt % APPPOO/20 wt % PDA, and (c) EPO/APPPOO, vertical burning tests: (a,b) 3.0-mm samples and (c) 1.6-mm samples.

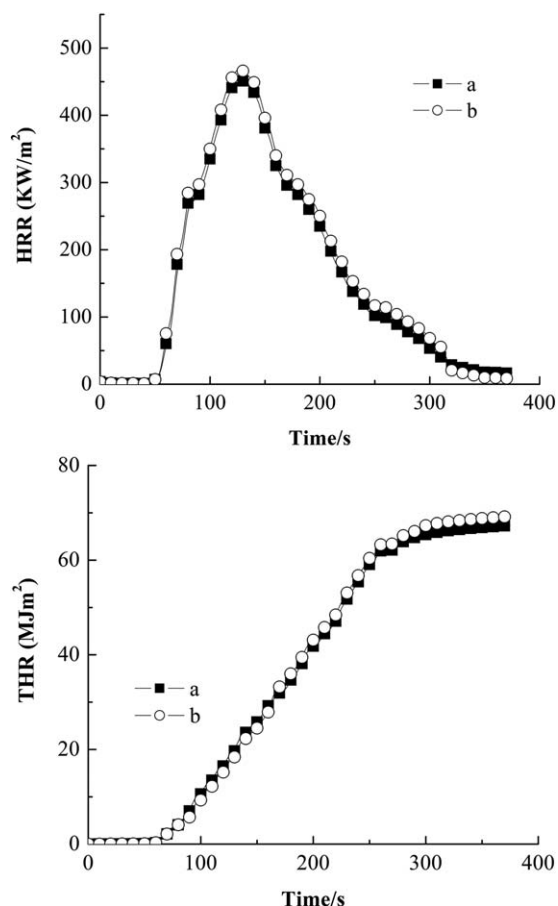


Figure 12. HRR and THR curves of EPO/APPPPO before and after water-resistance test. (a) Before the test and (b) after the test.

resins cured with APPPOO. For example, after the water-resistance test, the mass increase of EPO/APPPPO system was only 0.4% and the LOI value decreased to 33.6%. Although the LOI value decreased, EPO/80 wt % APPPOO/20 wt % PDA thermosets with 3.0-mm samples and EPO/APPPPO with 1.6 mm samples kept V-1 and V-2 rating, respectively. Figure 12 and Table VI shows and summarized the cone test results of EPO/APPPPO thermosets before and after the water-resistance

Table VI. Cone Results of EPO/APPPPO Thermosets Before and After Water-Resistance Test

Sample	Before the test	After the test
TTI (s)	50	50
PHRR ($\text{kW}\cdot\text{m}^{-2}$)	456	470
THR ($\text{MJ}\cdot\text{m}^{-2}$)	67	69
t_{PHRR} (s)	125	130
ASEA ($\text{m}^2\cdot\text{kg}^{-1}$)	686	697
AMLR ($\text{g}\cdot\text{s}^{-1}$)	0.08	0.09

test. TTI of the samples was not changed and the values of THR, PHRR, t_{PHRR} , AMLR, and ASEA increased slightly after the water-resistance test. Overall, the test did not deteriorate its flame retardancy although the sample was placed into hostile condition. Figure 13 shows SEM images of the char layer obtained from cone test of EPO/APPPPO thermosets before and after water-resistance test. It can be observed that the surface morphologies of the char layer kept continuous and dense, which indicated that the water-resistance test did not deteriorate the char layer formed after combustion. Consequently, the samples kept good flame retardancy after the water-resistance test.

Table VII summarizes the effect of the time on mechanical properties of the cured epoxy resins. It was obvious that the mechanical properties of the samples decreased with the extension of the test time. After 7 days, the tensile, flexural, and Izod impact strength of EPO/PDA thermoset reduced by 4.6, 4.0, and 26.8%, respectively. The tensile, flexural, and Izod impact strength of EPO/80 wt % APPPOO/20 wt % PDA composite reduced by 3.3, 3.5, and 23.1%, respectively, after the water-resistance test and for EPO/APPPPO system, the tensile, flexural, and Izod impact strength reduced by 3.0, 2.7, and 19.0%, respectively. As a result, the reduction of the mechanical properties of epoxy resins cured with APPPOO was slight and decreased with increasing the content of APPPOO.

Hergenrother et al.³⁰ reported that the mass increase of *N,N,N',N'*-tetraglycidyl-4,4'-methylenedianiline/*bis*(4-aminophenyl)

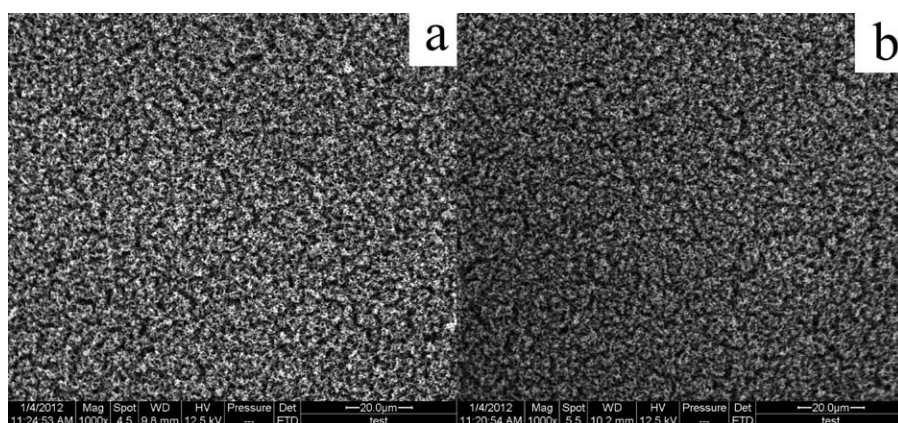


Figure 13. SEM of the char layer of EPO/APPPPO from combustion before and after water-resistance test: (a) before test and (b) after test.

Table VII. Mechanical Properties of EPO/PDA and EPO/APPPOO Thermosets During Water-Resistance Test

Samples	Time (days)	Mechanical properties		
		Tensile strength (MPa)	Flexural strength (MPa)	Izod impact strength (kJ·m ⁻²)
EPO/PDA	0	52.2 ± 0.1	55.3 ± 0.2	7.1 ± 0.1
	1	52.0 ± 0.2	55.1 ± 0.1	7.0 ± 0.1
	3	51.5 ± 0.2	54.7 ± 0.1	6.6 ± 0.2
	5	50.7 ± 0.1	54.0 ± 0.1	6.0 ± 0.2
	7	49.8 ± 0.1	53.1 ± 0.2	5.2 ± 0.3
EPO/80 wt % APPPOO/20 wt % PDA	0	44.9 ± 0.4	48.3 ± 0.1	5.2 ± 0.1
	1	44.8 ± 0.2	48.2 ± 0.1	5.2 ± 0.2
	3	44.5 ± 0.1	47.9 ± 0.1	5.0 ± 0.1
	5	44.0 ± 0.2	47.4 ± 0.2	4.6 ± 0.1
	7	43.3 ± 0.2	46.6 ± 0.2	4.0 ± 0.2
EPO/APPPOO	0	43.3 ± 0.2	46.8 ± 0.2	4.8 ± 0.3
	1	43.3 ± 0.1	46.8 ± 0.1	4.8 ± 0.2
	3	43.0 ± 0.1	46.5 ± 0.3	4.6 ± 0.3
	5	42.6 ± 0.2	46.1 ± 0.2	4.3 ± 0.2
	7	42.0 ± 0.1	45.5 ± 0.3	3.9 ± 0.2

methylphosphonate, diglycidylmethylphosphonate/4,4'-diaminodiphenyl sulfone, and triglycidylphosphate/4,4'-diaminodiphenyl sulfone were 2.6, 2.9, and 4.3%, respectively, after the water-resistance test. However, the mass increase of EPO/APPPOO thermoset was just only 0.4% in our study. At present, the effect of water resistance on flame retardancy and mechanical properties of cured epoxy resins has never been reported. In this study, the results of the water-resistance test indicated that the epoxy resins cured with APPPOO possessed excellent water resistance because of aromatic and P—C hydrophobic structures.^{23,33} The water resistance increased with increasing the content of APPPOO and it was demonstrated that the APPPOO played an important role in improving water resistance of the cured epoxy resins.

CONCLUSIONS

A novel amine-terminated and phosphorus-containing compound with P—C bond structure was successfully synthesized and used as curing and flame-retarding agent for preparing flame-retardant epoxy resin thermoset. The LOI value of EPO/APPPOO thermosets reached 34.8% and the samples with the thickness of 3.0 and 1.6 mm can pass UL-94 V-1 and V-2 rating, respectively. TGA test revealed that T_{initial} decreased when the phosphorus content increased, but the char residue increased at high temperature. A sufficient, compact, and homogeneous char layer formed through SEM micrographs after cone test of EPO/APPPOO thermosets, which can prevent the transfer of heat and oxygen into underlying polymer matrix. The result of mechanical properties test indicated that the incorporation of APPPOO slightly deteriorated the mechanical properties of the cured epoxy resins. The epoxy resin thermosets cured with APPPOO possessed excellent water resistance, and still remained excellent flame retardant and mechanical properties after water resistance testing.

ACKNOWLEDGMENTS

The authors are grateful for funding support by National Nature Science Foundation of China (Grant No. 21174025), China Postdoctoral Science Foundation (2012M510907, 2013T60339), Heilongjiang Postdoctoral Grant (LBH-Z11252), Youth Science Fund of Heilongjiang Province (QC2011C102), and Heilongjiang Major Research Projects (GA12A102).

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