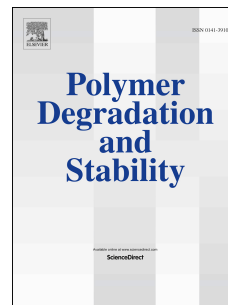# Accepted Manuscript

Ultra-low phosphorus loading to achieve the superior flame retardancy of epoxy resin

Junling Wang, Chao Ma, Peilong Wang, Shuilai Qiu, Wei Cai, Yuan Hu

Please cite this article as: Wang J, Ma C, Wang P, Qiu S, Cai W, Hu Y, Ultra-low phosphorus loading to achieve the superior flame retardancy of epoxy resin, *Polymer Degradation and Stability* (2018), doi: 10.1016/j.polymdegradstab.2018.01.024.

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Ultra-low phosphorus loading to achieve the superior flame retardancy of epoxy resin

Junling Wang[a], Chao Ma[a]*, Peilong Wang[a], Shuilai Qiu[a], Wei Cai[a], Yuan Hu[a]*

[a] State Key Laboratory of Fire Science, University of Science and Technology of China, Hefei 230026, China

---

* Corresponding author.

Tel/fax: +86-551-63601664. E-mail: mcsky@ustc.edu.cn (Chao Ma)

yuanhu@ustc.edu.cn (Yuan Hu)

Abstract

A novel phosphorus-containing compound (DOPO-THPO) is synthesized via the Atherton-Todd-reaction between 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) and trihydroxymethylphosphine oxide (THPO), and then employed as flame retardant for diglycidyl ether of bisphenol A/4-4 diaminodiphenylmethane epoxy resin (DGEBA/DDM). Based on the ultra-low phosphorus loading, the highly efficient flame retarded epoxy resin (EP) systems are successfully established in this work. Remarkable improvements in the limited oxygen index (LOI) values and UL-94 rating of flame retarded EP systems are observed. In detail, when the phosphorus content is only 0.33 wt%, the EP composite receives V-0 rating in the UL-94 vertical burning test with LOI value of 30%. Heat release of EP composites is obviously inhibited with the formation of intumescent char residue. Furthermore, TG-IR result of DOPO-THPO shows the generation of phosphorus containing products, which may provide a gaseous phase flame retardant function on EP. This work may open the new door for the construction of highly efficient flame retardant EP system based on the ultra-low phosphorus loading.

Key words: ultra-low phosphorus loading; flame retardancy; epoxy resin; UL-94 V-0 rating.

1. Introduction

Epoxy resin (EP) has attracted great attention from people since it was created, due to its outstanding properties, such as high transparency, excellent adhesion to substrates and superior electrical and mechanical performances. Thus, it has extensive applications in various industrial fields [1-7]. Unfortunately, EP is easy to ignite with low limited oxygen index (LOI) value and shows no rating in the UL-94 vertical burning test [8-10]. The flammability of EP restrains its further applications. Therefore, it is of great significance to improve the flame retardancy of EP.

Halogen-containing compounds are recognized to be efficient flame retardants for EP. However, the negative effect on the environment and ecological health is caused by the usage of these additives. Accordingly, the development of halogen-free flame retardants is necessary and other anti-flaming elements, such as phosphorus [11-13], boron [14, 15], silicon [16, 17] and nitrogen [18, 19], come into people's vision. Among these favored elements, phosphorus is the most used elements in flame retarded EP system, owing to its high flame retardant efficiency. Based on these literature, phosphorus-containing flame retardants function not only in gaseous phase but also in condensed phase. The former is originated from the radical scavenging effect of PO· radicals and the latter is achieved by the protective effect of phosphorus-containing char residue [20].

Owing to the remarkable gaseous fire-resistant performance, 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) and its derivatives have drew the extensive attention of researchers [19, 21-25]. Schäfer et al. have investigated the influence of DOPO on the flame retardancy of EP, and found that the flame retarded EP couldn't pass the UL-94 V-0 rating until 0.81 wt% phosphorus was added [24]. However, this flame retardant efficiency is dissatisfactory. Then, more effort is needed to achieve the high flame retardant efficiency, with simultaneously decreasing the phosphorus content as low as possible. Unfortunately, only a few works focus on the development of such highly efficient DOPO derivatives. Jian et al. have constructed a flame retardant EP system with a novel DOPO analogue (DOPO-ABZ). Under the same phosphorus loading (0.64 wt%), the composite containing DOPO-ABZ received the V-0 rating while the sample with DOPO failed to pass UL-94 rating [25]. To further improve the flame retardant efficiency for EP, another two works were conducted by them. The corresponding flame retarded EP system can pass the V-0 rating with very low phosphorus loading (0.56 and 0.49 wt%) [26, 27].

Thus, the aim of this work is the construction of highly efficient flame retardant EP system with ultra-low phosphorus loading. A novel phosphorus-containing compound (DOPO-THPO) is synthesized via Atherton-Todd-reaction [28-31] and used as flame retardant for EP systems. Results from ^{1}H and ^{31}P nuclear magnetic resonance spectroscopy (NMR), Fourier transform infrared spectroscopy (FTIR), electrospray

4

ionization mass spectrometry (ESI-MS) and elemental analyses confirm the complex structure of DOPO-THPO. Moreover, it is found that two different P-groups are presented in one molecule of DOPO-THPO. To date, introducing different P-groups into flame retardant has stimulated the wide interest of researchers, owing to its high flame retardant efficiency [9, 32-37]. The flame retardancy of EP is significantly improved after its incorporation. In detail, when only 0.33 wt% phosphorus was loaded, the flame retarded EP can pass the V-0 rating, suggesting the successful construction of highly efficient flame retardant EP system. The obvious decreases in heat release rate and total heat release values are found by cone calorimeter test. After combustion, more compact and intumescent char residue are observed for the flame retarded EP. It is believed that DOPO-THPO exhibits two flame retardant effects in gaseous and condensed phase, resulting in these significant enhancements in flame retardancy of polymer.

2. Experimental

2.1 Materials

A 75% tetrakis-(hydroxymethyl)phosphonium sulfate (THPS) aqueous solution was provided by Aladdin Chemistry Co., Ltd. (China). Potassium iodide starch test papers, barium hydroxide octahydrate, 30% hydrogen peroxide (H_2O_2) solution, triethylamine, dichloromethane (CH_2Cl_2), tetrachloromethane (CCl_4), anhydrous sodium sulfate,

5

hydrochloric acid, sodium bicarbonate and 4,4´-diaminodiphenylmethane (DDM) were bought from Sinopharm Chemical Reagent Co., Ltd. (China). DOPO was purchased by Energy Chemical (Shanghai, China). Diglycidyl ether of bisphenol A (DGEBA, E-44, epoxy value = 0.44 mol/100 g) was obtained from Hefei Jiangfeng Chemical Industry Co., Ltd. (China). Triethylamine, dichloromethane and tetrachloromethane were purified by distillation to remove water before use. All other chemicals were used as received.

2.2 Synthesis of DOPO-THPO

THPO was synthesized according to the literature [38, 39]. Before the reaction, the prepared THPO was heated at 100 $^\circ$C for 2 h and the traces of water in THPO were removed by sustained nitrogen gas flow. 2.8 g THPO, 19.44 g DOPO, 10.93 g triethylamine and 100 mL of dried CH_2Cl_2 were charged into 250 three-necked flask equipped with a mechanical stirrer and a dropping funnel. The reaction mixture was cooled in ice bath and the temperature was kept at 0-5 $^\circ$C. After the complete dissolution of DOPO, 16.63 g CCl_4 solution was slowly added into the flask in 1 h via the dropping funnel and the temperature was kept below 15 $^\circ$C. The mixture was then heated to 30 $^\circ$C and agitated for 12 h. The reaction mixture was washed with hydrochloric acid solution、sodium bicarbonate solution and deionized water to remove impurities. After that, the mixture was dried with anhydrous sodium sulfate, filtered, and evaporated under vacuum at 80 $^\circ$C for 24 h. A light yellow product with

the yield of 87% was obtained.

2.3 Preparation of pure EP and its composites

DGEBA and DOPO-THPO (0, 1.0, 1.5, 2.0, 2.5 wt% of the total thermoset) were mixed with a mechanical stirrer at 100 °C until DOPO-THPO was completely dissolved. Then, stoichiometric amount of DDM (relative to DGEBA) was added and dissolved. The hybrid was poured into the preheated stainless steel mold, cured at 100 °C for 2 h, and postcured at 150 °C for 2 h. Thereafter, the thermoset was naturally cooled slowly to room temperature to prevent cracking. These samples were named as EP-1, EP-2, EP-3, EP-4, EP-5, respectively.

2.4 Characterization

Nuclear magnetic resonance spectra were performed on a Bruker AV400 NMR spectrometer (400MHz) at room temperature. Fourier transform infrared (FTIR) spectra were recorded on a Nicolet 6700 FTIR spectrophotometer (Nicolet Instrument Co., U.S.). Elemental analysis was conducted via the Vario EL III elemental analyzer. Electrospray ionization mass spectrometry (ESI-MS) result was obtained by Agilent 6460 Triple Quadruple mass spectrometer equipped with an ESI source, and exact masses were measured by a Thermo Scientific LTQ Orbitrap Mass Spectrometer equipped with an electro-spray interface. Thermogravimetric analysis (TGA) was recorded on a TA Q5000IR thermo-analyzer (TA Instruments Inc., U.S.) with a heating rate of 20 °C/min. Differential scanning calorimetry was performed with a

DSC Q2000 (TA Instruments Inc., U.S.) at a heating rate of 10 $^{\circ}$C/min under a nitrogen atmosphere. Limited oxygen index (LOI) was obtained according to ASTM Standard D 2863 using a HC-2 oxygen index meter (Jiangning Analysis Instrument Company, China). The test specimens with dimension of $100 \times 6.5 \times 3.0$ mm^3 were burned in mixed atmosphere of oxygen and nitrogen. The UL-94 vertical burning test was performed on a CFZ-2 type instrument (Jiangning Analysis Instrument Co., China) according to ASTM D3801-1996 standard. Five specimens with dimension of $130 \times 13 \times 3$ mm^3 were tested for one group. Combustion test was performed on a cone calorimeter (FTT, Co., Ltd., UK) according to ISO-5660 standard. The specimen with the sizes of $100 \times 100 \times 3$ mm^3 was wrapped in an aluminum foil and exposed horizontally to a heat flux of 35 kW/m^2. Scanning electron microscopy (SEM) images of char residues were obtained on FEI Sirion 200 scanning electron microscope with an acceleration voltage of 20 kV. Raman spectra were obtained on a LabRAM-HR Confocal Raman Microprobe (JobinYvon Instruments, France) with a 514.5 nm argon ion laser. Thermogravimetric analysis/infrared spectrometry (TG-IR) was performed on a TA Q5000IR thermo-analyzer coupled with a Nicolet 6700 FTIR spectrophotometer. About 8.0-10.0 mg of the sample was heated from 30 to 800 $^{\circ}$C with the heating rate of 20 $^{\circ}$C/min, under N$_2$ atmosphere.

3. Results and discussion

3.1 Synthesis and structural characterization of DOPO-THPO

As shown in Fig. 1, two steps are required for the preparation of DOPO-THPO. THPO is first synthesized from THPS and alkali before the oxidation by H_2O_2. Then, the reaction between THPO and DOPO is carried out to get the final product. From the ^{31}P NMR spectra of THPO and DOPO-THPO presented in Fig. 2, a singlet at 44.9 ppm is observed for THPO while two peaks appear in the spectrum of DOPO-THPO. The signal at 11.4 ppm is attributed to the phosphorus of $-Ph-P(=O)-$ and the peak at 31.8 ppm is corresponding to the phosphorus of $-CH_2-P(=O)-$. The disappeared signal of phosphorus in THPO and the new signals of phosphorus in DOPO-THPO suggest the successful preparation of target product. In ^1H NMR spectrum of DOPO-THPO, the chemical shifts between 7.0 and 8.3 ppm are due to the the protons of phenyl rings while the peak around 4.4 is assigned to methylene protons.

FTIR spectrum of DOPO-THPO is given in Fig. 3. The adsorption bands at 2916 and 2967 cm^{-1} correspond to C-H vibration in methylene group while the peak at 3063 cm^{-1} belongs to C-H vibration in phenyl ring. The peaks at 1595 and 1476 cm^{-1} are attributed to the P-Ph vibration of phenyl group. The presence of P-O-C vibration can be observed at 1044 cm^{-1}. Moreover, the band at 750 cm^{-1} is assigned to P-C vibration [40, 41].

Elemental analysis results of DOPO-THPO are listed in Table 1. The calculated values are obtained according to the structural formula of the target product. Good consistency is found between the calculated and measured values, which suggests that

9

the target product of DOPO-THPO is successfully synthesized. Moreover, only C, H, O and P elements exist in the product and the high phosphorus content of 15.37 wt% is estimated (100 wt%-59.36 wt%-21.17 wt%-4.10 wt%). To further confirm the structure of DOPO-THPO, ESI-MS analysis was performed and the corresponding result is shown in Fig. 4. The ESI-MS result (*m/z*: calcd. for $[M + Na]^+$, 805.07000; found, 805.07025) also indicates the successful preparation of DOPO-THPO.

3.2 Thermal stability of pure EP and its composites

TGA and DTG curves of pure EP and its composites under air and N_2 are exhibited in Fig. 5. The decomposition temperature at 5% weight loss ($T_{5\%}$), the temperature at maximum weight loss rate (T_{max}), and char yield at 735 °C (CY) are obtained from these curves, and the relevant data are given in Table 2. In air, two-stage decomposition are observed for pure EP. The first one corresponds to the pyrolysis of epoxy chains while the second one is originated from the degradation of char residue [42]. Pure EP decomposes with $T_{5\%}$ of 374 °C and T_{max1} as well as T_{max2} of 387 and 568 °C, respectively. Whereas in EP composites, obvious decreases in $T_{5\%}$ and T_{max1} are presented, suggesting the ahead of degradation. This can be attributed to the unstable O=P-O bond in DOPO-THPO. Moreover, it's worth noting that EP composites show higher T_{max2} value than pure EP, which indicates that more thermal-stable char residue is formed under the presence of DOPO-THPO. Moreover, the increases in char yield and decreases in maximum mass loss rate (MMLR) are

10

observed. Similar phenomenon are also found in N_2. The decomposition of EP composites appears in advance with the increments in char yield and reductions in MMLR.

DSC was used to measure the glass transition temperature (T_g) of pure EP and its composites. The obtained DSC thermograms are shown in Fig. 6 and the corresponding data are listed in Table. 2. After the incorporation of DOPO-THPO, EP composites show higher T_g than pure EP. The rich and bulky aromatic DOPO pendant groups in flame retardant may hinder the mobility of EP molecular chains [9]. Then, the enhanced T_g is obtained, suggesting the enhanced thermal stability of EP.

3.3 Transmittance of pure EP and its composites.

As is well known, EP resins has wide applications in the field of optoelectronics because of its high transparency. However, the using of flame retardant additives often result in the reduction in transparency of EP. Then, it is of great importance to maintain the relative high transparency of materials, along with the markedly enhanced flame retardancy. UV-vis transmission spectra of EP and its composites are shown in Fig. 7 and their digital photos are also presented. Compared with pure sample, EP composites still show relative high transparency, which may be derived from the good compatibility between DOPO-THPO and EP matrix.

3.4 Combustion behavior of pure EP and its composites

To investigate the combustion behavior of the cured EP resins, LOI and UL-94 tests

11

were performed and the corresponding results are shown in Table 3. Pure EP is inherently flammable with a low LOI value of 26% and received no rating in the UL-94 test. The significant improvement in flame retardancy of EP is obtained after the incorporation of DOPO-THPO. In detail, with the loading of 1.0 wt% DOPO-THPO, the sample of EP-2 receives V-1 rating in UL-94 test and shows LOI value of 29%. When the loading of DOPO-THPO rises to 2.0 and 2.5 wt%, the samples of EP-4 and EP-5 can pass the UL-94 V-0 rating with further increased LOI values of 30 and 32%, respectively. Moreover, it is noteworthy that the phosphorus content in EP-4 and EP-5 are only 0.33 and 0.42 wt%, respectively, which based on the formulation of this two flame retarded EP systems and the phosphorus content in DOPO-THPO measured previously. These results reveal that the flame retardancy of EP composite is enhanced markedly, even with low phosphorus content. Thus, DOPO-THPO can be regarded as a highly efficient flame retardant for EP resins.

Cone calorimeter test, based on the well-known oxygen consumption principle, is widely used to evaluate the fire behavior of materials. Here, the flammability of pure EP and its composites is evaluated via this apparatus and the obtained data are given in Table 3. The heat release rate (HRR) and total heat release (THR) curves as a function of time are presented in Fig. 8. A high HRR peak appears in the curve of pure EP with a peak heat release rate (PHRR) of 1725 kW/m^2 and its THR is 60.2 MJ/m^2. Ahead of combustion is observed in EP composites, which can be attributed to the decomposition of unstable organic component. After the incorporation of

12

DOPO-THPO, the reductions in PHRR and THR values can be observed, suggesting the improved flame retardancy of polymer. When 2.5 wt% DOPO-THPO is added, the PHRR and THR values are decreased by 21.3 and 17.3%, respectively. During the combustion, the decomposition of DOPO-THPO may release the PO· radicals, which can quench the highly active H· and OH· radicals in the flame and hamper the radical chain reactions. Then, the combustion efficiency of EP resin is reduced. In addition, more thermal-stable and compact char residue is formed for the samples containing DOPO-THPO, as shown in Fig. 9. This char may insulate the flammable volatiles from heat and oxygen and protect the underlying polymer from degradation to leave more residue, further suppressing the burning of EP resins. Thus, it is believed that DOPO-THPO may exhibit two flame retardant effects in gaseous and condensed phase, resulting in the significant enhancements in flame retardancy of polymer.

Two parameters, the fire performance index (FPI) and fire growth index (FGI), are often used to assess the fire hazard of materials [43-45]. The FPI and FGI values are defined as the ratio of TTI (time to ignition) to PHRR and the ratio of PHRR to TTP (time to PHRR), respectively. There is a close relationship between FPI value and time to flashover. The decreased FPI value means the reduction in the time to flashover. Then, larger value of FPI is relevant to higher fire safety of materials. However, higher value of FGI represents the shorter time to arrive at PHRR. Thus, lower FGI value is corresponding to the more remarkable fire safety of samples. After the addition of DOPO-THPO, the increased FPI and decreased FGI values are

13

observed for EP composites, except for EP-2. This may be due to the minimal loading of DOPO-THPO in EP-2. In general, the fire hazard of EP resins is suppressed, even at low phosphorus content.

3.5 Analysis of char residues after combustion.

Digital photos and SEM images of char residues after cone calorimeter test are given in Fig. 9. The formed char residues often plays an important role in suppression on the burning of polymer, because of its barrier effect on the transfer of flammable volatiles and heat. Pure EP shows a kind of fragmentary and loose char residue from its front view, and this char cannot effectively insulate the combustible volatiles from the heat and oxygen. Then, the suppression effect on the burning of underlying polymer is marginal here. With the addition of DOPO-THPO, the continuous and compact char residues are observed in EP composites and it seem to be more intumescent compared to that of pure EP, from the side view of char, especially for EP-5. During the combustion of EP, many gaseous volatiles are released and the covered char serves as barrier on the diffusion of volatiles. More compact and thermal-stable char is formed in EP composites. Then, the gaseous volatiles are effectively trapped in condensed phase to form char instead of released to flame zone. Thus, the swelling of char residue is obtained. The microstructure of char residue is presented in SEM images. There are many holes and cracks in the char of pure EP while the smooth and unbroken char is found for EP composites. Therefore, adding

14

DOPO-THPO contributes to the generation of compact and intumescent char layer, which provides efficient suppression effect on the burning of EP.

Raman analysis is also employed to evaluate the quality of formed char residue and the relevant results are shown in Fig. 10. Two strong peaks located at 1360 and 1595 cm^{-1} are presented in the Raman spectra. The former corresponds to the vibration of carbon atoms with dangling bonds in the plane terminations of disordered graphite or glassy carbons (D band) and the latter is assigned to the vibration of sp^2-hybridized carbon atoms in a graphite layer (G band) [46, 47]. The ratio of integral intensity of D and G bands (I_D/I_G) is used to estimate the graphitization degree of char residue. Lower value of I_D/I_G represents higher graphitization degree of char, which can protect the polymer matrix more efficiently. The value of I_D/I_G of char residue is decreased after the incorporation of DOPO-THPO, suggesting the enhanced graphitization degree of char. Then, more protective char residue is formed in EP composites and then the burning of EP resin is inhibited effectively.

3.6 TG-IR analysis of DOPO-THPO

To better understand the flame retardant effect of DOPO-THPO in gaseous phase, FTIR spectra of its decomposed volatiles at different temperature are shown in Fig. 11. Accordingly, these main bands can be attributed to the functional groups with characteristic band positions, such as hydrocarbons (2800-2900 cm^{-1}), CO_2 (2310-2360 cm^{-1}), carbonyl compounds (1700-1780 cm^{-1}) [48], aromatic compounds

15

(1510 cm^{-1}) [49], P=O bonds (1237 cm^{-1}) and P-O bonds (1122 cm^{-1}) [25]. The absorbance of hydrocarbons appears in early decomposition stage and almost disappears at 458 $^{\circ}$C. However, more aromatic compounds are released with the increment of temperature. Moreover, the presence of phosphorus containing products, which may play an important role in flame inhibition through gaseous phase, can be observed.

4. Conclusions

In this work, a highly efficient flame retardant EP system based on the ultra-low phosphorus loading, is successfully constructed. The used flame retardant of DOPO-THPO is synthesized via the Atherton-Todd-reaction between THPO and DOPO. The structure of this compound is confirmed by NMR, FTIR, EA and ESI-MS analyses. After the incorporation of DOPO-THPO, the significant improvements in LOI values and UL-94 ratings are found for EP composites. With only 0.33 wt% phosphorus content, the flame retarded EP can pass the V-0 rating. The obvious decreases in PHRR and THR values are also observed with the formation of more compact and intumescent char residues, which can act as efficient shield for underlying EP matrix. This indicates the condensed phase fire resistant function of DOPO-THPO. Furthermore, TG-IR analysis of DOPO-THPO shows the release of phosphorus containing volatiles, which may endow this additive with gaseous phase flame retardant effect. The PO· radicals, released from the decomposition of

DOPO-THPO, can quench the highly active H· and OH· radicals in the flame and hamper the radical chain reactions, resulting in the suppression in the combustion of EP. This work may open the new door for the construction of highly efficient flame retardant EP system based on the ultra-low phosphorus loading.

Acknowledgements

Reference

[1] M. Rakotomalala, S. Wagner, M. Döring, Recent developments in halogen free flame retardants for epoxy resins for electrical and electronic applications, Materials 3 (2010) 4300-4327.

[2] S.A. Kumar, Z. Denchev, Development and characterization of phosphorus-containing siliconized epoxy resin coatings, Prog. Org. Coat. 66 (2009) 1-7.

[3] T. Mariappan, C.A. Wilkie, Flame retardant epoxy resin for electrical and

electronic applications, Fire Mater. 38 (2014) 588-598.

[4] J.-Y. Shieh, C.-S. Wang, Synthesis of novel flame retardant epoxy hardeners and properties of cured products, Polymer 42 (2001) 7617-7625.

[5] D.-H. Kuo, C.-C. Chang, T.-Y. Su, W.-K. Wang, B.-Y. Lin, Dielectric behaviours of multi-doped BaTiO 3/epoxy composites, J. Eur. Ceram. Soc. 21 (2001) 1171-1177.

[6] W. Dang, M. Kubouchi, S. Yamamoto, H. Sembokuya, K. Tsuda, An approach to chemical recycling of epoxy resin cured with amine using nitric acid, Polymer 43 (2002) 2953-2958.

[7] R.J. Jeng, G.S. Lo, C.P. Chen, Y.L. Liu, G.H. Hsiue, W.C. Su, Enhanced thermal properties and flame retardancy from a thermosetting blend of a phosphorus‐containing bismaleimide and epoxy resins, Polym. Advan. Technol. 14 (2003) 147-156.

[8] C. Ma, B. Yu, N. Hong, Y. Pan, W. Hu, Y. Hu, Facile synthesis of a highly efficient, halogen-free, and intumescent flame retardant for epoxy resins: thermal properties, combustion behaviors, and flame-retardant mechanisms, Ind. Eng. Chem. Res. 55 (2016) 10868-10879.

[9] X. Wang, Y. Hu, L. Song, H. Yang, W. Xing, H. Lu, Synthesis and characterization of a DOPO-substitued organophosphorus oligomer and its application in flame retardant epoxy resins, Prog. Org. Coat. 71 (2011) 72-82.

[10] Y. Zhang, B. Yu, B. Wang, K.M. Liew, L. Song, C. Wang, Y. Hu, Highly Effective P–P Synergy of a Novel DOPO-Based Flame Retardant for Epoxy Resin,

Ind. Eng. Chem. Res. 56 (2017) 1245-1255.

[11] Y.L. Liu, G.H. Hsiue, R.H. Lee, Y.S. Chiu, Phosphorus‐containing epoxy for flame retardant. III: Using phosphorylated diamines as curing agents, J. Appl. Polym. Sci. 63 (1997) 895-901.

[12] H. Ren, J. Sun, B. Wu, Q. Zhou, Synthesis and properties of a phosphorus-containing flame retardant epoxy resin based on bis-phenoxy (3-hydroxy) phenyl phosphine oxide, Polym. Degrad. Stab. 92 (2007) 956-961.

[13] R.-J. Jeng, S.-M. Shau, J.-J. Lin, W.-C. Su, Y.-S. Chiu, Flame retardant epoxy polymers based on all phosphorus-containing components, Eur. Polym. J. 38 (2002) 683-693.

[14] S.M. Unlu, S.D. Dogan, M. Dogan, Comparative study of boron compounds and aluminum trihydroxide as flame retardant additives in epoxy resin, Polym. Advan. Technol. 25 (2014) 769-776.

[15] C. Martin, G. Lligadas, J. Ronda, M. Galia, V. Cadiz, Synthesis of novel boron‐containing epoxy–novolac resins and properties of cured products, J. Polym. Sci. Pol. Chem. 44 (2006) 6332-6344.

[16] L. Mercado, M. Galia, J. Reina, Silicon-containing flame retardant epoxy resins: synthesis, characterization and properties, Polym. Degrad. Stab. 91 (2006) 2588-2594.

[17] G.-H. Hsiue, W.-J. Wang, F.-C. Chang, Synthesis, characterization, thermal and flame-retardant properties of silicon-based epoxy resins, J. Appl. Polym. Sci. 73 (1999) 1231-1238.

[18] T.S. Leu, C.S. Wang, Synergistic effect of a phosphorus–nitrogen flame retardant on engineering plastics, J. Appl. Polym. Sci. 92 (2004) 410-417.

[19] S. Yang, J. Wang, S. Huo, L. Cheng, M. Wang, Preparation and flame retardancy of an intumescent flame-retardant epoxy resin system constructed by multiple flame-retardant compositions containing phosphorus and nitrogen heterocycle, Polym. Degrad. Stab. 119 (2015) 251-259.

[20] S.-Y. Lu, I. Hamerton, Recent developments in the chemistry of halogen-free flame retardant polymers, Prog. Polym. Sci. 27 (2002) 1661-1712.

[21] J. Artner, M. Ciesielski, O. Walter, M. Döring, R.M. Perez, J.K. Sandler, V. Altstädt, B. Schartel, A Novel DOPO‐Based Diamine as Hardener and Flame Retardant for Epoxy Resin Systems, Macromol. Mater. Eng. 293 (2008) 503-514.

[22] B. Perret, B. Schartel, K. Stöß, M. Ciesielski, J. Diederichs, M. Döring, J. Krämer, V. Altstädt, Novel DOPO-based flame retardants in high-performance carbon fibre epoxy composites for aviation, Eur. Polym. J. 47 (2011) 1081-1089.

[23] W. Zhang, X. Li, R. Yang, Novel flame retardancy effects of DOPO-POSS on epoxy resins, Polym. Degrad. Stab. 96 (2011) 2167-2173.

[24] A. Schäfer, S. Seibold, W. Lohstroh, O. Walter, M. Döring, Synthesis and properties of flame‐retardant epoxy resins based on DOPO and one of its analog DPPO, J. Appl. Polym. Sci. 105 (2007) 685-696.

[25] R. Jian, P. Wang, W. Duan, J. Wang, X. Zheng, J. Weng, Synthesis of a novel P/N/S-containing flame retardant and its application in epoxy resin: thermal property,

flame retardance, and pyrolysis behavior, Ind. Eng. Chem. Res. 55 (2016) 11520-11527.

[26] R. Jian, P. Wang, L. Xia, X. Zheng, Effect of a novel P/N/S-containing reactive flame retardant on curing behavior, thermal and flame-retardant properties of epoxy resin, J. Anal. Appl. Pyrol. 127 (2017) 360-368.

[27] R. Jian, P. Wang, L. Xia, X. Yu, X. Zheng, Z. Shao, Low-flammability epoxy resins with improved mechanical properties using a Lewis base based on phosphaphenanthrene and 2-aminothiazole, J. Mater. Sci. (2017) 1-15.

[28] S.S. Le Corre, M. Berchel, H. Couthon-Gourvès, J.-P. Haelters, P.-A. Jaffrès, Atherton–Todd reaction: mechanism, scope and applications, Beilstein J. Org. Chem. 10 (2014) 1166-1196.

[29] M. Neisius, S. Liang, H. Mispreuve, S. Gaan, Phosphoramidate-containing flame-retardant flexible polyurethane foams, Ind. Eng. Chem. Res. 52 (2013) 9752-9762.

[30] N.M. Neisius, M. Lutz, D. Rentsch, P. Hemberger, S. Gaan, Synthesis of DOPO-based phosphonamidates and their thermal properties, Ind. Eng. Chem. Res. 53 (2014) 2889-2896.

[31] P. Jiang, X. Gu, S. Zhang, S. Wu, Q. Zhao, Z. Hu, Synthesis, characterization, and utilization of a novel phosphorus/nitrogen-containing flame retardant, Ind. Eng. Chem. Res. 54 (2015) 2974-2982.

[32] B. Schartel, B. Perret, B. Dittrich, M. Ciesielski, J. Krämer, P. Müller, V. Altstädt,

L. Zang, M. Döring, Flame retardancy of polymers: the role of specific reactions in the condensed phase, Macromol. Mater. Eng. 301 (2016) 9-35.

[33] X. Wang, L. Song, W. Xing, H. Lu, Y. Hu, A effective flame retardant for epoxy resins based on poly (DOPO substituted dihydroxyl phenyl pentaerythritol diphosphonate), Mater. Chem. Phys. 125 (2011) 536-541.

[34] L.-L. Wei, D.-Y. Wang, H.-B. Chen, L. Chen, X.-L. Wang, Y.-Z. Wang, Effect of a phosphorus-containing flame retardant on the thermal properties and ease of ignition of poly (lactic acid), Polym. Degrad. Stab. 96 (2011) 1557-1561.

[35] J. Zheng, X. Li, Y. Yu, X. Feng, Y. Zhao, Novel high phosphorus content phosphaphenanthrene-based efficient flame retardant additives for lithium-ion battery, J. Therm. Anal. Calori. 117 (2014) 319-324.

[36] K.A. Salmeia, S. Gaan, An overview of some recent advances in DOPO-derivatives: chemistry and flame retardant applications, Polym. Degrad. Stab. 113 (2015) 119-134.

[37] D.-Y. Wang, editor. Novel Fire Retardant Polymers and Composite Materials, Woodhead Publishing, 2016.

[38] Z. Tan, C. Wu, M. Zhang, W. Lv, J. Qiu, C. Liu, Phosphorus-containing polymers from tetrakis-(hydroxymethyl) phosphonium sulfate III. A new hydrolysis-resistant tris (allyloxymethyl) phosphine oxide and its thiol-ene reaction under ultraviolet

irradiation, RSC Adv. 4 (2014) 41705-41713.

[39] M.-J. Chen, C.-R. Chen, Y. Tan, J.-Q. Huang, X.-L. Wang, L. Chen, Y.-Z. Wang, Inherently flame-retardant flexible polyurethane foam with low content of phosphorus-containing cross-linking agent, Ind. Eng. Chem. Res. 53 (2014) 1160-1171.

[40] X. Wang, Y. Hu, L. Song, W. Xing, H. Lu, P. Lv, G. Jie, Flame retardancy and thermal degradation mechanism of epoxy resin composites based on a DOPO substituted organophosphorus oligomer, Polymer 51 (2010) 2435-2445.

[41] X. Chen, Y. Hu, C. Jiao, L. Song, Preparation and thermal properties of a novel flame-retardant coating, Polym. Degrad. Stab. 92 (2007) 1141-1150.

[42] X. Wang, Y. Hu, L. Song, W. Xing, H. Lu, Thermal degradation mechanism of flame retarded epoxy resins with a DOPO-substitued organophosphorus oligomer by TG-FTIR and DP-MS, J. Anal. Appl. Pyrol. 92 (2011) 164-170.

[43] C.I. Idumah, A. Hassan, S. Bourbigot, Influence of exfoliated graphene nanoplatelets on flame retardancy of kenaf flour polypropylene hybrid nanocomposites, J. Anal. Appl. Pyrol. 123 (2017) 65-72.

[44] M. Hassan, M. Nour, Y. Abdelmonem, G. Makhlouf, A. Abdelkhalik, Synergistic effect of chitosan-based flame retardant and modified clay on the flammability properties of LLDPE, Polym. Degrad. Stab. 133 (2016) 8-15.

[45] B. Yuan, A. Fan, M. Yang, X. Chen, Y. Hu, C. Bao, S. Jiang, Y. Niu, Y. Zhang, S. He, The effects of graphene on the flammability and fire behavior of intumescent

flame retardant polypropylene composites at different flame scenarios, Polym. Degrad. Stab. 143 (2017) 42-56.

[46] B. Yuan, Y. Hu, X. Chen, Y. Shi, Y. Niu, Y. Zhang, S. He, H. Dai, Dual modification of graphene by polymeric flame retardant and Ni (OH)$_2$ nanosheets for improving flame retardancy of polypropylene, Compos. Part. A-Appl. S. 100 (2017) 106-117.

[47] W. Cai, X. Feng, B. Wang, W. Hu, B. Yuan, N. Hong, Y. Hu, A novel strategy to simultaneously electrochemically prepare and functionalize graphene with a multifunctional flame retardant, Chem. Eng. J. 316 (2017) 514-524.

[48] G. Tullos, L. Mathias, Unexpected thermal conversion of hydroxy-containing polyimides to polybenzoxazoles, Polymer 40 (1999) 3463-3468.

[49] W. Wang, H. Pan, Y. Shi, Y. Pan, W. Yang, K. Liew, L. Song, Y. Hu, Fabrication of LDH nanosheets on β-FeOOH rods and applications for improving the fire safety of epoxy resin, Compos. Part. A-Appl. S. 80 (2016) 259-269.

Table captions

Table 1. Elemental analysis results of DOPO-THPO.

Table 2. Thermal parameters of the cured epoxy resins under air and N_2.

Table 3. LOI and UL94 test results of the cured epoxy resins.

Table 4. Combustion parameters of the cured epoxy resins obtained from cone calorimeter test.

Table 1. Elemental analysis results of DOPO-THPO.

Elements	C (wt%)	O (wt%)	P (wt%)	H (wt%)
Calculated	59.84	20.46	15.86	3.84
Measured	59.36	21.17	15.37[a]	4.10

[a] Estimated by 100 wt%-59.36 wt%-21.17 wt%-4.10 wt%.

Table 2. Thermal parameters of the cured epoxy resins under air and N$_2$.

Samples	T_g ($^\circ$C)	Air			N$_2$		
		$T_{5\%}$ ($^\circ$C)	T_{max1}, T_{max2} ($^\circ$C)	CY (wt%)	$T_{5\%}$ ($^\circ$C)	T_{max} ($^\circ$C)	CY (wt%)
EP-1	147	374	387, 568	1.29	373	393	16.2
EP-2	155	355	374, 631	1.44	356	377	17.2
EP-3	154	350	371, 616	1.56	355	374	17.4
EP-4	155	347	372, 617	1.77	348	374	18.1
EP-5	154	342	367, 619	2.26	342	382	18.7

Table 3. LOI and UL94 test results of the cured epoxy resins.

Sample	P content (wt%)	LOI (%)	UL 94 rating
EP-1	0	26	NR
EP-2	0.16	29	V-1
EP-3	0.25	29	V-1
EP-4	0.33	30	V-0
EP-5	0.41	32	V-0

Table 4. Cone calorimeter test results of the cured epoxy resins.

Sample	TTI (s)	TTP (s)	PHRR (kW/m^2)	THR (MJ/m^2)	FPI (m^2·s/kW)	FGI (kW/m^2·s)
EP-1	50	100	1725	60.2	0.029	17.25
EP-2	38	80	1488	56.4	0.025	18.60
EP-3	48	88	1450	56.8	0.033	16.47
EP-4	48	88	1357	52.4	0.035	15.42
EP-5	49	88	1375	49.8	0.036	15.62

Figure captions

Fig. 1. Scheme of the synthesis for DOPO-THPO.

Fig. 2. NMR spectra of THPO and DOPO-THPO.

Fig. 3. FTIR spectrum of DOPO-THPO.

Fig. 4. ESI-MS spectrum of DOPO-THPO.

Fig. 5. TGA and DTG curves of pure EP and its composites under air and N_2.

Fig. 6. DSC thermograms of the cured epoxy resins.

Fig. 7. Digital photos and UV-vis transmission spectra of the cured epoxy resins.

Fig. 8. HRR and THR curves of pure EP and its composites.

Fig. 9. Digital photos and SEM images of char residues after cone calorimeter test.

Fig. 10. Raman spectra of char residues.

Fig. 11. FTIR spectra of the evolved decomposed volatiles generated from

DOPO-THPO.
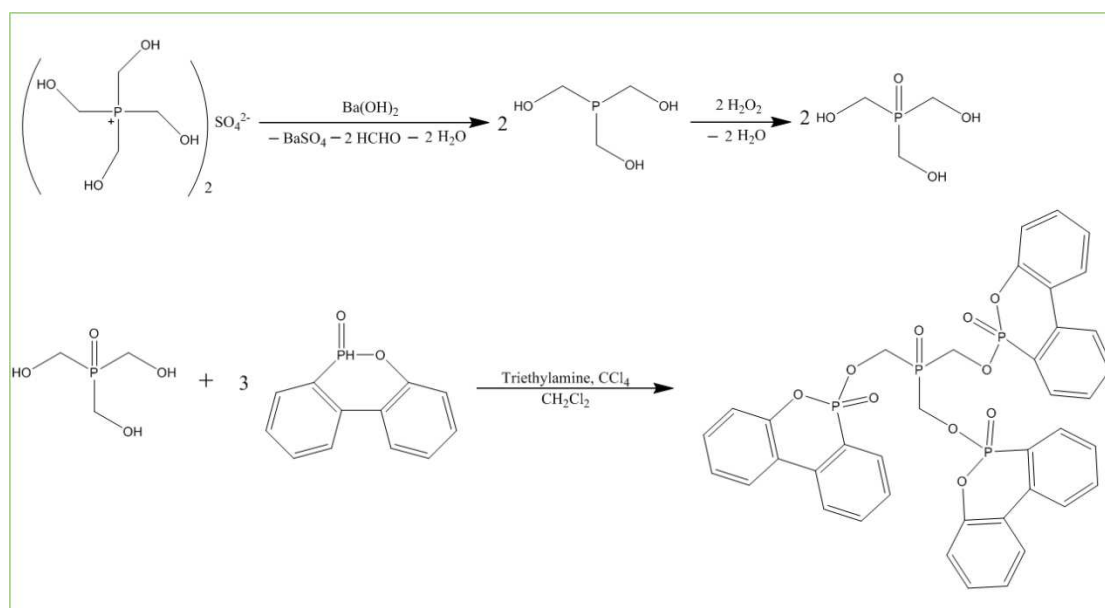
Fig. 1
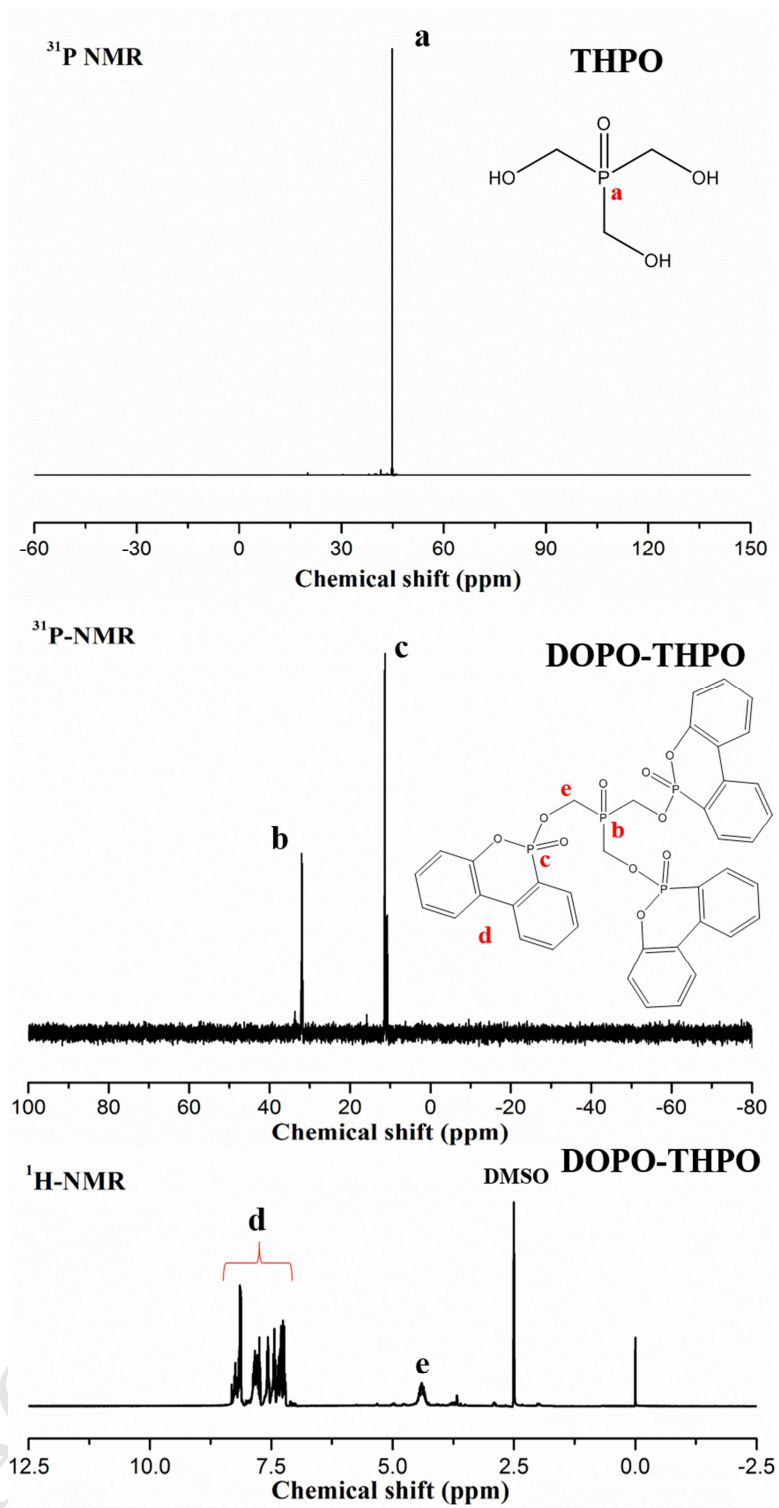
Fig. 2
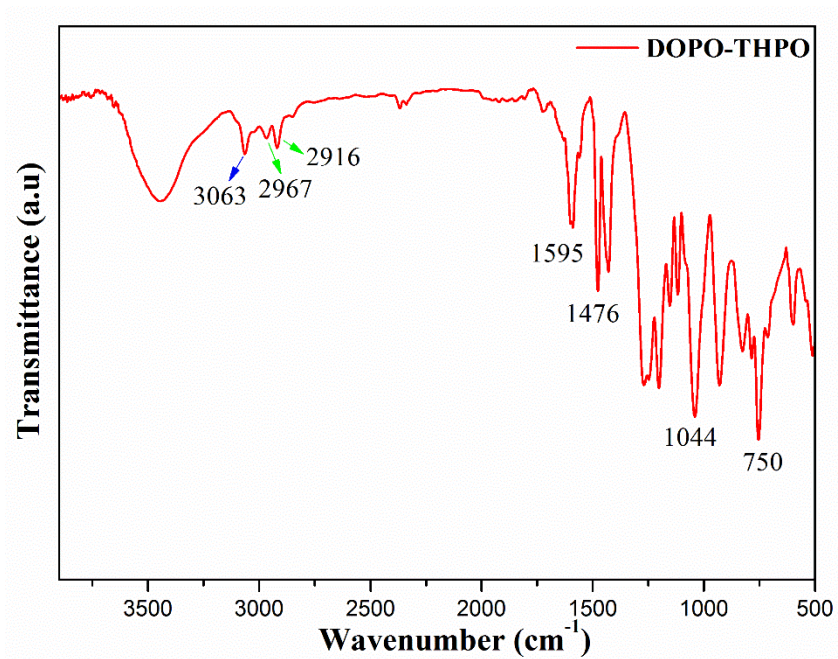
Fig. 3
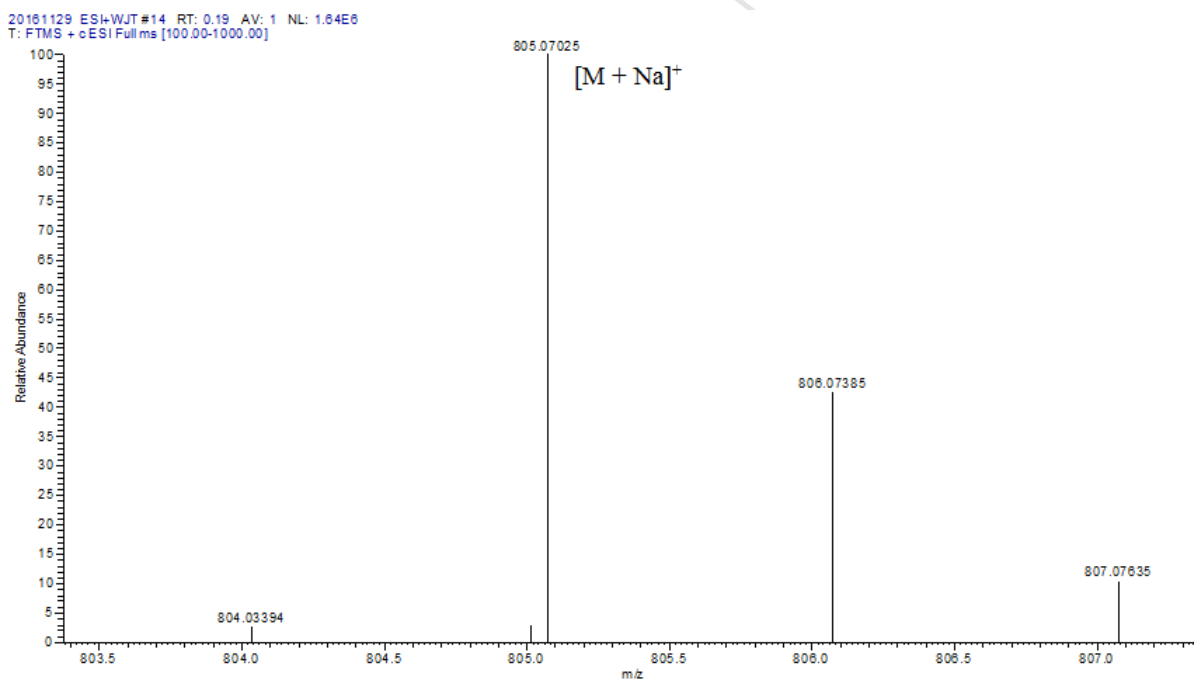
Fig. 4
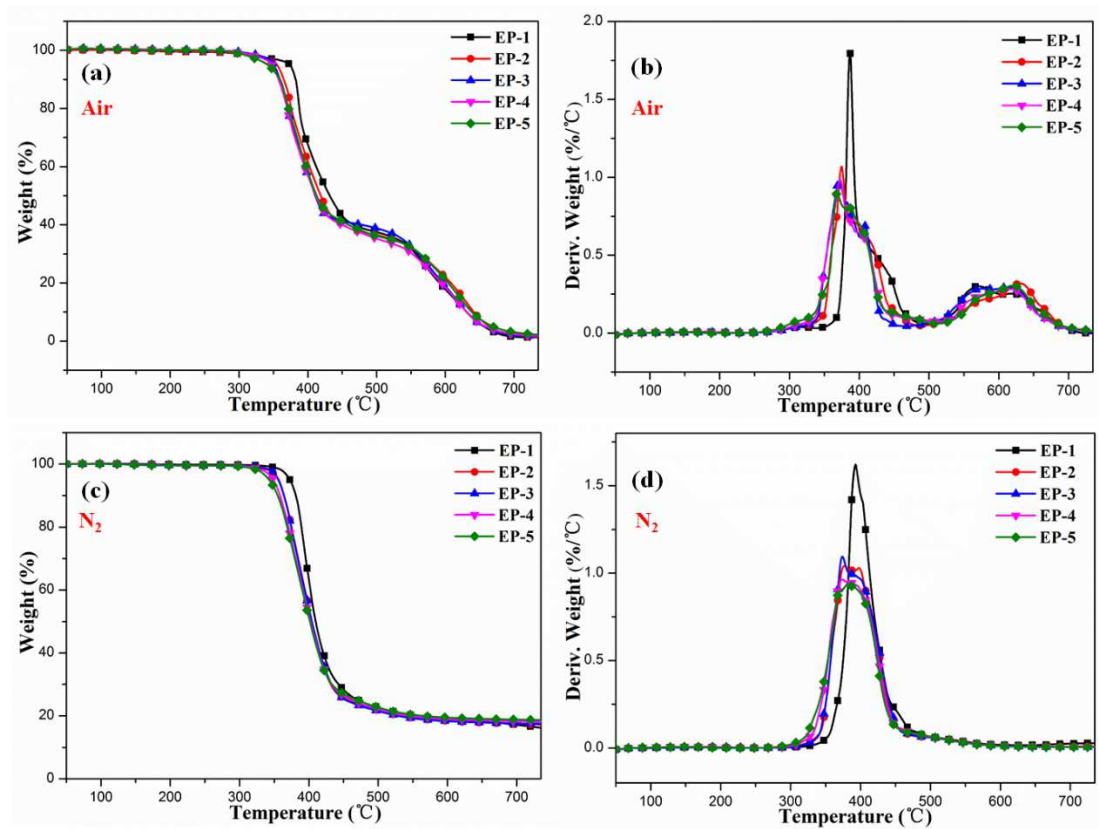
Fig. 5

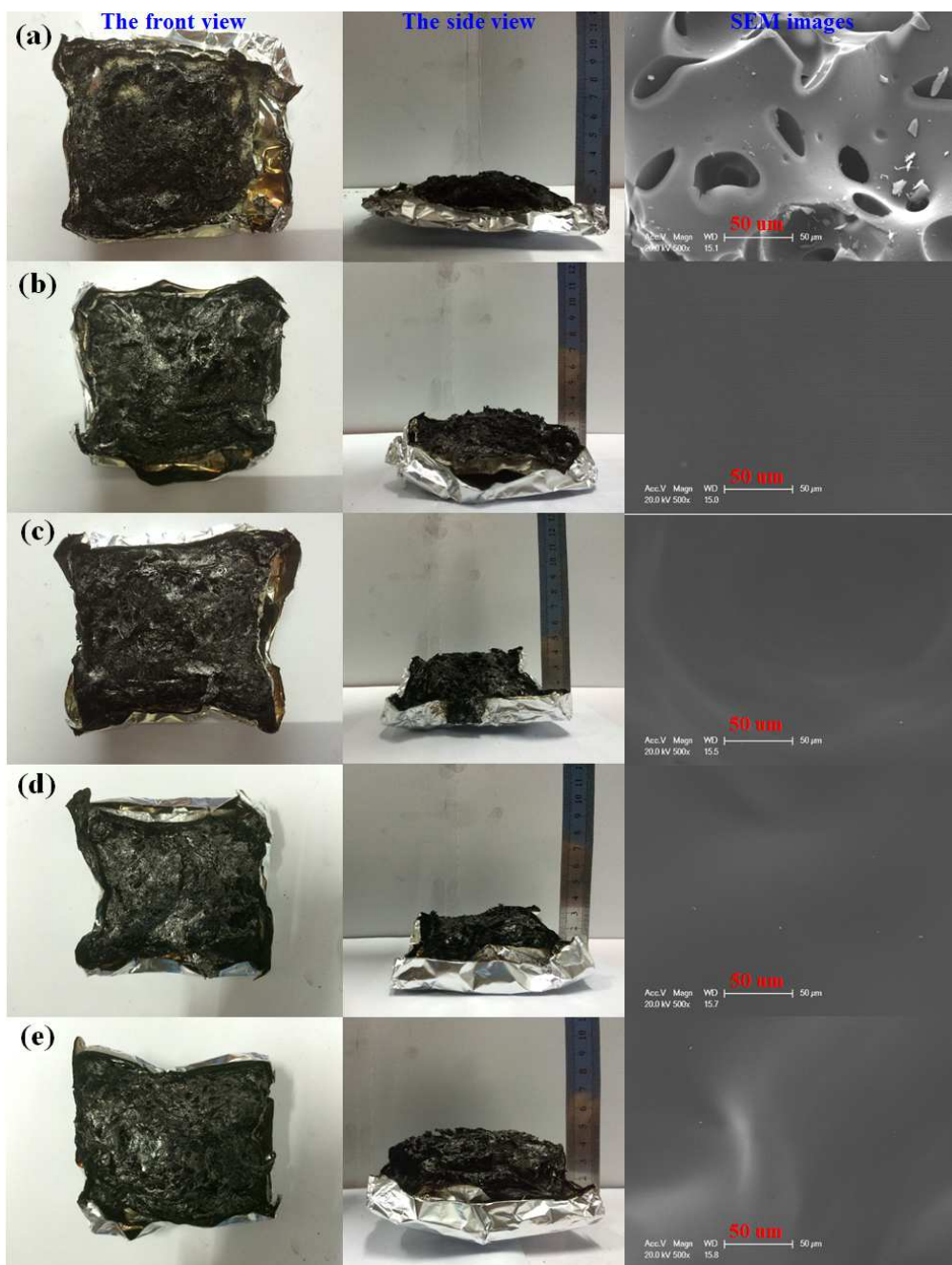**Fig. 6**
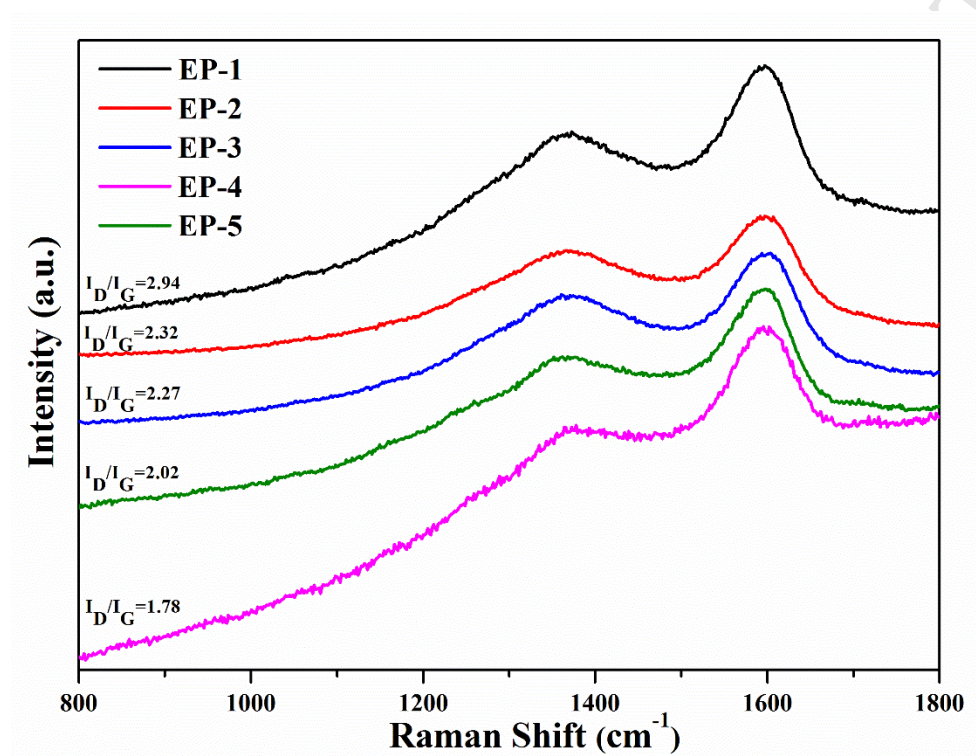
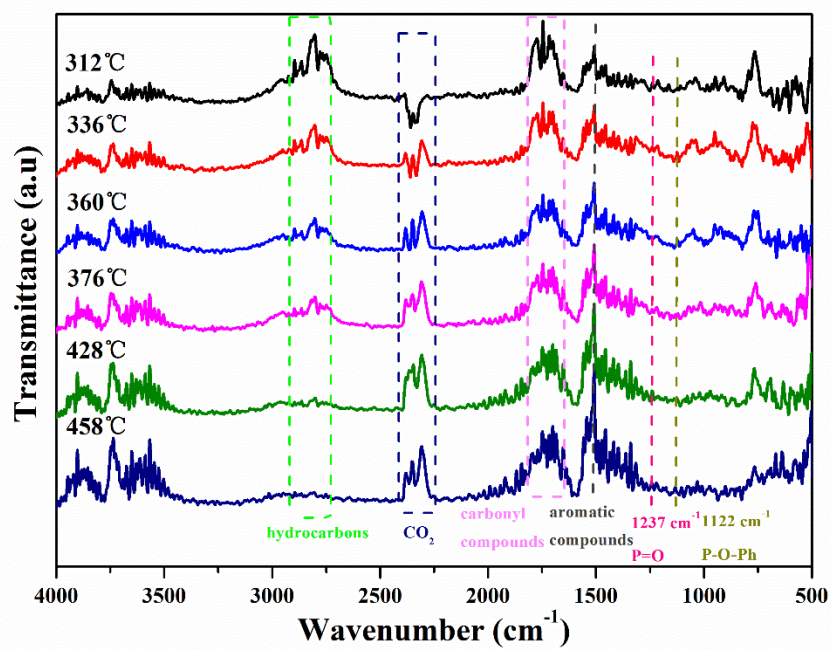**Fig. 7**

Fig. 8

36
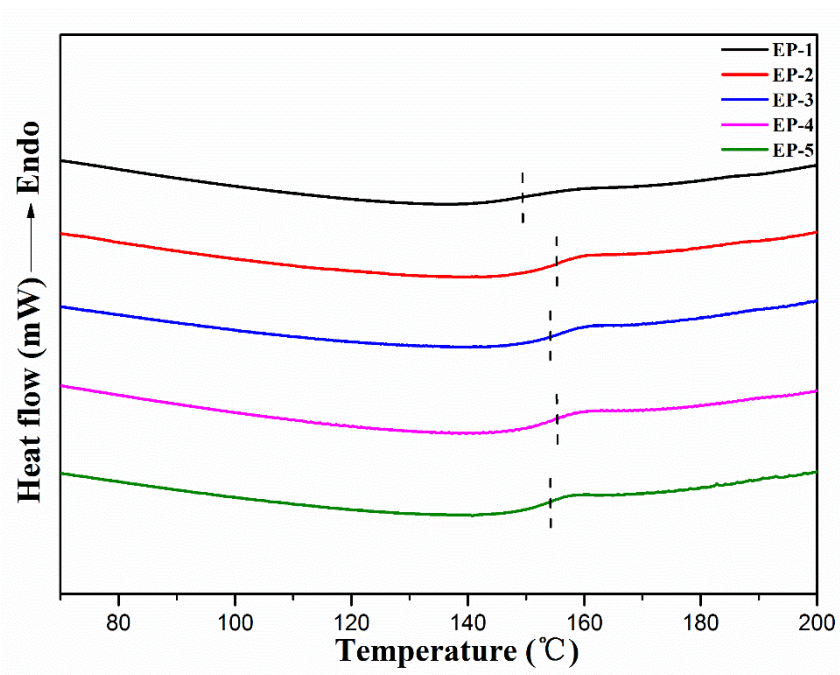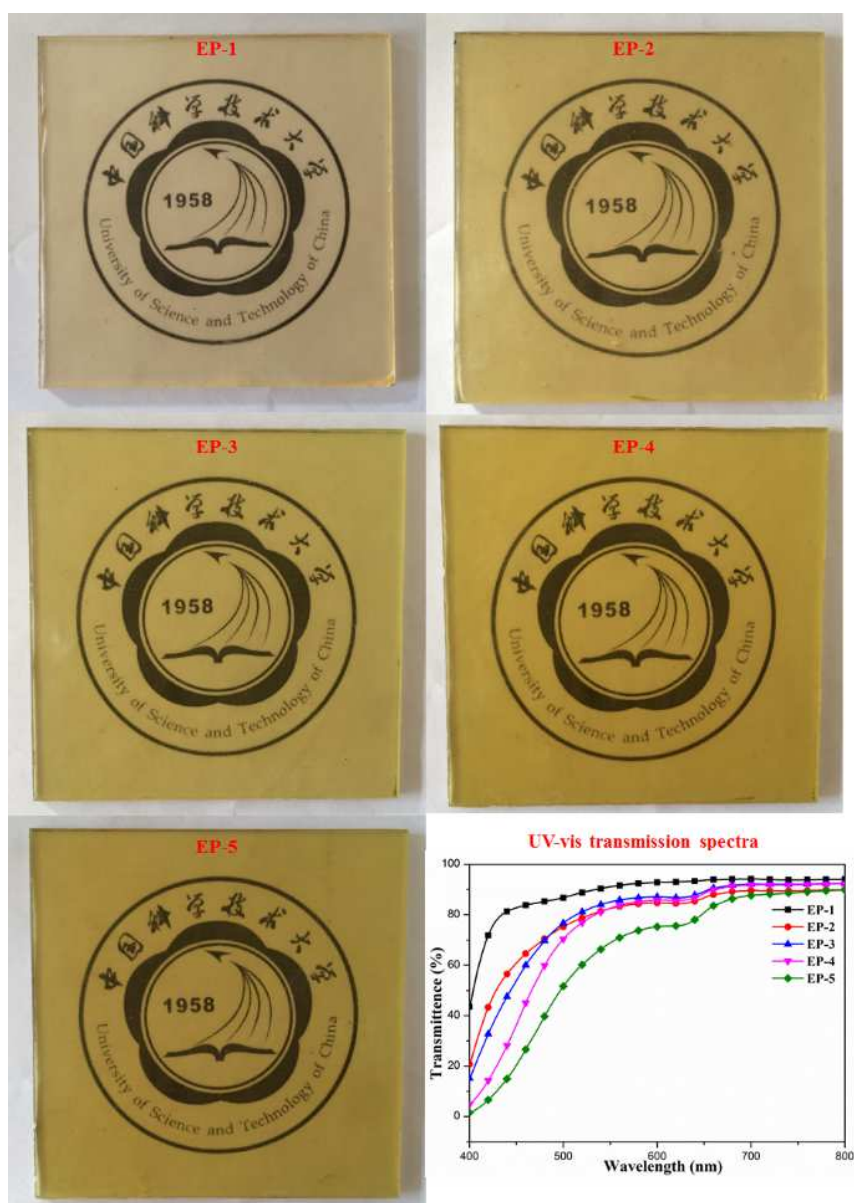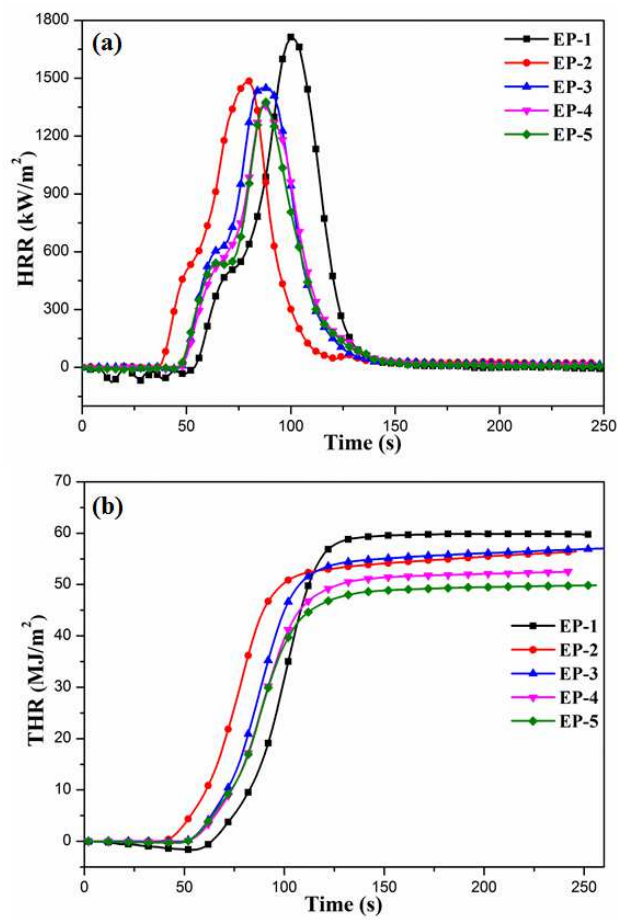
Fig. 9

Fig. 10

Fig. 11

Highlights

1. Highly efficient flame retarded epoxy resin (EP) systems are successfully established in this work, based on the ultra-low phosphorus loading.

2. When the phosphorus content is only 0.33 wt%, the EP composite receives V-0 rating in the UL 94 vertical burning test with LOI value of 30%.

3. Obviously decreased heat release rate and total heat release are also observed.

4. This flame retardant show very pronounced flame retardant effect both in gaseous and condensed phase.