

Synthesis of a novel phosphonate flame retardant and its application in epoxy resins

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ABSTRACT: A novel phosphonate flame retardant additive bis(2,6-dimethylphenyl) phenylphosphonate (BDMPP) was synthesized from phenylphosphonic dichloride and 2,6-dimethyl phenol, and its chemical structure was characterized by Fourier transform infrared (FTIR) spectroscopy, ¹H and ³¹P nuclear magnetic resonance. The prepared BDMPP and curing agent *m*-phenylenediamine were blended into epoxy resins (EP) to prepare flame retardant EP thermosets. The effect of BDMPP on fire retardancy and thermal degradation behavior of EP/BDMPP thermosets was investigated by limiting oxygen index (LOI), vertical burning test (UL-94), cone calorimeter and thermogravimetric analysis (TGA). The morphologies of char residues of the EP thermosets were investigated by scanning electron microscopy (SEM) and the water resistant properties of thermosets were evaluated by putting the samples into distilled water at 70°C for 168 h. The results demonstrated that the cured EP/14 wt % BDMPP composites with the phosphorus content of 1.11 wt % successfully passed UL-94 V-0 flammability rating and the LOI value was as high as 33.8%. The TGA results indicated that the introduction of BDMPP promoted EP matrix decomposed ahead of time compared with that of pure EP and led to a higher char yield at high temperature. The incorporation of BDMPP enhanced the mechanical properties and reduced the moisture absorption of EP thermosets. The morphological structures of char residue revealed that BDMPP benefited to the formation of a more compact and homogeneous char layer on the materials surface during burning, which prevented the heat transmission and diffusion, limit the production of combustible gases and then lead to the reduction of the heat release rate. After water resistance tests, EP/BDMPP thermosets still remained excellent flame retardancy. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42765.

KEYWORDS: degradation; flame retardance; thermogravimetric analysis; thermosets

Received 22 November 2014; accepted 21 July 2015

DOI: 10.1002/app.42765

INTRODUCTION

Epoxy resins (EP) have been widely used in surface coating, adhesives, laminates, encapsulates for semiconductor and insulating materials for electric devices due to their excellent mechanical and chemical properties.¹ However, conventional EP are very flammable and they can not satisfy some applications which require high flame retardant grade.² Therefore, the enhancement of the flame retardancy for EP is becoming an urgent problem and has attracted more and more attention. Traditionally, halogenated compounds have been widely used as co-monomers or additives with EP to obtain flame retardant materials. However, flame retardant EP containing bromine or chlorine can produce poisonous and corrosive smoke and may produce highly toxic halogenated dibenzodioxins and dibenzofurans.^{3–5} Thus, the development and application of halogen-free flame retardant has been a subject of extensive investigation for EP. A wide variety of halogen-free flame retardants contain-

ing silicon,^{6–8} phosphorus,^{9–12} nitrogen,¹³ carbon nanotube,¹⁴ boron,^{15,16} layer double hydroxide,¹⁷ montmorillonite¹⁸ etc. have been explored to improve their flame retardancy in the past decades. Among them, phosphorus-containing compounds is considered to be one promising method for flame retardant EP because the phosphorous-containing compounds can promote EP to form a carbonaceous char due to the excellent capacity of EP, which acts as a physical barrier to heat transfer from the flame to the matrix and the diffusion of combustible gas and smoke.^{10,11} On the other hand, 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.¹⁹

The phosphorus-containing compounds mainly including phosphates, ammonium polyphosphates and phosphate esters were used as flame retardants additive in EP.^{20,21} However,

phosphates and ammonium polyphosphates may disperse heterogeneously in matrices and greatly affect mechanical properties, and sometimes incompatible with matrices.²² Regarding to conventional phosphate esters which only containing P—O—C bond, most of them are liquid, which may resulting in volatility in processing and difficulty in transportation. In addition, these compounds which only containing P—O—C bond hydrolyze easily and have poor resistance to acid and base. However, the derivatives of phosphine alkane which only contain P—C bond,^{23,24} the flame retardant efficiency is not good enough although higher thermal stability and strong capability of hydrolysis resistance can be observed. In our previous work,²³ the curing agent of *m*-aminophenylene phenyl phosphine oxide oligomer (APPPOO) contain only P—C bond was synthesized and incorporated into EP, the EP thermosets cured with APPPOO passed UL-94 V-1 flammability rating, meanwhile the phosphorus content was as high as 3.3 wt % in composites. But the composites possess excellent water resistance and still maintained excellent flame retardancy after water resistance tests. In order to obtain the flame retardant EP thermosets with excellent comprehensive properties as well as flame and moisture resistance, the introduction of phosphorus containing flame retardant containing both P—O—C and P—C bonds may be an alternative approach.

In this work, a novel phosphonate flame retardant bis(2,6-dimethylphenyl) phenylphosphonate (BDMPP) including both P—O—C and P—C bonds was synthesized and confirmed by FTIR, ¹H NMR and ³¹P NMR. The prepared BDMPP flame retardant additive was incorporated into EP and cured with *m*-Phenylenediamine (PDA) to prepare flame retardant EP/BDMPP thermosets. The flame retardancy, details of fire behavior, thermal degradation behavior and moisture absorption of EP/BDMPP thermosets were investigated by limiting oxygen index (LOI), vertical burning test, cone calorimeter tests, thermogravimetric analysis and water resistance tests, respectively.

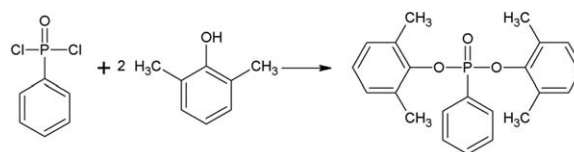
EXPERIMENTAL

Materials

Phenylphosphonic dichloridewas (DCPPO) purchased from Kaisai Chemicals (Shanghai, China). 2, 6-Dimethylphenol, magnesium sulfate (MgSO₄) and triethylamine (TEA) were purchased from Guangfu Fine Chemical Research Institute (Tianjin, China). Toluene was purchased from Baishi Chemicals (Tianjin, China). Sodium, calcium chloride and benzophenone were purchased from Yili Fine Chemicals (Beijing, China). PDA was obtained from Sinopharm Chemical Reagent (Shanghai, China). EP (E-44, epoxide equivalent weights = 213 g/epoxide) of technical grade was supplied by Fude Chemicals Industry (Guangzhou, China).

Synthesis of Bis(2,6-dimethylphenyl) Phenylphosphonate (BDMPP)

The synthetic route of BDMPP is shown in Scheme 1. In a 250 mL, four-necked flask equipped with thermometer, mechanical stirrer, reflux condenser and pressure-equalizing funnel, 2, 6-dimethylphenol (25.6 g, 0.21 mol), 29 mL of TEA and 100 mL of toluene were added. The reaction mixture was maintained at 3–5°C and DCPPO was added dropwise into the



Scheme 1. Synthetic route of BDMPP.

mixture with stirring. Thereafter, the reaction mixture was gradually heated to 80°C and maintained at that temperature for 8 h until no HCl gas emitted. The organic phase obtained by separating funnel was washed three times by water and then dried with MgSO₄ over night. The solvent was removed by rotary evaporator under reduced pressure and the precipitate was dried in a vacuum drying oven at 65°C for 12 h. Finally, the white crystals were obtained and the weight was 33.8 g (92.6%). The melt point of BDMPP was 115.5°C.

FTIR (KBr, cm⁻¹): 3063, 3051 (aromatic C—H); 2960, 2926 (methyl C—H); 1592, 1471 (aromatic C—C); 1443 (P—Ph). ¹H NMR (300 MHz, DMSO-*d*₆, ppm): 2.2 (proton of methyl); 7.0–8.1 (aromatic proton). ³¹P NMR (300 MHz, DMSO-*d*₆, ppm): 9.8 (O=P—O).

Characterization

The chemical structure of the synthesized BDMPP was determined by a combination of Fourier transform infrared (FTIR) spectroscopy and nuclear magnetic resonance (NMR) spectroscopy tests. FTIR spectra were recorded from samples pressed into pellets with KBr powder using a Nicolet Avator 360 spectrometer. NMR spectra were obtained using 10–25% solutions in deuterium dimethyl sulfoxide (DMSO-*d*₆) and Bruker 300 NMR (300 MHz) spectrometer (Germany). 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.

Preparation of EP Thermosets

To prepare cured EP/BDMPP composites with different content of BDMPP additive, the flame retardant additive of BDMPP, EP and the curing agent (PDA) were mixed homogeneously in an epoxide/amino equivalent ration of 1/1 by mechanical stirrer at 120°C. The liquid mixtures were poured into a mold, cured at 105°C for 2 h and post cured at 150°C for 2 h. After curing, all samples were cooled to room temperature and carried out the LOI and UL-94 tests. The content of BDMPP additive in the composites was listed in Table I.

Flame Retardancy Tests

The 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 mm³. Vertical burning (UL-94) tests were performed on a CZF-2-type instrument (Jiangning Analysis Instrument Company, China) according to UL-94 test standard with specimen dimension of 130 × 13 × 3.2 mm³. 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.

Table I. Formulations and Flame Retardancy for Cured EP Composites

Sample	Components (wt %)			Flame retardancy	
	EP	BDMPP	Phosphorus content	UL-94	LOI (%)
EP-0	100	0	0	No rating	20.3 ± 0.2
EP-6	94	6	0.47	No rating	29.7 ± 0.2
EP-8	92	8	0.63	No rating	31.4 ± 0.1
EP-10	90	10	0.79	V-1	32.5 ± 0.2
EP-12	88	12	0.94	V-1	33.1 ± 0.2
EP-14	86	14	1.11	V-0	33.8 ± 0.2
EP-16	84	16	1.27	V-0	34.3 ± 0.2
EP-18	82	18	1.43	V-0	35.0 ± 0.1

Cone Calorimeter Tests

The combustion behavior under ventilated conditions was measured using cone calorimeter (West Sussex, UK), in conformance with ISO 5660-1 standard. Samples with size of $100 \times 100 \times 4 \text{ mm}^3$ 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 (SEM)

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.

Thermalgravimetric Analysis

The thermalgravimetric analysis (TGA) was carried out using a Perkin Elmer Pyris 1 Thermal Gravimetric Analyzer (Massachusetts, USA) at a heating rate of $10^\circ\text{C min}^{-1}$, heating from 50 to 700°C under nitrogen with a flow rate of 20 mL min^{-1} . The weight of the samples was kept within 4–5 mg. All thermal degradation data were obtained from the TGA and derivative thermal gravimetric analysis (DTG) curves.

Mechanical Properties Test

Tests of tensile strength and flexural strength of all samples were performed by Regeer computer controlled mechanical instrument (Shenzhen, China) and Notched Izod impact instrument (Chengde, China), respectively, according to 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.

Moisture Resistance Test

In order to perform the hydrolysis resistance test, the cured EP specimens were kept in water at 70°C for 168 h and the water was replaced every 24 h, then the water on the surface of the specimens was wiped by filter paper. The moisture absorption was evaluated in terms of mass increase of samples. The specimens for flame retardancy tests were dried in a vacuum oven at 105°C for 72 h. Mass increase of the samples was tested with the dimension of $50 \times 50 \times 1 \text{ mm}^3$. Flame retardancy was tested with the same dimension as previously mentioned.

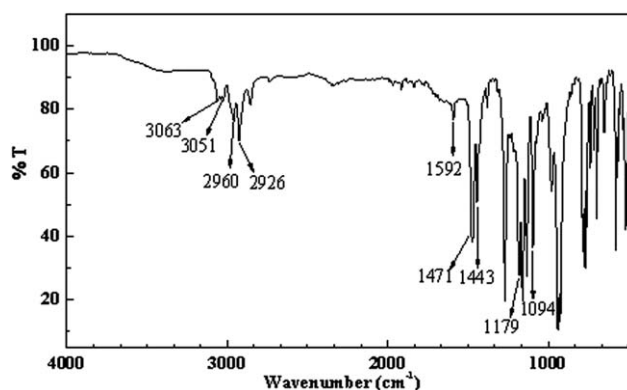
RESULTS AND DISCUSSION

Characterization

The chemical structure of the prepared BDMPP was characterized by FTIR, ^1H NMR, and ^{31}P NMR, respectively. As shown in Figure 1, the FTIR spectra of BDMPP with characteristic peaks as follows: the peaks at 3063 and 3051 cm^{-1} were attributed to the aromatic C—H stretching vibration, 2960 and 2926 cm^{-1} were assigned to the C—H stretching for methyl. The absorption peaks at 1592 and 1471 cm^{-1} corresponding to phenyl nucleus, 1443 cm^{-1} was assigned to P—Ph stretching. The ^1H NMR spectrum of the synthesized BDMPP was shown in Figure 2. The chemical shifts of protons (a) of methyl at 2.2 ppm, and the chemical shifts of the protons (b), (c) and (d) of the aromatic ring were observed at 7.0, 7.5–7.6, and 8.0–8.1 ppm, respectively. As revealed in Figure 3, the ^{31}P NMR spectrum of BDMPP appeared a single resonance at 9.8 ppm, which suggested that there exists only unique phosphorus containing compound. The characterization results of FTIR and NMR confirmed the chemical structure of BDMPP.

Flame Retardancy

The effect of the BDMPP on the LOI values and UL-94 vertical burning tests of the EP thermosets were presented in Table I. It can be seen that the pure EP thermosets is highly combustible with the LOI value of 20.3%. The LOI value of the cured EP/BDMPP composite is dramatically increased from 20.3% for pure EP to 29.7% when the loading amount of BDMPP is only

**Figure 1.** FTIR spectrum of BDMPP.

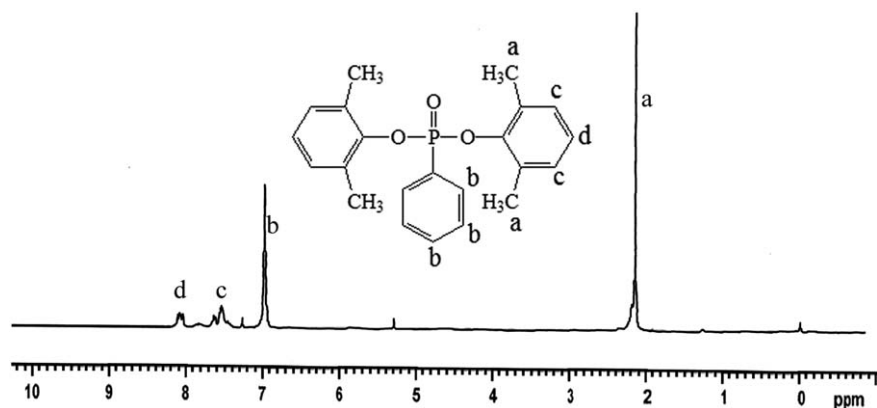


Figure 2. ^1H NMR spectrum of BDMPP.

6 wt % (sample EP-6), meanwhile the phosphorus content is merely 0.47 wt % in the thermosets. The flame retardancy of the EP/BDMPP thermosets gradually increases with the improvement of the BDMPP and phosphorus content in the composite. The sample of EP-14 can successfully pass UL-94 V-0 flammability rating and the LOI value is as high as 33.8% when the BDMPP content is 14 wt % with the phosphorus content of 1.11 wt % in the EP thermosets, which indicates that the BDMPP additive is effective for flame retardant EP materials. The LOI value of EP-18 sample is increased to 35.0% and the sample pass UL-94 V-0 when the load amount of BDMPP is 18 wt %. The fact can be attributed that the BDMPP flame retardant additive in EP can act as acid precursors and decompose to phosphoric and polyphosphoric acid during combustion which promotes the formation of char layer in the condensed phase.²⁵ 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 BDMPP 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.¹⁹ The reaction can interrupt the exothermic processes and suppress combustion by a radical mechanism.

Whilst the LOI and UL 94 tests are useful small-scale test for flame retarded polymer. The cone calorimeter measurement,

which can provide a wealth of information to simulate real fire conditions,²⁶ is used to investigate the effect of BDMPP on the fire behavior of the EP thermosets. The related combustion 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 produce rate (SPR), total smoke produce (TSP), CO production rate (COPR), CO₂ production rate (CO₂PR) and effective heat combustion (EHC) are determined and used to predict the combustion behavior of materials in real fires. The plots and the detailed information of combustion behavior for cured pure EP (sample EP-0) and EP/14 wt % BDMPP thermosets (sample EP-14) obtained from the cone calorimeter test at a heat flux of 50 kW·m⁻² are presented in Figures 4–6 and Table II.

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 reveals in Table II, TTI of EP-14 decrease from 75 s for EP-0 to 65 s. The phenomenon may be attributed that the BDMPP flame retardant additive not only decompose ahead of time itself but also promote the EP 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 EP-14.

The HRR is recognized to be the most important parameter to quantify the size of fire and an effective flame retardant system

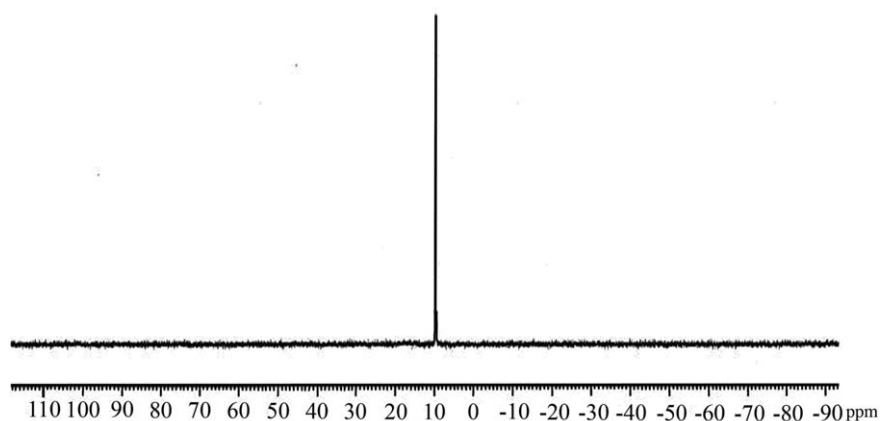


Figure 3. ^{31}P NMR spectrum of BDMPP.

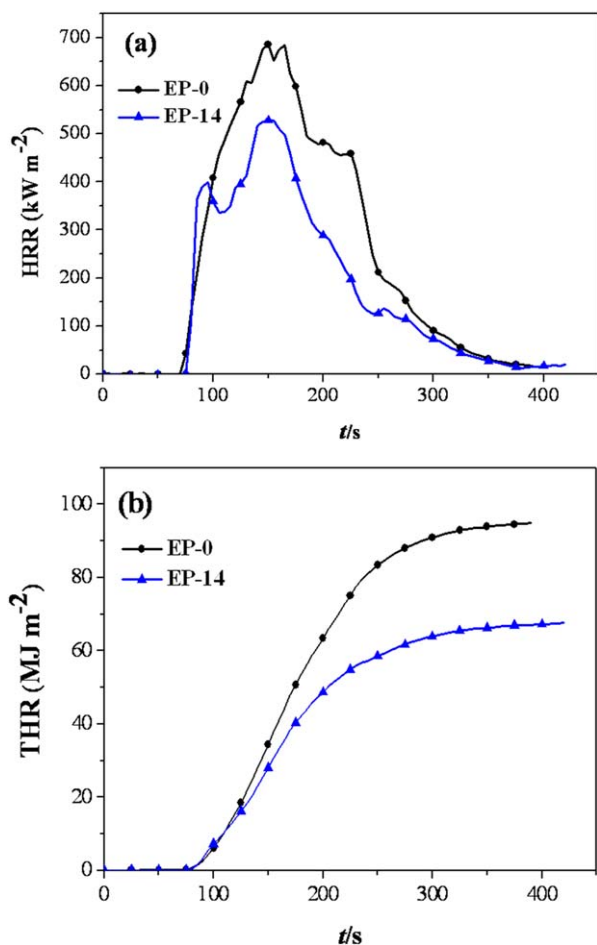


Figure 4. HRR (a) and THR (b) curves of cured EP-0 and EP-14 thermosets. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. CONE Data of EP-0 and EP-14 Thermosets

Sample	EP-0	EP-14
TTI (s)	75	65
Peak ₁ -HRR (kW·m ⁻²)	685	398
t peak ₁ -HRR(s)	150	92
Peak ₂ -HRR (kW·m ⁻²)	–	528
t peak ₂ -HRR(s)	–	155
THR (MJ·m ⁻²)	95	68
PHRR/TTI (kW·m ⁻² ·s ⁻¹)	10.5	7.0
Mean EHC (MJ·kg ⁻¹)	20.03	16.47
peak ₁ -SPR (m ² ·s ⁻¹)	0.32	0.30
t peak ₁ -SPR (s)	160.4	84.1
peak ₂ -SPR (m ² ·s ⁻¹)	–	0.45
t peak ₂ -SPR (s)	–	143.9
TSP (m ² ·kg ⁻¹)	45.89	48.34
peak ₁ -COPR (g·s ⁻¹)	0.042	0.027
t peak ₁ -copr (s)	150.2	89.3
peak ₂ -COPR (g·s ⁻¹)	0.003	0.039
t peak ₂ -copr (s)	307.1	149.4

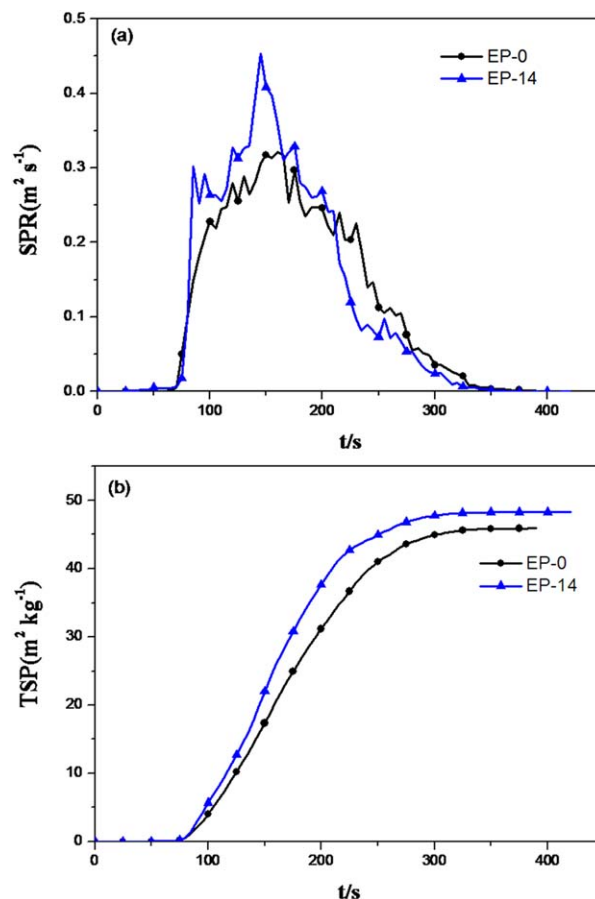


Figure 5. SPR (a) and TSP (b) curves of cured EP-0 and EP-14 thermosets. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

normally shows a lower HRR value. Figure 4(a) gives the HRR curves of EP-0 and EP-14, and the results reveal that the cured pure EP burns rapidly after ignition and only one sharp HRR peak appears with a PHRR of $685 \text{ kW} \cdot \text{m}^{-2}$ at 150 s. However, the HRR curve of EP-14 shows two peaks. The first HRR peak appears at 92 s and earlier than that of EP-0, which may be corresponding to the BDMPP additive decomposes itself at the early stage on heating and stimulates the EP matrix to degrade and charring at lower temperature. The insulation of char layer formed on the surface of matrix, that is, the heat insulating char causes a rapid rise in the surface temperature and accelerates the decomposition of EP matrix on the surface of the composites. Peak₁-HRR value of EP-14 is $398 \text{ kW} \cdot \text{m}^{-2}$, which is much lower than that of EP-0 due to the surface decomposition and burning of EP-14. The second HRR peak of EP-14 can be observed at 155 s, the time is similar to that of EP-0. However, the PHRR is obviously decreased from $685 \text{ kW} \cdot \text{m}^{-2}$ for EP-0 to $528 \text{ kW} \cdot \text{m}^{-2}$. It is confirmed that the phosphonate compound of BDMPP can promote EP thermosets to char due to the charring capacity of EP themselves, which prevents the transfer of heating during the ignition process from the samples. On the other hand, the BDMPP additive both containing P–C and P–O–C bonds can produce PO, P, and P₂ species which likely to react with H and OH radicals to form HPO and interrupt

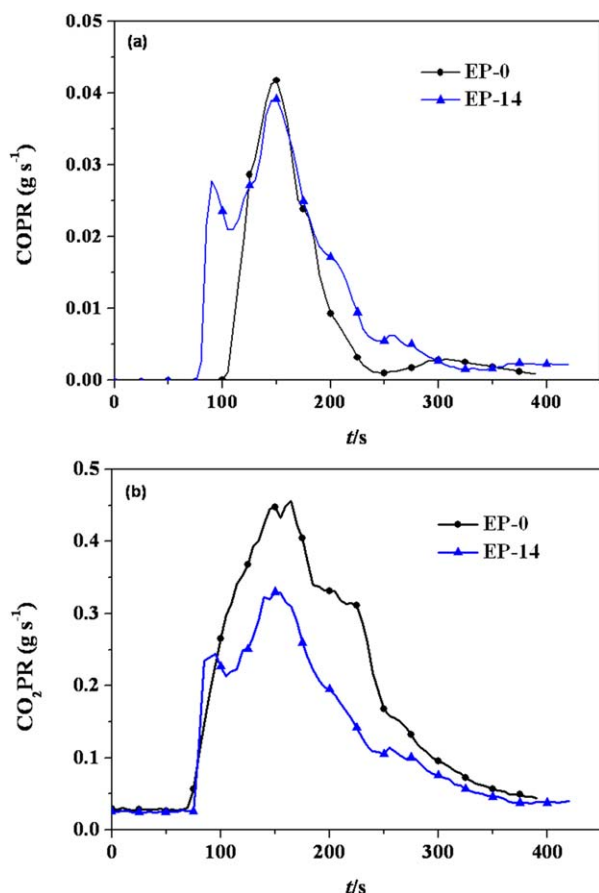


Figure 6. COPR (a) and CO_2PR (b) curves of cured EP-0 and EP-14 thermosets. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the exothermic processes and suppress combustion by a radical mechanism.¹⁹ Consequently, the intensity of combustion pyrolysis reactions is degraded and the release of the quantity of heat is also decreased. With the incorporation of BDMPP into EP, the THR is decreased from $95 \text{ MJ}\cdot\text{m}^{-2}$ for EP-0 to $68 \text{ MJ}\cdot\text{m}^{-2}$, as revealed in Figure 4(b) and Table II. The lower THR values indicate that a part of EP-14 has not completely combusted and possibly undergoing a char-forming process.

The smoke production along with the HRR is also considered as another critical parameter in fire. The SPR and TSP curves of the cured pure EP and EP-14 are presented in Figure 5. Compared with the SPR curve of pure EP, the value of EP-14 composites with the BDMPP loading of 14 wt % appears higher and the peak appears earlier due to the rapid decomposition of BDMPP on the sample surface at the initial stage on heating, as revealed in Figure 5(a). The main decomposition products of BDMPP are probably PO, P and P₂ species which likely to react with H and OH radicals produced from the decomposition of EP to form HPO during combustion process.¹⁹ The reaction can inhibit the further degradation of EP and act the gas phase flame retardant mechanism, resulting in amount of smoke emission. The value of TSP of EP-14 composite increase from $45.89 \text{ m}^2\cdot\text{kg}^{-1}$ for cured pure EP to $48.49 \text{ m}^2\cdot\text{kg}^{-1}$, as reveals in Figure 5(b).

The COPR and CO_2PR curves for EP-0 and EP-14 thermosets are similar to the HRR curves, as reveals in Figure 6, and the first peaks of COPR and CO_2PR for EP-14 composite appear earlier than that of the cured pure EP due to the incorporation of BDMPP stimulates the decomposition of EP at earlier stage on heating. It is speculated that BDMPP can accelerate the release of CO and CO_2 . According to the previous discussion, the introduction of BDMPP can stimulate EP matrix to form more sufficient carbonaceous char and lead to the lower mass loss rates. The COPR is obtained from the product of the CO yield (kg/kg) and the mass loss rate (g/s), thus the lower mass loss rate give higher COPR and the peak value of EP-14 is almost as high as that of EP-0. As a result, the increased char yield of the EP with 14 wt % BDMPP content induces the potential decrease of the CO_2PR , as reveals in Figure 6(b).

The EHC is heat released from combustion of the volatile portion of the material. The lower EHC value indicated that non-combustible gas exist in gas phase. As revealed in Table II, the averaged value of EHC of EP/14 wt % BDMPP thermosets decreases from $20.03 \text{ MJ}\cdot\text{kg}^{-1}$ for cured pure EP system to $16.47 \text{ MJ}\cdot\text{kg}^{-1}$. The fact is mainly attributed that the BDMPP both containing P—C and P—O—C bonds decompose and produce PO, P and P₂ species which likely to react with H and OH radicals to form HPO during combustion process.¹⁹ The action of the BDMPP compounds can take place in the vapor phase by a radical mechanism to interrupt the exothermic processes and suppress combustion. The another reason is that the thermosets containing BDMPP release noncombustible gases, such as CO_2 during the combustion process, which can dilute flammable gases and reduce the oxygen concentration around the material. The nonflammable gases can play an important role in the gas phase.

Thermal Degradation Behavior

A sample loses mass with increasing temperature can be measured by TGA, which provides direct information about the thermal stability, char formation and the degradation behavior of samples. It also can provide indirect information about the potential flame retardancy of the cured EP largely related to the formation of a char residue on heating. The initial decompose temperature defined as the temperature at which 1 wt % weight loss occurs and T_{max} defined as the temperature at maximum weight loss rate. The TGA and DTG curves of BDMPP, cured pure EP (sample EP-0) and EP/14 wt % BDMPP thermosets (sample EP-14) under nitrogen atmosphere are presented in Figure 7, and the related thermal degradation data are summarized in Table III. BDMPP begins to decompose at 227.6°C and almost decompose completely below 350°C , consequently the char yield of BDMPP is 0 wt % at 700°C . The thermal decomposition process of BDMPP appears one step, as revealed in DTG curves of BDMPP in Figure 7(b), the main weight loss in the temperature range of $230\text{--}310^\circ\text{C}$ associated with the thermal decomposition of BDMPP. The pure EP thermosets starts to decompose at 357.2°C and the char yield is 14.6 wt % at 700°C , the thermal degradation process exist one step and the peak of maximum thermal decomposition rate appears at 383°C with the loss weight rate of $17.9\% \text{ min}^{-1}$. However, the initial thermal decomposition temperature of EP-14 greatly decreased from

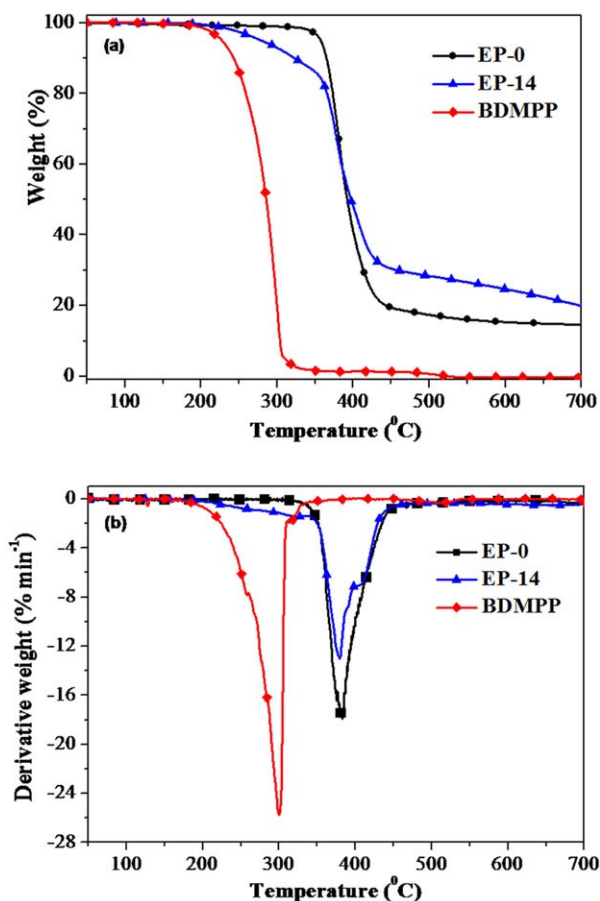


Figure 7. TGA (a) and DTG (b) curves of BDMPP, EP-0 and EP-14. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

357.2°C for pure EP to 279.2°C due to the incorporation of BDMPP into EP composites. The phenomenon may be attributed that the cured EP including BDMPP could undergo degradation and produce phosphoric, polyphosphoric acid at a relative low temperature, and then the produced acid accelerated the decomposition of the EP.²⁵ The reaction stimulates the EP degrade at earlier stage on heat to form sufficient char. As a result, the char yield of EP-14 is enhanced from 14.6 wt % for pure EP to 20.0 wt %. The T_{max} of EP-14 appears at 380°C and the maximum weight loss rate decrease from 17.9% min⁻¹ for pure EP to 13.0% min⁻¹ due to the formed char layer protect the underlying EP matrix from further degradation. 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 the surface of the EP materials. The higher char yield will enhance the flame retardancy of EP thermosets. The thermal degradation results coincide with the flame retardancy tests discussed above.

Morphologies of the Char Residue

In order to further investigate the relationship between the microstructure of the char layers and flame retardant properties of the cured EP composites, the morphologies of the char residues of cured EP-0 and EP-14 after cone calorimeter tests were measured by SEM magnified by 1000 times, as shown in Figure 8. It can be observed that the surface morphology of the char layer for cured pure EP presents an inhomogeneous, relatively loose structure including some small crevasses and holes on the surface [see Figure 8(a)] due to insufficient char formation during combustion, consequently heat and flammable volatiles can penetrate the char layer into the flame zone. On the contrary, the char layer for EP-14 thermosets appears more uniform and compact than that of cured pure EP, as revealed in Figure 8(b). The results suggest that the incorporation of BDMPP additive stimulates the formation of higher char yield and phosphorus rich char residue, which resulting in a more compact char layer and consequently the char layer possesses higher strength and thermal stability, which may effectively stop the transfer of heat and flammable volatiles during combustion. Thus the EP thermosets containing BDMPP obtain excellent flame retardancy.

Mechanical Properties

The mechanical properties of pure EP and EP/BDMPP thermosets with different content of BDMPP additive are presented in Table IV. The tensile and flexural strength of pure EP thermosets are 57.2 MPa and 102.3 MPa, respectively. To our surprise, the tensile and flexural strength of the cured EP/6 wt % BDMPP composite enhance to 72.6 MPa and 115.4 MPa, and increase by 26.9% and 12.8% comparing to that of pure EP thermosets, respectively. With the increase of BDMPP content in EP/BDMPP composite, the tensile and flexural strength of materials gradually increase. The tensile and flexural strength of the cured EP/18 wt % BDMPP composites are as high as 83.4 MPa and 125.8 MPa, respectively. In previously reported works,^{27–30} the triphenyl phosphine (Ph₃P) was used as a curing accelerator during the curing procedure of EP. In this work, the chemical structure of the synthesized BDMPP was similar with Ph₃P. As a result, this phenomenon may be attributed to that the incorporation of BDMPP flame retardant additive stimulate the formation of the intercrosslinking network of EP thermosets and then increase the molecular rotational barrier of EP, consequently enhance the mechanical properties of the EP/BDMPP composite thermosets.

Table III. TGA and DTG Data of BDMPP and Cured EP Under Nitrogen

Sample	$T_{initial}$ (°C)	R_{peak}/T_{peak} (% min ⁻¹ /°C)	Char residue (wt %)
			700°C
BDMPP	228	-25.9/300	0
EP-0	357	-17.9/383	14.7
EP-14	279	-13.0/380	20.0

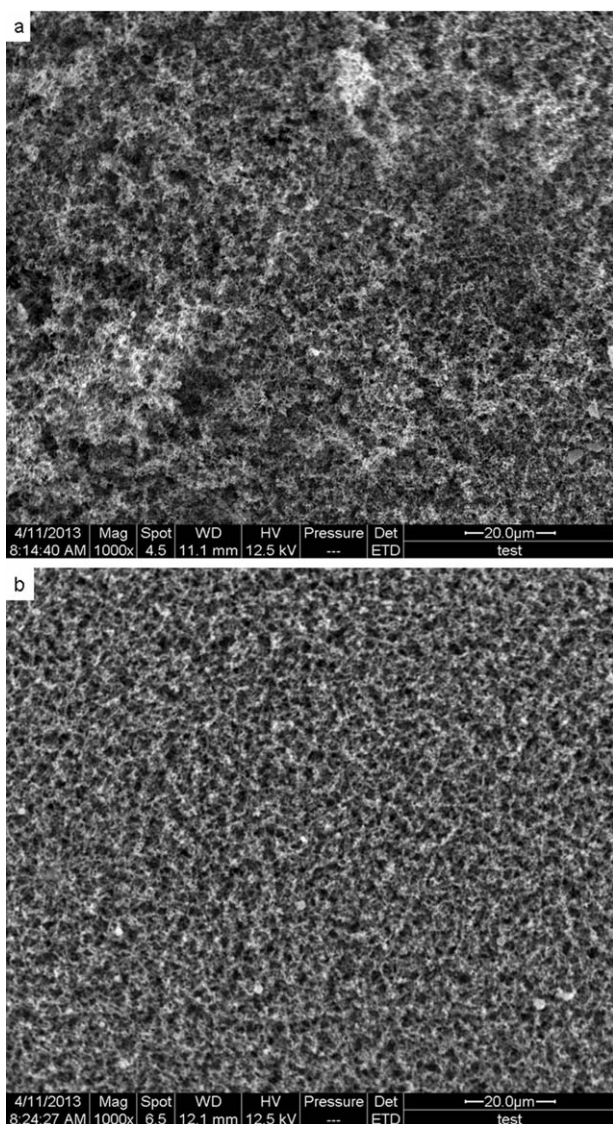


Figure 8. SEM images of the char residues of (a) EP-0, 1000 \times ; (b) EP-14, 1000 \times .

Table IV. Mechanical Properties of Cured Pure EP and EP/BDMPP Composites

Samples	Mechanical Properties	
	Tensile strength (MPa)	Flexural strength (MPa)
EP-0	57.2 \pm 3.2	102.3 \pm 5.3
EP-6	72.6 \pm 4.1	115.4 \pm 6.1
EP-8	74.8 \pm 4.3	117.9 \pm 5.2
EP-10	76.1 \pm 3.8	118.6 \pm 6.4
EP-12	78.4 \pm 4.1	120.1 \pm 5.4
EP-14	81.7 \pm 4.2	123.2 \pm 5.6
EP-16	82.2 \pm 3.4	124.6 \pm 5.1
EP-18	83.4 \pm 3.6	125.8 \pm 4.8

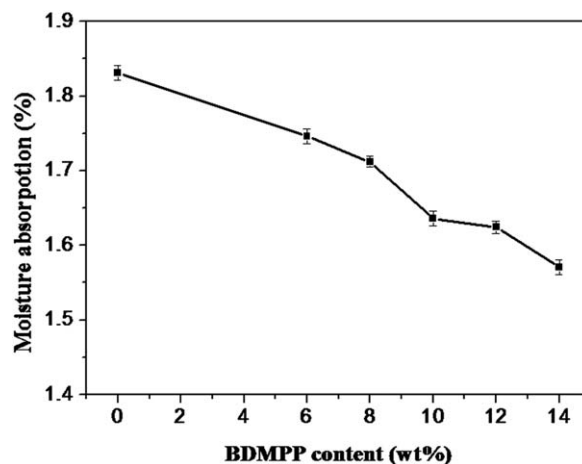


Figure 9. The relationship between the moisture absorption and BDMPP content in EP composites.

Moisture Resistance

EP are hygroscopic because of their inherent hydrophilic nature, and the moisture adsorption would have negative impact on the flame retardancy and mechanical property of the material. The relationship between the moisture absorption and BDMPP content in EP composites is presented in Figure 9. It can be observed that the incorporation of BDMPP into EP reduce the moisture adsorption behavior. For example, the percentage of moisture uptake for the pure EP thermosets is 1.83%, whereas for EP/6 wt % BDMPP composite, it becomes 1.74%. The percentage of moisture adsorption of the cured EP/BDMPP composites gradually decrease with the increase of the BDMPP content in the EP thermosets and the percentage of moisture uptake of EP/14 wt % BDMPP thermosets decrease to 1.57%. It can be deduced that the BDMPP incorporation plays an important role in improving the resistance to moisture absorption of EP/BDMPP thermosets. This may be contributed that the rigid aromatic hydrophobic structure of BDMPP additive.³¹

Table V gives the results of the LOI and UL-94 vertical burning tests of different cured EP/BDMPP composites after water resistance tests. Compared with the results before water resistance tests (see Table I), the corresponding LOI values marginally decrease and the UL-94 rating do not change, which indicate that the cured EP/BDMPP composites possess excellent water resistance. This may be due to the combined effect of the P—C

Table V. Flame Retardancy of Cured EP After Water Resistance Test

Samples	LOI (%)	UL-94
EP-0	20.2 \pm 0.2	No rating
EP-6	29.5 \pm 0.2	No rating
EP-8	31.1 \pm 0.2	No rating
EP-10	32.0 \pm 0.1	V-1
EP-12	32.6 \pm 0.2	V-1
EP-14	33.1 \pm 0.1	V-0
EP-16	33.8 \pm 0.2	V-0
EP-18	34.3 \pm 0.1	V-0

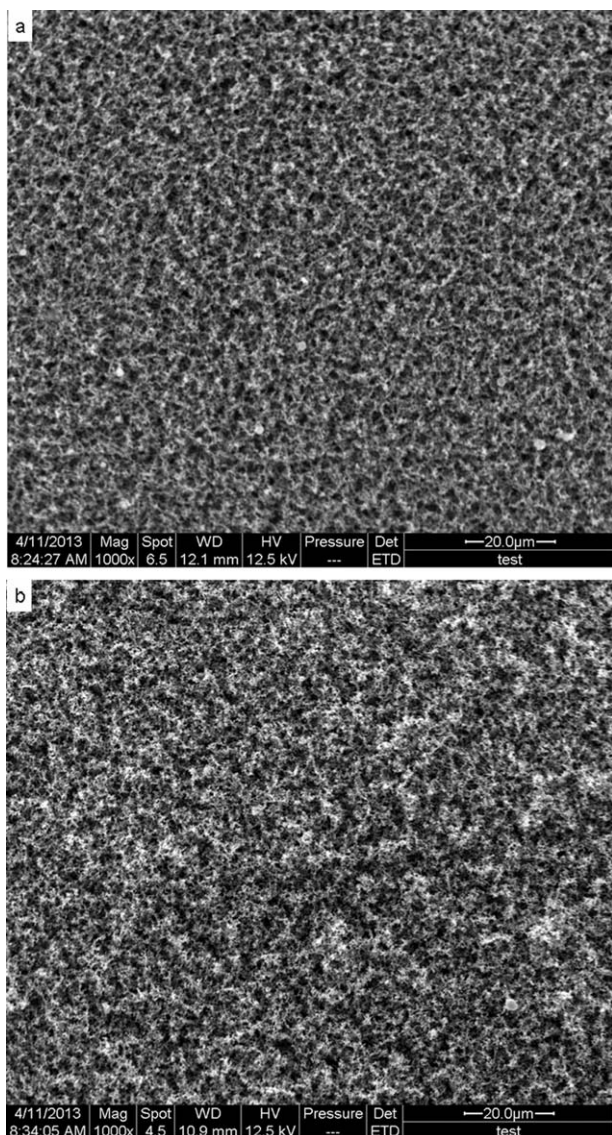


Figure 10. SEM images of the char residues of EP-14 before (a) and after (b) water resistance test.

bond with good thermal stability and strong capability of moisture resistance and the hydrophobic aromatic structure in BDMPP.

Figure 10 shows SEM images of the char layer obtained from cone test of EP-14 thermosets before and after water resistance tests. It can be observed that the surface morphologies of the char layer maintain continuous and compact, which indicated that the water resistance tests do not deteriorate the char layer formed after combustion. This may be attributed that the flame retardant additive of BDMPP in EP-14 composite is scarcely extracted during water resistance tests due to the rigid and hydrophobic aromatic structure of BDMPP. Consequently, the samples still maintain excellent flame retardancy after water resistance test.

CONCLUSIONS

A novel flame retardant additive BDMPP containing both P—C and P—O—C bonds has been successfully synthesized and the

structure is confirmed. The EP/14 wt % BDMPP thermosets with 1.11 wt % phosphorus content in composites reach UL-94 V-0 flammability rating and its LOI value is as high as 33.8%. The incorporation of BDMPP into EP stimulates EP matrix to decompose ahead of time, enhance the char yield at high time. Meanwhile, the mechanical properties of EP/BDMPP thermosets is also increased due to the introduction of BDMPP with reasonable melting point into EP and form cross-linking network structure. Moreover, the moisture absorption of EP/BDMPP thermosets decrease due to the rigid aromatic hydrophobic structure of BDMPP, and the thermosets still maintain excellent flame retardancy after water resistance tests. The BDMPP which incorporated into EP thermosets plays an important role both in condensed and gas phase, consequently reduce the heat transmission and the rate of heat release during combustion, resulting in an efficient flame retardancy for EP/BDMPP composites.

ACKNOWLEDGMENTS

The authors are grateful for funding supported 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 NEFU Innovation Foundation for Postgraduates (ST1P 10).

REFERENCES

1. Wang, X.; Song, L.; Xing, W.; Lu, H. D.; Hu, Y. *Mater. Chem. Phys.* **2011**, *125*, 536.
2. Lu, S. Y.; Hamerton, I. *Prog. Polym. Sci.* **2002**, *27*, 1661.
3. Wang, J. S.; Liu, Y.; Zhao, H. B.; Liu, J.; Wang, D. Y.; Song, Y. P. *Polym. Degrad. Stab.* **2009**, *94*, 625.
4. Chow, W. S.; Neoh, S. S. *J. Appl. Polym. Sci.* **2009**, *114*, 3967.
5. Becker, L.; Lenoir, D.; Matuschek, G.; Kettrup, A. *J. Anal. Appl. Pyrolysis.* **2001**, *60*, 55.
6. Sponton, M.; Mercado, L. A.; Ronda, J. C.; Galia, M.; Cadiz, V. *Polym. Degrad. Stab.* **2008**, *93*, 2025.
7. Mercado, L. A.; Reina, J. A.; Galia, M. *J. Polym. Sci.: Polym. Chem.* **2006**, *44*, 5580.
8. Canadell, J.; Mantecon, A.; Cadiz, V. *Polym. Degrad. Stab.* **2007**, *92*, 1934.
9. Li, X.; Ou, Y. X.; Shi, Y. *Polym. Degrad. Stab.* **2002**, *77*, 383.
10. Artner, J.; Ciesielski, M.; Walter, O.; Doring, M.; Perez, R. M.; Sandler, J. K. W.; Altstadt, V.; Schartel, B. *Macromol. Mater. Eng.* **2008**, *293*, 503.
11. Alcon, M. J.; Ribera, G.; Galia, M.; Cadiz, V. *J. Polym. Sci.: Polym. Chem.* **2005**, *43*, 3510.
12. Wu, C. S.; Liu, Y. L.; Chiu, Y. C.; Chiu, Y. S. *Polym. Degrad. Stab.* **2002**, *78*, 41.
13. Gao, M.; Yang, S. S. *J. Appl. Polym. Sci.* **2010**, *115*, 2346.
14. Winey, K. I.; Kashiwagi, T.; Mu, M. F. *MRS Bull.* **2007**, *32*, 348.

15. Martin, C.; Lligadas, G.; Ronda, J. C.; Galia, M.; Cadiz, V. J. *Polym. Sci.: Polym. Chem.* **2006**, *44*, 6332.
16. Martin, C.; Ronda, J. C.; Cadiz, V. J. *Polym. Sci.: Polym. Chem.* **2006**, *44*, 1701.
17. Tseng, C. H.; Hsueh, H. B.; Chen, C. Y. *Compos. Sci. Technol.* **2007**, *67*, 2350.
18. Guo, B. C.; Jia, D. M.; Cai, C. G. *Eur. Polym. J.* **2004**, *40*, 1743.
19. Lu, S. Y.; Hamerton, I. *Prog. Polym. Sci.* **2002**, *27*, 1661.
20. Gao, M.; Yang, S. J. *Appl. Polym. Sci.* **2010**, *115*, 2346.
21. Gao, M.; Wu, W.; Yan, Y. J. *Therm. Anal. Calorim.* **2009**, *95*, 605.
22. Lin, H.; Yan, H.; Liu, B.; Wei, L.; Xu, B. *Polym. Degrad. Stab.* **2011**, *96*, 1382.
23. Xu, M. J.; Zhao, W.; Li, B. *J. Appl. Polym. Sci.* **2014**, DOI: 10.1002/app.41159.
24. Xu, M. J.; Zhao, W.; Li, B.; Yang, K.; Lin, L. *Fire Mater.* **2014**, DOI: 10.1002/fam.2252.
25. Zhang, W. C.; Li, X. M.; Guo, X. Y.; Yang, R. J. *Polym. Degrad. Stab.* **2010**, *95*, 2541.
26. Zhang, W.; Li, X. M.; Yang, R. J. *Polym. Degrad. Stab.* **2011**, *96*, 2167.
27. Wang, C. S.; Shieh, J. Y. *Eur. Polym. J.* **2000**, *36*, 443.
28. Ren, H.; Sun, J. Z.; Wu, B. J.; Zhou, Q. Y. *Polym. Degrad. Stab.* **2007**, *92*, 956.
29. Deng, J.; Shi, W. F. *Eur. Polym. J.* **2004**, *40*, 1137.
30. Shieh, J. Y.; Wang, C. S. *Polym.* **2001**, *42*, 7617.
31. Kumar, S. A.; Denchev, Z. *Prog. Org. Coat.* **2009**, *66*, 1.