

Accepted Manuscript

Economical and environment-friendly synthesis of a novel hyperbranched ploy(aminomethylphosphine oxide-amine) as co-curing agent for simultaneous improvement of fire safety, glass transition temperature and toughness of epoxy resins

Chao Ma, Shuilai Qiu, Bin Yu, Junling Wang, Chengming Wang, Wenru Zeng, Yuan Hu

PII: S1385-8947(17)30613-7
DOI: <http://dx.doi.org/10.1016/j.cej.2017.04.070>
Reference: CEJ 16824

To appear in: *Chemical Engineering Journal*

Received Date: 2 January 2017
Revised Date: 6 April 2017
Accepted Date: 13 April 2017

Please cite this article as: C. Ma, S. Qiu, B. Yu, J. Wang, C. Wang, W. Zeng, Y. Hu, Economical and environment-friendly synthesis of a novel hyperbranched ploy(aminomethylphosphine oxide-amine) as co-curing agent for simultaneous improvement of fire safety, glass transition temperature and toughness of epoxy resins, *Chemical Engineering Journal* (2017), doi: <http://dx.doi.org/10.1016/j.cej.2017.04.070>

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.



Economical and environment-friendly
synthesis of a novel hyperbranched
poly(aminomethylphosphine oxide-amine) as
co-curing agent for simultaneous improvement
of fire safety, glass transition temperature and
toughness of epoxy resins

Chao Ma^a, Shuilai Qiu^b, Bin Yu^d, Junling Wang^b, Chengming Wang^e, Wenru Zeng^{b,c,*},
and Yuan Hu^{b,*}

^a CAS Key Laboratory of Soft Matter Chemistry, Department of Polymer Science and
Engineering, University of Science and Technology of China, 96 Jinzhai Road,
Hefei, Anhui 230026, P.R. China

^b State Key Laboratory of Fire Science, University of Science and Technology of China,
96 Jinzhai Road, Hefei, Anhui 230026, P.R. China

^c National Synchrotron Radiation Laboratory, University of Science and Technology of
China, Hefei, Anhui 230029, P.R. China

^d Institute of Textiles & Clothing, Hong Kong Polytechnic University, Hunghom,
Kowloon, Hong Kong, P.R. China

^e Instruments' Center For Physical Science/Structure Research Laboratory, University
of Science and Technology of China, 96 Jinzhai Road, Hefei, Anhui 230026, P.R. China

* Corresponding authors.

E-mail addresses: wrzeng@ustc.edu.cn (W. Zeng), yuanhu@ustc.edu.cn (Y. Hu).

ABSTRACT

Epoxy resins inherently suffer flammability and brittleness. Various approaches have been used to improve their fire safety or toughness, however, glass transition temperature (T_g) is always deteriorated concomitantly. Herein, a novel hyperbranched poly(aminomethylphosphine oxide-amine) (HPAPOA) was synthesized from α -aminomethylation reaction of trihydroxymethylphosphine (THP) with piperazine before oxidation. THP was prepared from tetrakis(hydroxymethyl)phosphonium sulfate and barium hydroxide to avoid the usage of organic solvent in the synthesized process. When HPAPOA was utilized as co-curing agent for epoxy resins, T_g and impact strength of epoxy thermosets are improved due to the increased cross-linking density and the multiple toughening mechanisms. Simultaneously, fire safety include flame retardancy, smoke suppression and toxicity reduction is raised (except 1.0 wt% added). The condensed phase flame retardant mechanism is verified as increased char yield and protective and barrier effect of the formed char layer and the gas phase for release of phosphorus-containing species of HPAPOA. With as low as 3.0 wt% HPAPOA incorporated, epoxy thermoset achieved vertical burning V-0 rating with a limited oxygen index of 30.7. The blowing-out effect for upgradation of vertical burning rating is elucidated. Moreover, the curing reactivity of epoxy systems is slightly changed and the reaction activation energy is elevated. The thermal decomposition temperature of epoxy thermoset diminishes. With 2.0 wt% HPAPOA added, tensile and flexural properties are improved and those with other contents are

slightly depressed. The practical HPAPOA modified epoxy thermosets with obvious disadvantage conquered and higher T_g can be used in industries for high-performance applications.

Keywords: Hyperbranched polymer, Poly(aminomethylphosphine oxide-amine), Epoxy resin, Fire safety, Glass transition temperature, Toughening

1. Introduction

Epoxy resins are widely used in areas such as coatings, adhesives, structural applications and electronics due to their thermal and chemical resistance, superior electrical properties, relatively low shrinkage and good adhesion to many substrates. However, they suffer two main drawbacks: the inherent flammability and brittleness. Epoxy resins are more combustible than similar thermosets since they have a reduced tendency to carbonize [1], while their poor impact resistance comes from the fact that they are highly cross-linked rigid thermosets [2].

At present, the efficient halogen-containing flame retardants have been restricted by legislations because that corrosive and toxic gas, such as hydrogen halide, dibenzo-p-dioxin and dibenzofuran [3], and large amount of smoke are produced during combustion. As a kind of substitute of halogen-containing flame retardants, organophosphorus compounds are of great interest for their high efficiency, low toxicity and environment-friendliness. And they are particularly effective in oxygen-rich polymers, for example, epoxy resins [4]. Organophosphorus flame

retardants can influence the gas phase via radical scavenging to interrupt the burning reactions [5]. Nevertheless, it is generally accepted that they act predominantly in the condensed phase by transformation into phosphoric acid and polyphosphoric acid, which alter the rate and pathway of matrix decomposition and promote the formation of more shielding char residue [6]. The use of organophosphorus additives for flame retarded epoxy resins harbors the merit of low cost for the less change of the manufacturing process, however, they are of poor compatibility and easy to be lost by leaching. In contrast, the reactive strategy, chemically attaching organophosphorus moieties into epoxy backbones, is more attractive due to the sustainable fire resistance. Unfortunately, improving flame retardancy of epoxy resins by organophosphorus compounds is always accompanied by the deterioration of glass transition temperature (T_g) [7-11], which is a critical parameter for high-performance applications of epoxy resins. 9,10-dihydro-9-oxa-10-phosphaphenanthrene 10-oxide (DOPO) derivatives exhibit good ability in maintaining or increasing T_g of epoxy thermosets [12-14] due to the hindrance of bulky rigid DOPO groups on molecular chains mobility.

As is well known, a P–C bond is more stable to hydrolysis than a P–O–C bond, thus phosphine oxides containing complete P–C bonds can maintain functions more effectively. Aryl phosphine oxides [15-18] and isobutylbis(glycidylpropylether)phosphine oxide [1,19] (IHPO-Gly) were reported to improve fire resistance of epoxy resins. The dominated gas phase flame retardant mechanism of bis(3-aminophenyl)phenylphosphine oxide in epoxy resins is demonstrated by Braun et al. [15] and various UL-94 V-0 rating epoxy thermosets

were obtained with IHPO-Gly. Nevertheless, only little papers studied the flame retardant application of aminomethyl phosphine oxide. Morpholinomethylphosphine oxide, piperidinomethylphosphine oxide and bis(2-hydroxyethyl)aminomethylphosphine oxide were prepared and used to improve the fire resistance of polyurethane [20-22]. And other aliphatic aminomethylphosphine oxides were synthesized without flame retardant application like 1,3,5-triaza-7-phosphatrimethyldecane 7-oxide [23] and tris(thiomorpholinomethyl)phosphine oxide [24]. These small molecular compounds were obtained from the highly efficient α -aminomethylation reaction of trihydroxymethyl phosphine (THP) and aliphatic amine in water [25] before oxidation. However, THP was prepared from tetrakis(hydroxymethyl)phosphonium chloride with sodium hydroxide or triethylamine, which brought about the removal of chloridion with organic solvent. Chen et al. synthesized trihydroxymethyl phosphine oxide (THPO) utilizing tetrakis(hydroxymethyl)phosphonium sulfate and barium hydroxide and the precipitate of barium sulfate can be simply centrifuged [26].

On the other hand, the brittleness of epoxy resins restricts their applications. As a result, tremendous efforts have been made to enhance toughness by blending them with various modifiers such as low molecular weight rubbers and functionally terminated thermoplastics [27]. Recently, hyperbranched polymers have found use as a novel class of epoxy modifiers to improve impact resistance. They don't reduce processability of epoxy resins for their tailorable compatibility with uncured resins and low viscosity-to-molecular weight ratios, which are due to a lack of restrictive

interchain entanglements [28]. Furthermore, the highly functionalized nature of the shell surfaces of hyperbranched polymers enhances the interfacial adhesion of particles and matrix, which is vital for toughness improvement [29]. However, when the toughness of epoxy resins is elevated by hyperbranched polymers, their T_g are always sacrificed due to the flexible chains incorporated [27,29-33]. Several papers show that addition of epoxy-terminated hyperbranched molecules with stiff backbone can improve toughness without sacrificing T_g [34-36].

The motivation of this research is to develop practical modifiers to overcome flammability and brittleness of epoxy resins without damaging T_g . Therefore, a novel hyperbranched poly(aminomethylphosphine oxide-amine) (HPAPOA) was synthesized from the polycondensation of piperazine and THP before oxidation by hydrogen peroxide. THP was prepared from THPS and barium hydroxide to realize the synthesis of aminomethylphosphine oxide without organic solvent. And the synthesis of HPAPOA is also characterized by nontoxic and environmental-friendly THPS, low-cost industrial raw materials and reaction under room temperature, in other words, it has great industrialized potential. We first utilized α -aminomethylation reaction of THP to synthesize hyperbranched polymers. With more than 1.0 wt% HPAPOA co-cured into epoxy thermosets, fire safety (flame retardancy, CO reduction and smoke suppression), T_g and toughness were concurrently optimized. To the best of our knowledge, no papers reported similar results. Moreover, the curing behavior, thermal stability and tensile and flexural properties were also investigated.

2. Experimental section

2.1. Materials

75 wt% THPS aqueous solution was purchased from Aladdin Chemistry Co. Ltd., China. Barium hydroxide octahydrate, piperazine, 30% hydrogen peroxide aqueous solution, methanol, tetrahydrofuran and 4,4'-diaminodiphenylmethane (DDM) were provided by Sinopharm Chemical Reagent Co. Ltd., China. Diglycidyl ether of bisphenol A (DGEBA, E-44, epoxy value = 0.44 mol/100 g) was bought from Hefei Jiangfeng Chemical Industry Co. Ltd., China. All chemical reagents were used without further purification.

2.2. Synthesis of THP

The preparation of THP was modified with THPS and barium hydroxide [26,37]. A mixture of 101.4 g 75% THPS aqueous solution and 100 mL water was deoxidized with nitrogen for 0.5 h before 60.2 g barium hydroxide octahydrate was added. Then the turbid solution was stirred for 2 h under nitrogen and centrifuged to separate the precipitate of barium sulfate. After water was evaporated, the crude product was dried at 100 °C under vacuum for 24 h to remove formaldehyde from the hemiacetal adduct of THP and it [38,39]. Then THP was almost quantitatively yielded (96%) as a colorless viscous liquid.

2.3. Synthesis of HPAPOA

35.3 g (0.284 mol) THP and 49.0 g (0.569 mol) piperazine were dissolved in water predeoxidized by nitrogen separately. Then THP solution was added dropwise into

piperazine solution under nitrogen. After the mixture was agitated overnight, nitrogen was removed and 32.2 g 30% hydrogen peroxide aqueous solution was slowly dropped into it. The reaction mixture was maintained for 2 h and concentrated on a rotary evaporator. Then, it was dropped into 1 L tetrahydrofuran and the precipitate was filtered and washed with tetrahydrofuran. After drying in a vacuum oven at 80 °C for 24 h, HPAPOA was yielded as a slightly yellow solid (78%).

2.4. Preparation of Epoxy Thermosets

DGEBA and HPAPOA (1.0, 2.0, 3.0 and 3.5 percent of the total weight of DGEBA/DDM/HPAPOA curing system) were mixed at 100 °C until a homogeneous solution was obtained. Then DDM was added and the total amount of amino groups of DDM and HPAPOA were equivalent to that of DGEBA epoxy groups. After the complete dissolution of DDM, the mixture was degassed for 3 min in a vacuum oven at 100°C and then poured into a preheated stainless steel mold. A three-step curing procedure was carried out: 120 °C for 2 h, 150 °C for 2 h and 180 °C for another 2 h. Finally, the thermoset was cooled slowly to room temperature to avoid cracking. The neat epoxy thermoset was prepared via the same method without adding HPAPOA and it is represented as EP. The modified epoxy thermoset with X wt% HPAPOA was denoted as EPX.

2.5. Characterization

Nuclear magnetic resonance (NMR) was measured on a Bruker AV400 NMR spectrometer (400 MHz) at room temperature.

Fourier transform infrared (FTIR) spectroscopy was obtained on a Nicolet 6700 spectrometer (Nicolet Instrument Company, U.S.).

Elemental analysis was performed with a Vario EL III elemental analyzer.

Gel permeation chromatography (GPC) was performed on an Agilent 1260 apparatus. A mixture of acetic acid and sodium acetate aqueous solution was used as eluent and polyethylene glycol standards were employed for calibration.

Differential scanning calorimetry (DSC) was measured with a DSC Q2000 (TA Instruments Inc., USA) under nitrogen. T_g of epoxy thermoset was measured at a heating rate of 10 °C/min and recorded at the mid-point of the inflexion curve from the second heating run. For studying the curing kinetics, DGEBA and curing agent were dissolved in a minor amount of methanol and then the mixture was evaporated under vacuum at room temperature. The freshly prepared samples were enclosed in aluminum pans. The DSC curves of each system were recorded at four different heating rates of 5, 10, 15 and 20 °C/min from room temperature to 250 °C.

Thermogravimetric analysis (TGA) was conducted with a Q5000 thermal analyzer (TA Co., U.S.) at a heating rate of 20 °C/min.

Limited oxygen index (LOI) was obtained according to ASTM D 2863 with a HC-2 oxygen index meter (Jiangning Analysis Instrument Company, China). The dimension of specimens is $100 \times 6.5 \times 3.0 \text{ mm}^3$.

Vertical burning test (UL-94) was carried out using a CFZ-2 type instrument (Jiangning Analysis Instrument Co., China) and the sample dimension is $130 \times 13 \times 3 \text{ mm}^3$. In the test, the specimens were subjected to two 10 s flame application, and t_1

and t_2 were obtained as the two self-extinguish times. Epoxy thermoset attains UL-94 V-0 rating if each t_1 and t_2 of five samples don't exceed 10 s and the total burning time for five samples does not exceed 50 s without any dropping.

Scanning electron microscopy (SEM) photograph was obtained on a FEI Sirion 200 scanning electron microscope.

Cone calorimetry was performed on an apparatus of Fire Testing Technology according to ISO 5660. The samples are of dimension $100 \times 100 \times 3 \text{ mm}^3$ and burnt under an external heat flux of 35 kW/m^2 . The measurement for each specimen was repeated three times, and the error values of the typical cone calorimeter were reproducible within $\pm 5\%$.

The pyrolysis photoionization time-of-flight mass spectrometry (PY-PI-TOFMS) is described elsewhere [40,41].

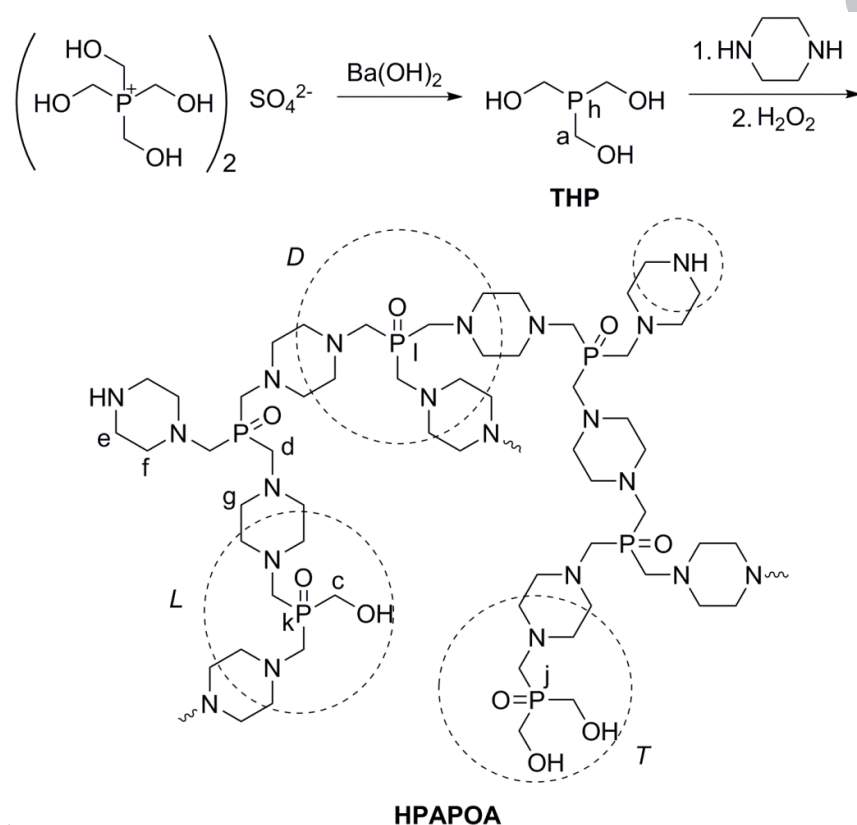
Dynamic mechanical analysis (DMA) was carried out on TA DMA Q800. Specimens were tested in a tensile mode at a heating rate of $5 \text{ }^\circ\text{C/min}$ and a fixed frequency of 1 Hz.

Tensile and flexural properties were measured at room temperature with a CMT6104 universal testing machine (MTS Systems Co., Ltd., China). The dumb-bell shaped tensile samples were tested according to ASTM D638. Flexural property was determined in three-point bending mode according to ASTM D790 and flexural strength was reported as the load at break or at yield measured at 5% deformation of the outer surface of the unbroken sample. The unnotched Izod impact strength test was performed on a ZBC1400-A impact tester (MTS Systems Co., Ltd., China) as per

ASTM D256. Results are presented as the energy to break per fractured area. For mechanical property tests, an average of five specimens was taken for each set.

3. Results and discussion

3.1. Synthesis and Characterization of THP and HPAPOA



Scheme 1. Synthetic Routes of THP and HPAPOA.

THP was first prepared from THPS and barium hydroxide, which was used not only as an alkali but also a precipitator of sulfate ions. Afterwards, HPAPOA was synthesized from the polycondensation of THP and piperazine before oxidation by

hydrogen peroxide. The synthetic routes are presented in Scheme 1 and Fig. 1 shows ^1H and ^{31}P NMR spectra of THP and HPAPOA in deuterium oxide. In the ^1H NMR spectrum of THP, an intense doublet located at 4.06 ppm (peak a) corresponds to the methylene protons of $\text{P}-\text{CH}_2-\text{O}$. The neighboring very weak peak at 4.12 ppm (peak b) is observed for the methylene protons of THPO formed during dissolution in NMR testing due to the easy conversion of THP to THPO by oxygen [38,42]. As for that of HPAPOA, the peak at 2.91 ppm (peak d) is attributed to the methylene protons of $\text{N}-\text{CH}_2-\text{P}=\text{O}$ and the emergence of this peak proves the reaction successfully proceeded. The chemical shift at 4.05 ppm (peak c) was due to the methylene protons of residual hydroxymethyl. The peaks between 2.3 and 2.8 ppm are ascribed to the hydrogen on the six-membered cycles. In detail, the signal at 2.70 ppm (peak e) reveals the contribution of methylene protons on $\text{C}-\text{CH}_2-\text{NH}$. The peaks at 2.61 ppm (peak f) and 2.53 (peak g) correspond to the methylene protons of $\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}$ and $\text{N}-\text{CH}_2-\text{CH}_2-\text{N}$ respectively. The ratio of integrated intensity of peak d to f and g is 1:2, which verifies the correct assignment of these peaks. Besides, the integrated intensity ratio of peak e to f and g is 35.6:64.4, which indicates the ratio of secondary to tertiary amino groups in HPAPOA is 35.6:64.4.

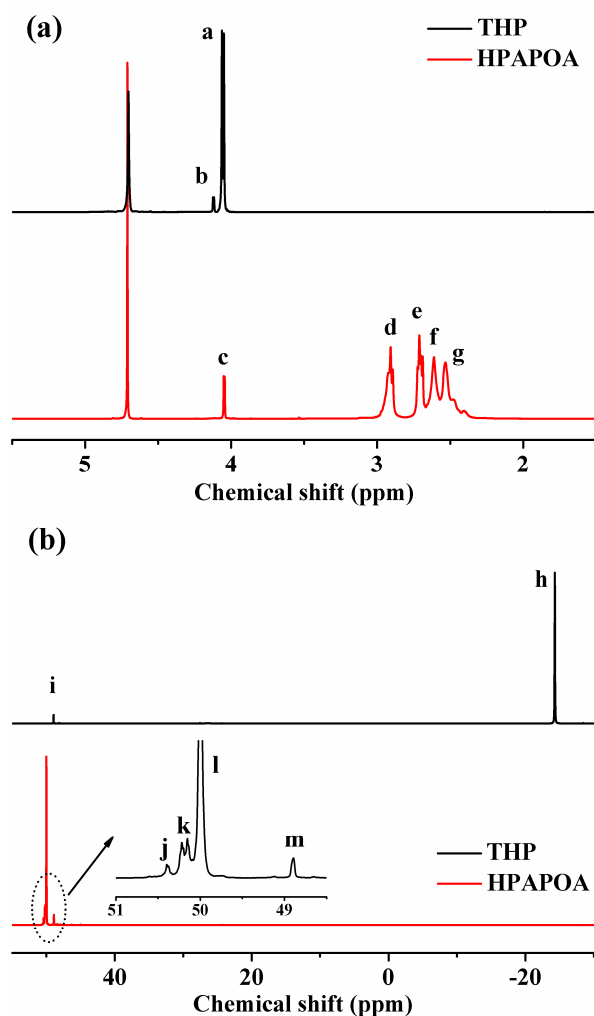


Fig. 1. ^1H (a) and ^{31}P (b) NMR spectra of THP and HPAPOA in deuterium oxide.

In the ^{31}P NMR spectra, THP is characterized by the singlet at -24.3 ppm (peak h) due to phosphorus of $\text{P}-(\text{CH}_2)_3$. Correspondingly, the phosphorus signal of THPO was found at 48.9 ppm (peak i). In the case of HPAPOA, the intense peak at 50.0 ppm (peak l) is ascribed to the phosphorus of $\text{O}=\text{P}-(\text{CH}_2-\text{N})_3$. The signal at 50.2 ppm (peak k) is attributed to the phosphorus of $\text{HO}-\text{CH}_2-\text{P}(=\text{O})-(\text{CH}_2-\text{N})_2$ while the peak at 50.4 ppm (peak j) corresponds to the phosphorus of $(\text{HO}-\text{CH}_2)_2-\text{P}(=\text{O})-\text{CH}_2-\text{N}$. The appearance of these signals indicates the successful reaction. And the above three

structures are distinguished as dendritic (*D*), linear (*L*) and terminal (*T*) units in a hyperbranched polymer respectively [43]. The structural perfection of a hyperbranched polymer is usually characterized by degree of branching (DB), which is determined by the following equation:

$$DB = \frac{D + T}{D + L + T} \quad (1)$$

The DB value can be estimated by the integral intensity of peak j, k and l in the ^{31}P NMR spectrum of HPAPOA to be 0.77. Moreover, the weak singlet at 48.9 ppm (peak m) for THPO was in virtue of the partial oxidation of THP by oxygen despite the care taken during the polycondensation reaction and its very similar solubility with HPAPOA. From the area ratio of peak m to peaks j, k and l, it can be computed that 2.0% phosphorus exists in the form of THPO. As a consequence, the influence of little THPO in HPAPOA can be neglected.

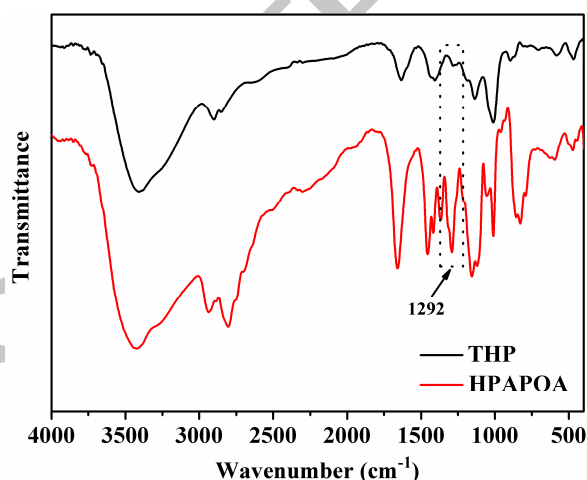


Fig. 2. FTIR spectra of THP and HPAPOA.

FTIR spectra of THP and HPAPOA are presented in Fig. 2. The broad absorption

around 3400 cm^{-1} is ascribed to the stretching vibration of N–H and O–H and the two peaks between 2700 and 3000 cm^{-1} are assigned to C–H stretching vibration of methylene groups. The bending vibration of N–H and O–H and methylene C–H occurred around 1630 and 1420 cm^{-1} respectively. The peak at 1292 cm^{-1} is attributed to P=O stretching vibration, which is intense for HPAPOA and weak for THP (due to little THPO). And the absorption around 1130 cm^{-1} reveals the contribution of C–C, C–N and C–P stretching vibration. Moreover, the peak at 1011 cm^{-1} is relative to C–O stretching vibration [44].

Table 1

Element Contents of HPAPOA.

HPAPOA	C (wt %)	H (wt %)	N (wt %)	O (wt %)	P (wt %)
Calculated	49.40	8.84	20.50	8.97	12.27
Found	49.49	8.75	20.59	9.08	12.09 ^a

^a Estimated from 1 - 49.49% - 8.75% - 20.59% - 9.08%.

Elemental contents of HPAPOA from elemental analysis and calculation are listed in Table 1. The calculated values are based on the structure in Scheme 1 (*D*, *L*, *T* and terminal $-\text{CH}_2-\text{NH}-\text{CH}_2-$ units in the circles and THPO as components) and the ratios are obtained from NMR analysis. Results show that the calculated values are in good accordance with the measured values for C, H, N and O, which further verifies the structure of HPAPOA as shown in Scheme 1. HPAPOA only consists of C, H, N, O and P, thus the phosphorus content of it can be estimated to be 12.09% from the measured values. Moreover, from N content and the ratio of secondary to tertiary

amino groups (35.6:64.4), the amine equivalent weight of HPAPOA is calculated to be 190.8 g/mol. The formulations of epoxy thermosets are shown in Table 2.

Table 2

Formulations of Epoxy Thermosets.

Sample	DGEBA (g)	DDM (g)	HPAPOA (g)
EP	100	21.8	0
EP1	100	21.5	1.23
EP2	100	21.2	2.47
EP3	100	20.8	3.74
EP3.5	100	20.7	4.38

GPC was utilized to measure the molecular weight of HPAPOA and its number-average molecular weight is 2100 g/mol with the polydispersity index of 1.19. The molecular weight of HPAPOA should be larger because that the hydrodynamic radius of hyperbranched polymers is smaller than liner polymers with the same molecular weight.

3.2. Nonisothermal Curing Behaviors

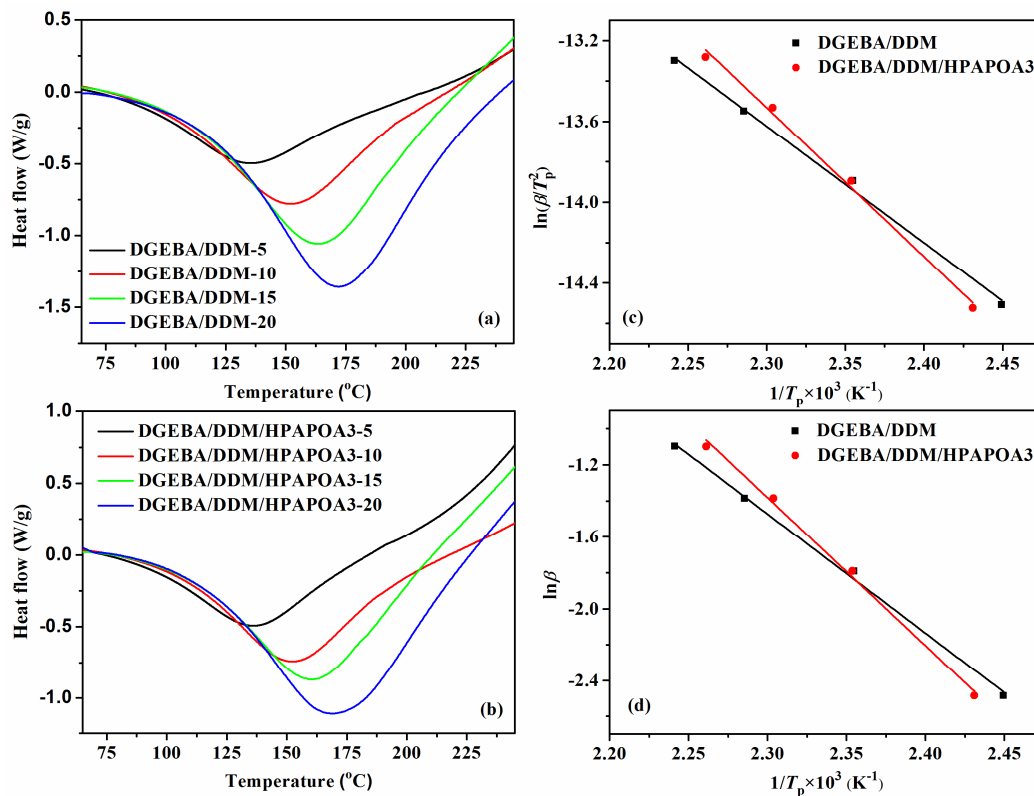


Fig. 3. DSC curves of DGEBA/DDM (a) and DGEBA/DDM/HPAPOA3 (b) curing systems at different heating rates, plots of $\ln(\beta/T_p^2)$ (c) and $\ln\beta$ (d) against $1/T_p$.

Dynamic DSC scan was used to trace the nonisothermal curing process and Fig. 3a and b shows the DSC thermograms of DGEBA/DDM and DGEBA/DDM/HPAPOA3 curing systems (the number after HPAPOA refers to the weight percent of it in the curing system) at different heating rates (β). Similar behaviors of DGEBA/DDM and DGEBA/DDM/HPAPOA curing systems are observed. The curing processes are all characterized by single exothermic peaks and the exothermic peak temperatures and curing heats are recorded as T_p and ΔH respectively (listed in Table 3). T_p shift to higher temperatures with increasing heating rate for all curing systems, which is owing to the less prompt respond of reaction

mixture to faster heating rate. This systematic peak evolution depends on the apparent reaction activation energy and pre-exponential factor. The well-known Kissinger's and Ozawa's methods are usually used to evaluate them [45,46]. In the case of Kissinger's method, T_p is related to the heating rate using the equation:

$$\ln\left(\frac{\beta}{T_p^2}\right) = \ln\left(\frac{AR}{E_k}\right) - \frac{E_k}{RT_p} \quad (2)$$

where A , R and E_k are pre-exponential factor, ideal gas constant and activation energy respectively. Accordingly, the plot of $\ln(\beta/T_p^2)$ versus $1/T_p$ should be linear and E_k and A can be calculated from the slope and intercept of the straight line. Similarly, the activation energy derived from Ozawa's method is estimated from the slope in the plot of $\ln\beta$ versus $1/T_p$ according to the following equation:

$$\ln\beta = -1.052 \frac{E_o}{RT_p} + \ln\left(\frac{AE_o}{R}\right) - 5.331 \quad (3)$$

where E_o is the activation energy. Fig. 3c and d illustrate the linear relationship of $\ln(\beta/T_p^2)$ and $\ln\beta$ against $1/T_p$ in DGEBA/DDM and DGEBA/DDM/HPAPOA curing systems. And the calculated activation energies and frequency factors are listed in Table 3.

Table 3

Curing Kinetic Parameters Obtained from Nonisothermal DSC Scans.

Curing system	β (°C/min)	T_p (°C)	ΔH (J/g)	E_k (kJ/mol)	A (s ⁻¹)	E_o (kJ/mol)
DGEBA /DDM	5	135.1	212.3	47.9	4.00×10^3	52.3
	10	151.5	217.4			
	15	164.4	254.7			
	20	173.0	314.6			
DGEBA /DDM /HPAPOA1	5	136.8	220.3	49.1	5.27×10^3	53.4
	10	154.0	230.8			
	15	166.2	261.4			
	20	174.2	316.4			
DGEBA /DDM /HPAPOA2	5	139.3	214.8	55.7	3.88×10^4	59.8
	10	153.7	222.9			
	15	164.5	236.3			
	20	173.1	280.7			
DGEBA /DDM /HPAPOA3	5	138.2	222.1	61.3	2.27×10^5	65.0
	10	151.7	236.8			
	15	160.9	255.0			
	20	169.1	303.9			
DGEBA /DDM /HPAPOA3.5	5	136.9	235.6	64.4	6.25×10^5	67.9
	10	150.1	245.9			
	15	158.4	274.3			
	20	166.3	315.1			

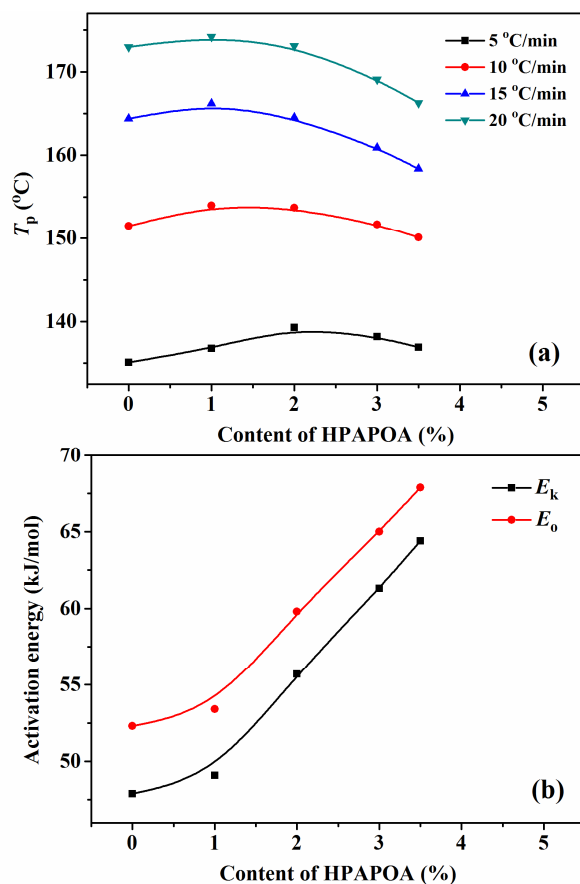


Fig. 4. Curves of T_p at different heating rate (a) and activation energy (b) versus content of HPAPOA.

Fig. 4 shows the dependence of T_p at different heating rate and activation energy on content of HPAPOA. T_p at a given heating rate exhibits similar variation tendency that they increase first and then decrease. The curing system with lower T_p under the same condition indicates higher reactivity of curing agent towards epoxy resin. The variation of reactivity can be associated with the integrate function of multiple factors. The electron cloud density on the nitrogen of HPAPOA is enriched by two electron-donating alkyls while the electron-withdrawing phenyl reduces that of DDM. The enhanced electron density facilitates the nucleophilic attack of amino groups

towards oxirane rings, which elevates the reactivity. Moreover, the catalytic effect of tertiary aliphatic amino and the unreacted terminal hydroxyl groups in HPAPOA is also responsible for the improvement of reactivity. However, the larger steric hindrance of secondary amine in HPAPOA leads to lower reactivity compared to the primary amine in DDM. At last, DGEBA/DDM/HPAPOA3.5 system exhibits higher reactivity of curing agent in contrast with DGEBA/DDM system at heating rates of 10, 15 and 20 °C/min. On the other hand, the calculated apparent activation energy falls into the typical range (50-70 kJ/mol) of epoxy-amine curing systems [47]. A good coincidence between Kissinger's and Ozawa's methods is observed that activation energy increase with the increase of HPAPOA content and E_o is higher than E_k for the same system. The variation tendency of activation energy doesn't correspond to that of T_p because reactivity is also influenced by temperature. Furthermore, activation energy can be used to interpret the fact that T_p of DGEBA/DDM/HPAPOA2 curing system is higher than that of DGEBA/DDM/HPAPOA1 at 5 °C/min while the opposite phenomenon occurs at higher heating rates. At 5 °C/min, the reactivity of DGEBA/DDM/HPAPOA2 curing system is lower. When higher heating rate is applied, higher curing temperature range (Fig. 3a, b) and reactivity can be attained. And the curing system with higher activation energy can afford more reactivity improvement. With obviously increased activation energy, the reactivity improvement of DGEBA/DDM/HPAPOA2 curing system is so significant that it is higher than that of DGEBA/DDM/HPAPOA1. Thus T_p of it is lower at higher heating rates.

3.3. Thermal Properties of Epoxy Thermosets

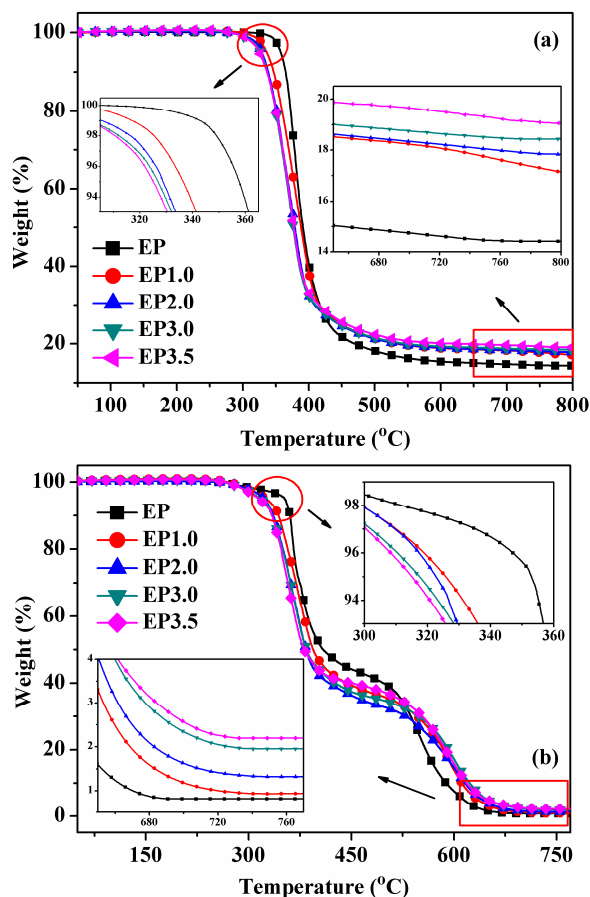


Fig. 5. TGA curves of epoxy thermostets under nitrogen (a) and air (b).

Thermal properties of epoxy thermostets were first assessed by thermogravimetric analysis. TGA curves under nitrogen and air are presented in Fig. 5. Main parameters include the decomposition temperature at 5% weight loss (T_d), the temperature at maximum weight loss rate (T_{max}) and the char yield (CY) at 750 °C are listed in Table 4. With the incorporation of HPAPOA, the T_d values of epoxy thermostets under nitrogen and air both decrease because of the existence of P–C bonds with low bond energy. Nevertheless, epoxy thermostets with T_d higher than 315 °C under nitrogen and air are high enough for applications. On the contrary, the T_{max} values of flame retardant epoxy resins in the second-stage degradation under air exceed that of EP by

more than 45 °C. This result means that the thermo-oxidative stability of char residue at high temperature is significantly enhanced. Furthermore, the CY values under both nitrogen and air increase with more HPAPOA added. Thus, HPAPOA improves thermal and thermal-oxidative stability of char residue and promotes to form more char residue, which is beneficial for the increment of flame retardancy.

Table 4

Thermal and Flame Retardant Properties of Cured Epoxy Resins.

Sample	Nitrogen			Air			T_g^a (°C)	T_g^b (°C)	v_e (mol/m ³)	LOI (%)	UL-94
	T_d (°C)	T_{max} (°C)	CY (%)	T_d (°C)	T_{max} (°C)	CY (%)					
EP	357	380	14.5	353	370, 555	0.82	156.6	157.2	2177	24.3	NR ^c
EP1.0	336	382	17.7	326	382, 611	0.93	157.1	158.3	2199	27.4	V-1
EP2.0	329	377	18.0	323	377, 609	1.32	157.3	159.9	2212	29.5	V-1
EP3.0	327	372	18.5	318	370, 610	1.95	160.5	165.9	2321	30.7	V-0
EP3.5	325	373	19.3	316	371, 601	2.20	164.0	167.8	2452	30.9	V-0

^a T_g from DSC. ^b T_g from DMA. ^c No rating.

DSC was then employed to determine T_g of HPAPOA and the cured epoxy resins. The DSC profiles are presented in Fig. 6 and the T_g values of epoxy thermosets are listed in Table 4. HPAPOA exhibits a T_g of 54 °C and the existence of T_g indicates the formation of macromolecular. For epoxy thermosets, T_g increases with increasing HPAPOA fraction and T_g of EP3.5 exceeds that of EP by 7.4 °C.

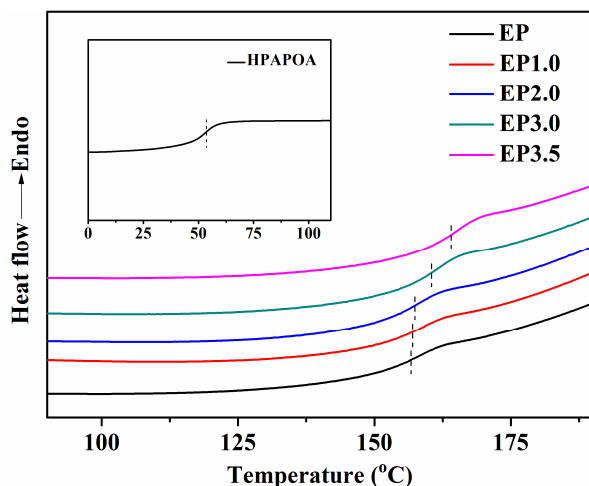


Fig. 6. DSC thermograms of HPAPOA and cured epoxy resins.

3.4. Combustion Behaviors of Epoxy Thermosets

3.4.1. LOI and UL-94

LOI and UL-94 tests were first conducted to investigate the flame retardant effect of HPAPOA in epoxy resins and the related results are shown in Table 4. EP is combustible with an LOI value of 24.3% and no UL-94 rating. When HPAPOA was added, modified epoxy resins achieved higher LOI values and UL-94 rating. V-0 rating was obtained for EP3.0 and EP3.5 and 3.0 wt% is just slightly higher than the reported lowest loading amount (2.5 wt%) for DGEBA/DDM epoxy resins to afford V-0 rating [48,49]. Therefore, HPAPOA endows epoxy resins excellent flame retardancy.

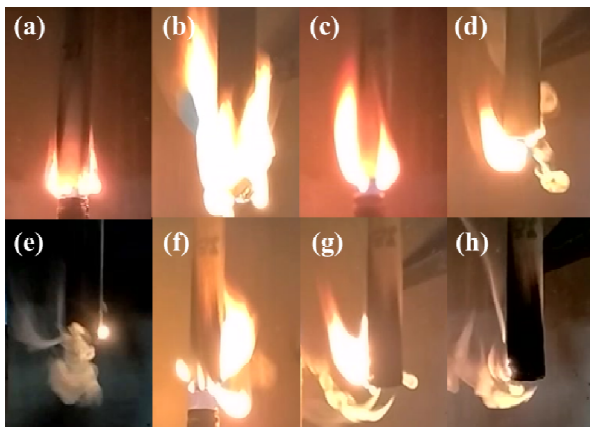


Fig. 7. Video screenshots of EP for the first 10 s ignition (a, b), EP3.0 for the first 10 s ignition (c, d, e) and EP3.0 for the second 10 s ignition (f, g, h) during UL-94 test.

During UL-94 test, the blowing-out effect of HPAPOA flame retardant epoxy resins is observed as shown in Fig. 7. For EP, after the first 10 s ignition, the fire propagated quickly (Fig. 7b) and the sample was burnt out. In the case of HPAPOA modified epoxy resins, obviously spurring fire occurred during the first and second 10 s ignition (Fig. 7c, f). After removal of the igniter, frequent and high-speed jetting of pyrolytic gas persisted (Fig. 7d, g) and ultimately blew out the fire (Fig. 7e, h), which is the so-called blowing-out effect [50,51]. Jet of pyrolytic gas is easier to be observed after the flame extinction. To further elucidate the blowing-out effect, char residue of EP and EP3.0 after UL-94 test were subjected to SEM measurement, which is shown in Fig. 8. The char surface of EP is flat (Fig. 8a) while a series of tiny convexities are distributed on that of EP3.0. Jet of pyrolytic gas can be explained through the SEM image of the convexity [48,49], which is marked in the red circle in Fig. 8d. A char layer first formed during combustion and the decomposed volatiles accumulated under it. Then the char layer was deformed under high temperature and pressure and

the convexity was produced. When the pressure was high enough, the char layer was broken and the pyrolytic gas was quickly jetted under high pressure. The pore left can be clearly seen in the convexity. When SEM images of char residue are magnified, compact and continuous char layer is observed for EP3.0 (Fig. 8f). The dense char layer can effectively seal the pyrolytic gas to attain a high pressure. While the char layer of EP is loose (Fig. 8c) and it couldn't render gas accumulation. Thus, no rating was achieved for EP and HPAPOA flame retarded epoxy resins afford UL-94 rating with obvious blowing-out effect.

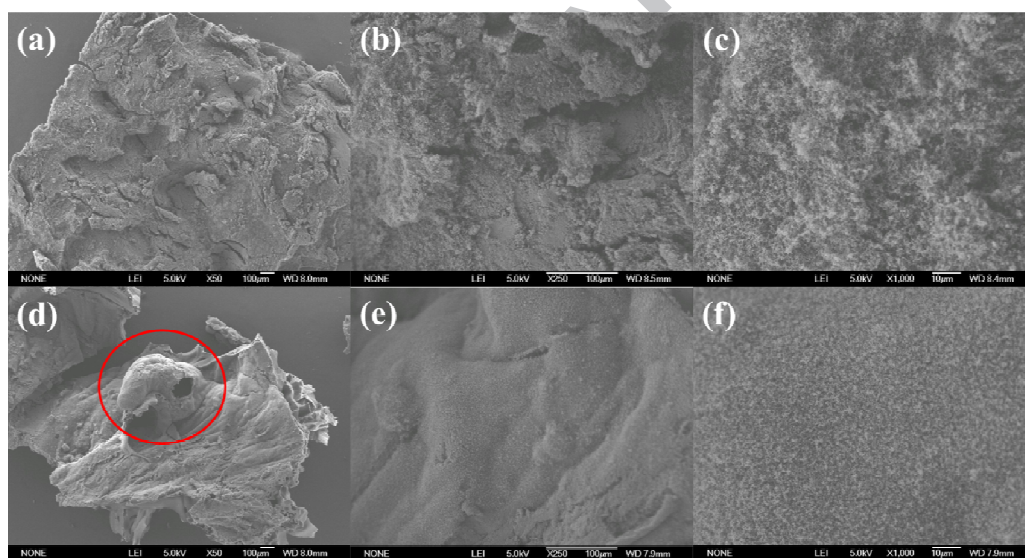


Fig. 8. SEM images of char residue after UL-94 test: EP-50 \times (a), EP-250 \times (b), EP-1000 \times (c), EP3.0-50 \times (d), EP3.0-250 \times (e) and EP3.0-1000 \times (f).

Besides, for HPAPOA modified epoxy resins, more significant blowing-out effect and shorter combustion time were found for samples containing more HPAPOA. This is mainly attributed to the following two aspects: more HPAPOA promoted epoxy

resin matrix to degrade faster and more volatiles were jetted; more compact char formed with more HPAPOA facilitated the production of higher pressure and more rapid spurting. Therefore, with increasing HPAPOA ratio, UL-94 rating is upgrade and EP3.0 and EP3.5 afford V-0 rating.

3.4.2. Cone Calorimetry

Table 5

Combustion Parameters of Cured Epoxy Resins from Cone Calorimetry.

Sample	TTI (s)	p-HRR (kW/m ²)	THR (MJ/m ²)	CY (%)	p-COPR (g/s)	TCOP (g)	TCO ₂ P (g)	p-SPR (m ² /s)	TSP (m ²)
EP	58	1790	68.9	9.1	0.070	2.44	52.2	0.58	30.2
EP1.0	51	1920	57.0	14.6	0.091	2.39	47.6	0.62	28.1
EP2.0	55	1164	53.0	15.5	0.058	2.35	42.1	0.49	27.4
EP3.0	60	1106	47.4	16.9	0.052	2.21	36.4	0.47	26.6
EP3.5	62	966	46.2	17.6	0.045	2.01	35.5	0.40	23.6

The flame retardant effect of HPAPOA in epoxy resins was further investigated with cone calorimeter. Characteristic parameters include time to ignition (TTI), peak of heat release rate (p-HRR), total heat release (THR), CY, peak of CO production rate (p-COPR), total CO production (TCOP), total CO₂ production (TCO₂P), peak of smoke production rate (p-SPR) and total smoke production (TSP) are listed in Table 5.

Plots of HRR and THR versus time are presented in Fig. 9.

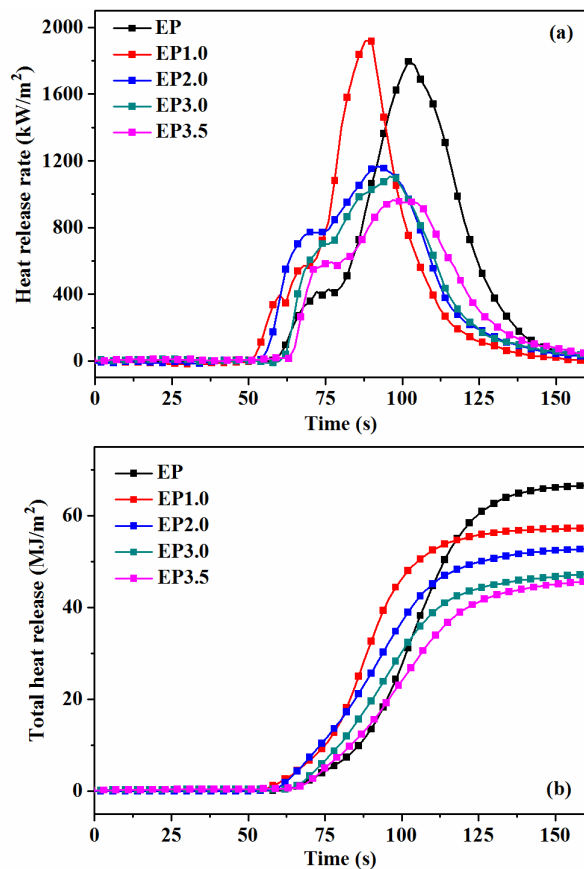


Fig. 9. HRR (a) and THR (b) curves of epoxy thermostets.

TTI values show a variation tendency of initial decrement and subsequent increment as HPAPOA content increases. On the one hand, TTI was declined due to the earlier degradation of epoxy resin matrix promoted by HPAPOA. On the other hand, HPAPOA released phosphorus-containing substances during decomposition (see the pyrolysis of HPAPOA). They are speculated to produce PO type radicals under thermal-oxidative conditions, which can quench the active H and OH radicals and interrupt the chain reaction for combustion. Therefore, TTI was delayed. Ultimately, the ignition of EP3.0 and EP3.5 is harder than that of EP. For p-HRR and THR, their values depress significantly with increasing HPAPOA ratio except EP1.0.

P-HRR of EP3.5 decreases by 46.0% in comparison with that of EP and THR 32.9%.

The lowered p-HRR and THR can be partially attributed to the increased CY, which reduced flammable volatiles and suppressed the intensity of combustion. In addition, morphology of char residue after cone test also provides information about flame retardant mechanism. Their digital photographs are shown in Fig. 10. The little char residue of EP is fragmentary and fragile. However, the intumescent char residue of EP2.0, EP3.0 and EP3.5 is continuous, compact and rigid. This kind of char residue not only hindered flammable gas from heat and oxygen, but also slowed their release. The protective and barrier effect of char layer further declined p-HRR and THR. Therefore, condensed phase flame retardant mechanism of HPAPOA is verified as increased char yield and protective and barrier effect of char layer.

As for EP1.0, its p-HRR is higher than that of EP and THR lower. Firstly, the decomposition of epoxy resin matrix was promoted by HPAPOA and combustible gas was produced faster. Nevertheless, with only 1.0 wt% HPAPOA, the char amount and strength of EP1.0 was not high enough and closed char layer couldn't be formed as illustrated in Fig. 10 (from side view). Without protective and barrier effect, the concentrated combustion of volatiles led HRR to reach a higher peak value while THR still decreased due to the obviously increased CY.

In fires, smoke and toxic CO lead to asphyxia and play the most important role in human casualties [52]. As HPAPOA content increases, p-COPR and p-SPR show the same variation trend with p-HRR. This is because more volatile burned brings about more heat release and combustion product (CO and smoke). P-COPR of EP3.5 is

depressed by 35.7% in contrast to that of EP and p-SPR 31.0%. Similarly, TCOP and TSP decrease as THR behaves. TCOP of EP3.5 diminishes by 17.6% and TSP 21.9%. Therefore, HPAPOA exhibits smoke suppression and toxicity reduction effect in epoxy resin combustion except 1.0 wt% added.

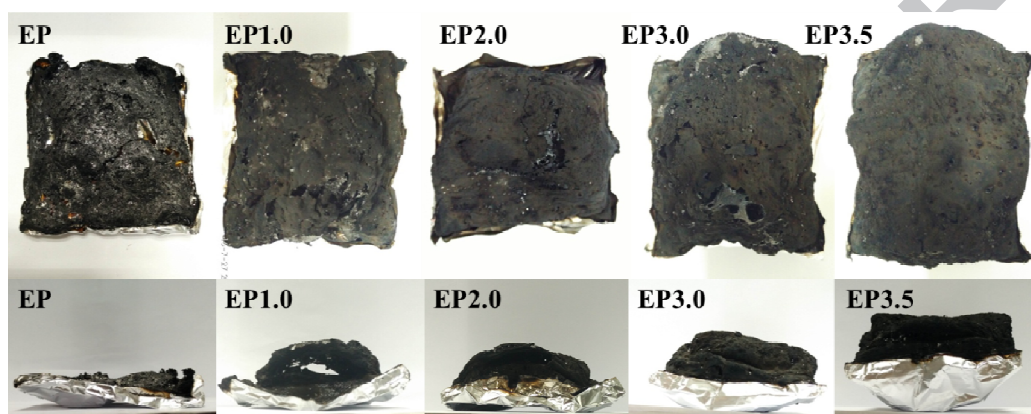


Fig. 10. Front and side view of char residue after cone test.

To summarize above combustion behaviors, fire safety of epoxy resins is improved with higher LOI value and UL-94 rating and declined heat, smoke and toxicity hazards when HPAPOA content exceeds 1.0 wt%.

3.5. Pyrolysis of HPAPOA

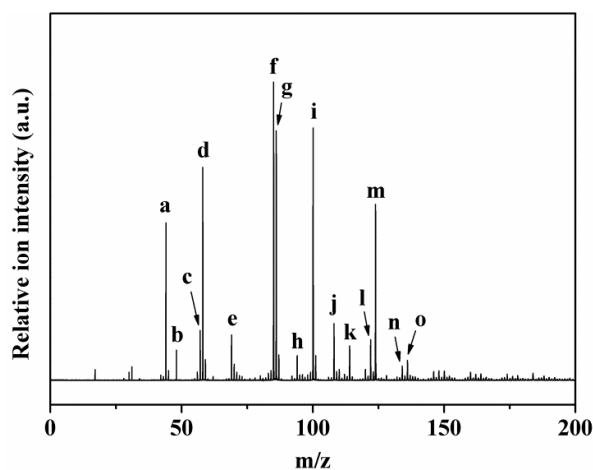


Fig. 11. PY-PI-TOFMS of HPAPOA.




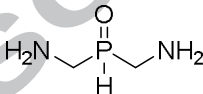

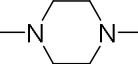

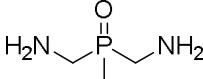
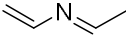

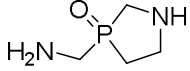

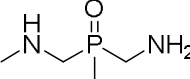
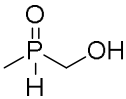
PY-PI-TOFMS was utilized to analyze the pyrolytic volatiles of HPAPOA. 20.0 mg HPAPOA was introduced into a tubular furnace preset at 500 °C with nitrogen as the carrier gas. The accumulated signal was recorded until no decomposition product released. The mass spectra are depicted in Fig. 11. Thanks to the near-threshold “soft” photoionization, nearly all mass peaks can be assigned as fragment-free parent ions [40,41]. Table 6 lists the assignments of mass peaks.

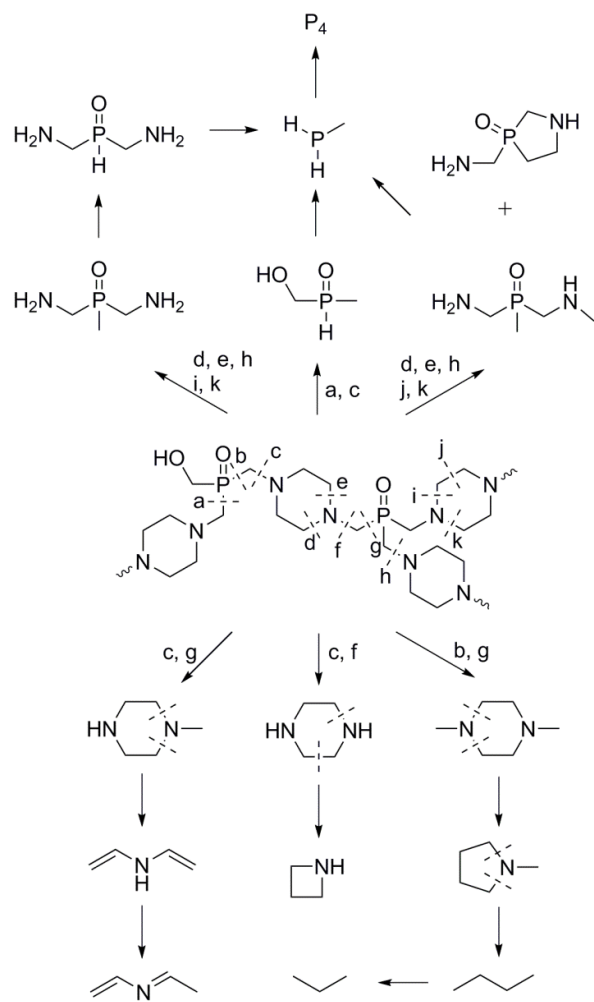
The decomposition products of HPAPOA can be categorized as piperazine-based compounds and phosphorus-containing species. Piperazine and its derivatives were released and further decomposed to produce compounds of smaller molecular weight. Phosphine oxides were also generated and transformed to methylphosphine and elemental phosphorus afterwards. The proposed pyrolytic mechanism is presented in Scheme 2. According to the positions of chemical bond cleavage, HPAPOA cured into epoxy networks could still release phosphorus-containing species. Thus, the gas phase flame retardant mechanism of HPAPOA is speculated as the flame inhibition

effect of PO type radicals generated from them during combustion [53,54].

Table 6

Assignments of the Mass Peaks in PY-PI-TOFMS.

Peak	m/z	Structure	Peak	m/z	Structure
a	44.04		i	100.08	
b	48.00		j	108.04	
c	57.05		k	114.09	
d	58.06		l	122.06	
e	69.04		m	123.86	P ₄
f	85.06		n	134.05	
g	86.06		o	136.07	
h	94.03				



Scheme 2. Proposed Pyrolytic Mechanism of HPAPOA.

3.6. Mechanical Properties of Epoxy Thermosets

3.6.1. Dynamic Mechanical Analysis

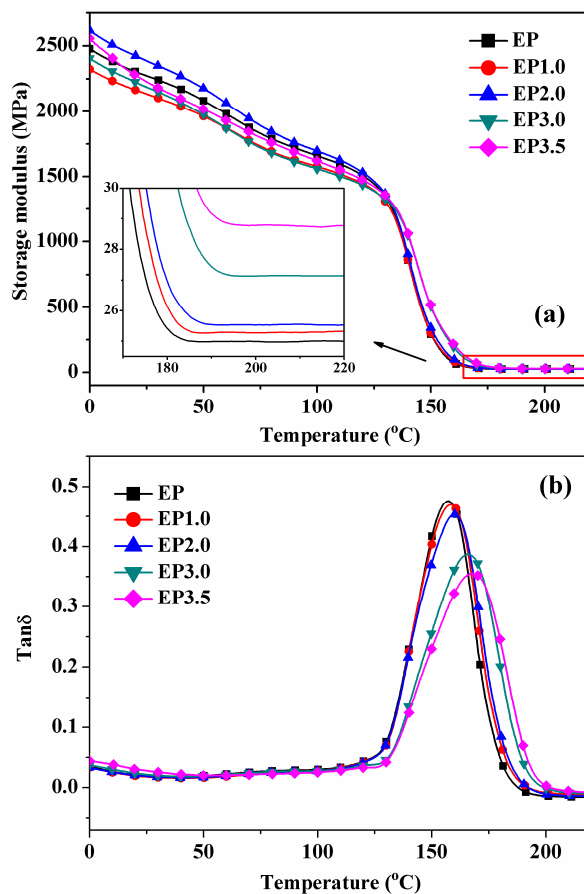


Fig. 12. Storage modulus (a) and $\tan\delta$ (b) of cured epoxy resins.

Dynamic mechanical behavior of cured epoxy resins was obtained by DMA and the plots of storage modulus (E') and loss factor ($\tan\delta$) versus temperature are presented in Fig. 12. In the $\tan\delta$ curve, the peak temperature of α relaxation is defined as T_g and the corresponding data are listed in Table 4. They show close values and variation trend with the results of DSC. In addition, T_g of epoxy thermosets with low HPAPOA loading significantly deviates from that of EP and no relaxation peak around T_g of HPAPOA (54 °C) can be detected. Thus, it is proved that HPAPOA is miscible with epoxy resins after curing [32].

On the other side, preliminary insight into mechanical properties can be achieved

through storage modulus. E' values of epoxy thermosets below 50 °C increase in the order: EP1.0 < EP3.0 < EP3.5 < EP < EP2.0 (interpreted in 3.6.2). Besides, curing density (ν_e) can be estimated from the storage modulus in the rubber plateau by the equation derived from the classic theory of rubber elasticity [55]:

$$\nu_e = E'/3RT \quad (4)$$

where E' is the storage modulus taken 30 °C above T_g , R is the ideal gas constant and T is the thermodynamic temperature of $T_g + 30$ °C. The calculated ν_e values are presented in Table 4. It is shown that cross-linking density of epoxy thermosets is elevated as HPAPOA content increase. This can be attributed to the polyfunctionality and short chain length between branching points of HPAPOA and leads to the improvement of T_g .

3.6.2. Tensile, Flexural and Impact Properties

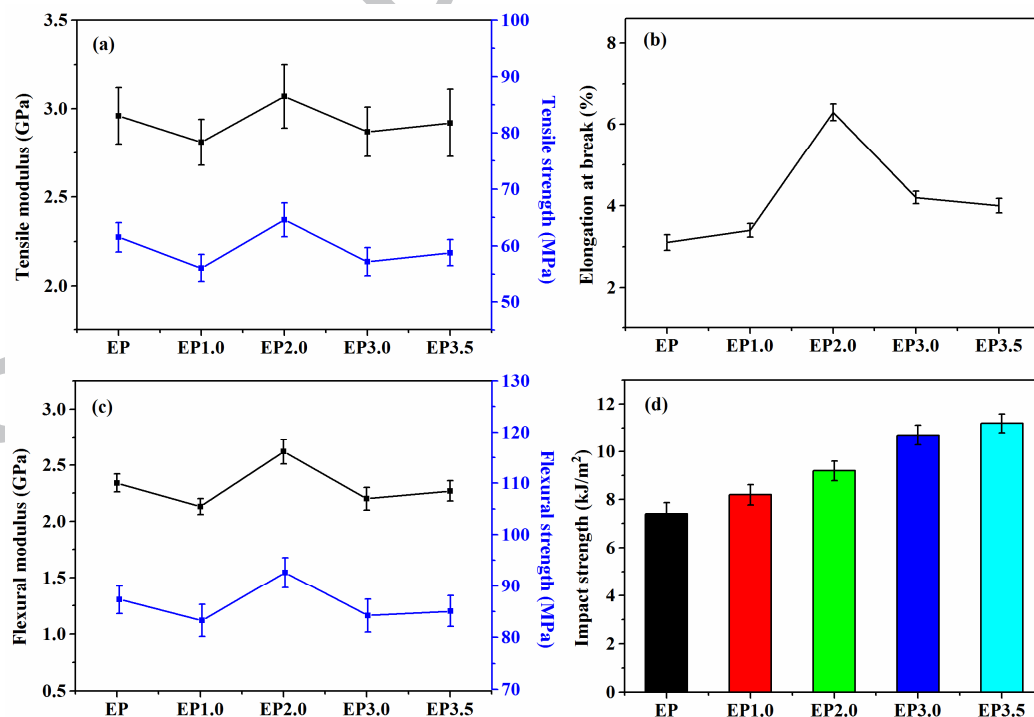


Fig. 13. Tensile modulus and strength (a), elongation at break (b), flexural modulus

and strength (c) and impact strength (d) of epoxy thermosets.

Fig. 13 depicts the change of tensile modulus and strength, elongation at break, flexural modulus and strength and impact strength of cured epoxy resins as the content of HPAPOA increase. The modulus and strength of tension and bending demonstrate the same variation with storage modulus in DMA and break strain increases first and decreases later. These variations are mainly determined by molecular chain rigidity, cross-linking density and internal stress. EP1.0 shows depressed modulus and strength and improved break strain in comparison with those of EP for that the plastification of flexible aliphatic chains of HPAPOA dominates. As for EP2.0, its modulus and strength, and failure strain are all higher than those of EP1.0, which mainly derives from the increased cross-linking density [36], and the improved fractional free volume from intra-molecular and inter-molecular cavities within and between hyperbranched molecules [34-35] and flexible chain content, respectively. However, those of EP3.0 all diminish. The flexible chains decline modulus and strength while the obviously increased cross-linking density decreases break strain. EP3.5 exhibits higher modulus and strength and lower failure strain due to the more significantly raised cross-linking density.

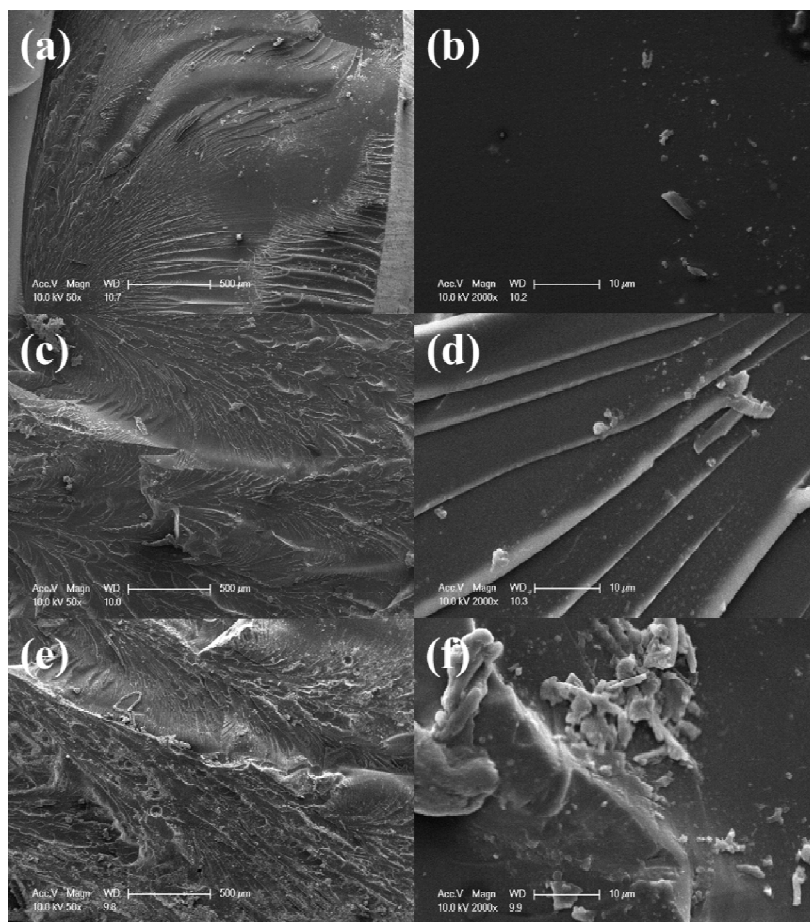


Fig. 14. SEM images of fracture surfaces after impact testing: EP-50 \times (a), EP-2000 \times (b), EP2.0-50 \times (c), EP2.0-2000 \times (d), EP3.5-50 \times (e) and EP3.5-2000 \times (f).

Impact strength of epoxy thermosets is improved with increasing HPAPOA fraction and a 51% increment is obtained for EP3.5 compared to EP. The impact behavior can be explained in terms of fracture surface morphology. The SEM images of fracture surfaces of EP, EP2.0 and EP3.5 are presented in Fig. 14. The smooth cross-sectional surface of EP indicates that brittle failure occurred during its impact testing. Nevertheless, ductile fracture feature can be observed in the SEM micrographs of EP2.0 and EP3.5 for their rough and irregular surfaces and substantial

plastic deformation on them and this feature is more obvious for EP3.5 than EP2.0. Furthermore, no phase separation can be seen in the SEM images of EP2.0 and EP3.5. Therefore, HPAPOA is compatible with cured epoxy resins. The possible toughening mechanisms are proposed: the aliphatic chains of HPAPOA provide greater flexibility between crosslinks and an increased number of conformational rearrangement modes during a fracture event, or in situ energy dissipation[30]; the deformation capability of intra-molecular cavities within and inter-molecular free volume between hyperbranched molecules improves toughness; the very small distance between cavities due to the small size of HPAPOA promotes shear deformation or yielding; the crack blunting by cavities may also operate in hybrids; during cooling, the higher local free volume in the vicinity of hyperbranched crosslinks than the bulk can induce compressive stresses on the surrounding regions of the network, which can promote yielding and thus improve toughness[36].

4. Conclusions

A novel hyperbranched poly(aminomethylphosphine oxide-amine) was prepared via an economical and environment-friendly route and it was used as co-curing agent for epoxy resins. The structure of HPAPOA is characterized by NMR, FTIR, elemental analysis and GPC. The nonisothermal DSC results show that the reactivity of epoxy curing system containing 1.0 and 2.0 wt% HPAPOA is slightly decreased in contrast to that of DGEBA/DDM. While those containing 3.0 and 3.5 wt% exhibit increased reactivity at higher heating rate. The curing activation energy is improved

with increasing HPAPOA content. After curing, thermal decomposition temperature of epoxy thermosets is depressed while char yield is significantly elevated. Both T_g measured by DSC and DMA are raised due to the improved cross-linking density (calculated from DMA). When as low as 3.0 wt% HPAPOA was loaded, epoxy thermoset passed UL-94 V-0 rating with an LOI value of 30.7 and the blowing-out effect is responsible for the upgradation of UL-94 rating. Cone calorimetry shows reduced p-HRR, THR, p-COPR, TCOP, p-SPR and TSP except p-HRR of EP1.0. The condensed phase flame retardant mechanism of HPAPOA in epoxy resins is verified as increased char yield and protective and barrier effect of the formed char layer. And the gas phase flame retardant mechanism is speculated as release of phosphorus-containing species of HPAPOA, which is detected by PY-PI-TOFMS. In comparison with EP, EP2.0 exhibits better tensile and flexural properties while those of others are depressed. The impact strength of epoxy thermosets is raised with increasing HPAPOA fraction and the possible toughening mechanisms are proposed. To sum up, when the content of HPAPOA in epoxy thermosets exceeds 1.0 wt%, fire safety, T_g and toughness are simultaneously improved. And EP2.0 exhibits excellent comprehensive property as raised fire safety, T_g and mechanical properties with nearly maintained curing reactivity and thermal stability.

Acknowledgements

The authors would like to acknowledge the support from National Key Research and Development Program of China (2016YFC0800605), National Natural Science

Foundation of China (21374111), USTC-NSRL Joint Funds (KY2320000007) and Fundamental Research Funds for the Central Universities (WK2320000032).

ORCID

Chao Ma: 0000-0003-0101-9945

References

- [1] M.J. Alcón, G. Ribera, M. Galià, V. Cádiz, Synthesis, characterization and polymerization of isobutylbis(glycidylpropylether) phosphine oxide, *Polymer* 44 (2003) 7291-7298.
- [2] D. Foix, X. Ramis, F. Ferrando, A. Serra, Improvement of epoxy thermosets using a thiol-ene based polyester hyperbranched polymer as modifier, *Polym. Int.* 61 (2012) 727-734.
- [3] C. Martín, G. Lligadas, J.C. Ronda, M. Galia, V. Cadiz, Synthesis of novel boron-containing epoxy-novolac resins and properties of cured products, *J. Polym. Sci., Part A: Polym. Chem.* 44 (2006) 6332-6344.
- [4] S. Hörold, Phosphorus flame retardants in thermoset resins, *Polym. Degrad. Stab.* 64 (1999) 427-431.
- [5] S.Y. Lu, I. Hamerton, Recent developments in the chemistry of halogen-free flame retardant polymers, *Prog. Polym. Sci.* 27 (2002) 1661-1712.
- [6] I.D. Carja, D. Serbezeanu, T. Vlad-Bubulac, C. Hamciuc, A. Coroaba, G. Lisa, C.G. López, M.F. Soriano, V.F. Pérez, M.D.R. Sánchez, A straightforward,

- eco-friendly and cost-effective approach towards flame retardant epoxy resins, *J. Mater. Chem. A* 2 (2014) 16230-16241.
- [7] C.H. Lin, C.S. Wang, Novel phosphorus-containing epoxy resins part I. synthesis and properties, *Polymer* 42 (2001) 1869-1878.
- [8] R.M. Perez, J.K.W. Sandler, V. Altstädt, T. Hoffmann, D. Pospiech, M. Ciesielski, M. Döring, Effect of DOP-based compounds on fire retardancy, thermal stability, and mechanical properties of DGEBA cured with 4,4'-DDS, *J. Mater. Sci.* 41 (2006) 341-353.
- [9] H.C. Chang, H.T. Lin, C.H. Lin, W.C. Su, Facile preparation of a phosphinated bisphenol and its low water-absorption epoxy resins for halogen-free copper clad laminates, *Polym. Degrad. Stab.* 98 (2013) 102-108.
- [10] D.C. Sun, Y.W. Yao, Synthesis of three novel phosphorus-containing flame retardants and their application in epoxy resins, *Polym. Degrad. Stab.* 96 (2011) 1720-1724.
- [11] R.M. Perez, J.K.W. Sandler, V. Altstädt, T. Hoffmann, D. Pospiech, J. Artner, M. Ciesielski, M. Döring, A.I. Balabanovich, B. Schartel, Effective halogen-free flame retardancy for a monocomponent polyfunctional epoxy using an oligomeric organophosphorus compound, *J. Mater. Sci.* 41 (2006) 8347-8351.
- [12] J.Y. Shieh, C.S. Wang, Synthesis of novel flame retardant epoxy hardeners and properties of cured products, *Polymer* 42 (2001) 7617-7625.
- [13] S.X. Cai, C.H. Lin, Flame-retardant epoxy resins with high glass-transition temperatures from a novel trifunctional curing agent: dopotriol, *J. Polym. Sci.*,

Part A: Polym. Chem. 43 (2005) 2862-2873.

- [14] M. Ciesielski,; A. Schäfer,; M. Döring, Novel efficient DOPO-based flame-retardants for PWB relevant epoxy resins with high glass transition temperatures, Polym. Adv. Technol. 19 (2008) 507-515.
- [15] U. Braun, A.I. Balabanovich, B. Scharrel, U. Knoll, J. Artner, M. Ciesielski, M. Döring, R. Perez, J.K.W. Sandler, V. Altstädt, T. Hoffmann, D. Pospiech, Influence of the oxidation state of phosphorus on the decomposition and fire behaviour of flame-retarded epoxy resin composites, Polymer 47 (2006) 8495-8508.
- [16] M.D. Shau, T.S. Wang, Syntheses, structure, reactivity, and thermal properties of new cyclic phosphine oxide epoxy resins cured by diamines, J. Polym. Sci., Part A: Polym. Chem. 34 (1996) 387-396.
- [17] P. Jain, V. Choudhary, I.K. Varma, Effect of structure on thermal behaviour of epoxy resins, Eur. Polym. J. 39 (2003) 181-187.
- [18] M. Sponton, L.A. Mercado, J.C. Ronda, M. Galia, V. Cadiz, Preparation, thermal properties and flame retardancy of phosphorus- and silicon-containing epoxy resins, Polym. Degrad. Stab. 93 (2008) 2025-2031.
- [19] M.A. Espinosa, M. Galia, V. Cadiz, Novel phosphorilated flame retardant thermosets: epoxy-benzoxazine-novolac systems, Polymer 45 (2004) 6103-6109.
- [20] H. Sivriev, V. Kaleva, G. Borissov, Synthesis of polyurethanes from phosphorus- and nitrogen-containing diols obtained on the basis of

- tetrakis(hydroxymethyl)phosphonium chloride, Eur. Polym. J. 22 (1986) 761-765.
- [21] H. Sivriev, G. Borissov, L. Zabski, W. Walczyk, Z. Jedlinski, Synthesis and studies of phosphorus-containing polyurethane foams based on tetrakis(hydroxymethyl)phosphonium chloride derivatives, J. Appl. Polym. Sci. 27 (1982) 4137-4147.
- [22] H. Sivriev, V. Kaleva, G. Borissov, L. Zabski, Z. Jedlinski, Rigid polyurethane foams with reduced flammability, modified with phosphorus- and nitrogen-containing polyol, obtained from tetrakis(hydroxymethyl)phosphonium chloride. Eur. Polym. J. 24 (1988) 365-370.
- [23] D.J. Daigle, T.J. Decuir, J.B. Robertson, D.J. Darensbourg, 1,3,5-Triaza-7-phosphatricyclo[3.3.1.1^{3,7}]decane and derivatives, Inorg. Synth. 32 (1998) 40-45.
- [24] R. Starosta, U.K. Komarnicka, M. Puchalska, M. Barys, Solid state luminescence of copper(I) (pseudo)halide complexes with neocuproine and aminomethylphosphanes derived from morpholine and thiomorpholine, New J. Chem. 36 (2012) 1673-1683.
- [25] J.G.E. Krauter, M. Beller, An easy and practical synthetic route to electron rich water soluble ligands: α -aminomethylation of trishydroxymethylphosphine, Tetrahedron 56 (2000) 771-774.
- [26] 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.
- [27] D.M. Dhevi, S.N. Jaisankar, M. Pathak, Effect of new hyperbranched polyester of varying generations on toughening of epoxy resin through interpenetrating polymer networks using urethane linkages, *Eur. Polym. J.* 49 (2013) 3561-3572.
- [28] G. Xu, W.F. Shi, M. Gong, F. Yu, J.P. Feng, Curing behavior and toughening performance of epoxy resins containing hyperbranched polyester, *Polym. Adv. Technol.* 15 (2004) 639-644.
- [29] R.J. Varley, W. Tian, Toughening of an epoxy anhydride resin system using an epoxidized hyperbranched polymer, *Polym. Int.* 53 (2004) 69-77.
- [30] Q. Jin, J.M. Misasi, J.S. Wiggins, S.E. Morgan, Simultaneous reinforcement and toughness improvement in an aromatic epoxy network with an aliphatic hyperbranched epoxy modifier, *Polymer* 73 (2015) 174-182.
- [31] D.H. Zhang, Y.K. Chen, D.M. Jia, Toughness and reinforcement of diglycidyl ether of bisphenol-A by hyperbranched poly(trimellitic anhydride-butanediol glycol) ester epoxy resin, *Polym. Compos.* 30 (2009) 918-925.
- [32] D. Ratna, G.P. Simon, Thermomechanical properties and morphology of blends of a hydroxy-functionalized hyperbranched polymer and epoxy resin, *Polymer* 42 (2001) 8833-8839.
- [33] J. Zhang, Q.P. Guo, B. Fox, Thermal and mechanical properties of a dendritic hydroxyl-functional hyperbranched polymer and tetrafunctional epoxy resin

- blends, *J. Polym. Sci., Part B: Polym. Phys.* 48 (2010) 417-424.
- [34] L.J. Luo, Y. Meng, T. Qiu, X.Y. Li, An epoxy-ended hyperbranched polymer as a new modifier for toughening and reinforcing in epoxy resin, *J. Appl. Polym. Sci.* 130 (2013) 1064-1073.
- [35] X.P. Miao, Y. Meng, X.Y. Li, A novel all-purpose epoxy-terminated hyperbranched polyether sulphone toughener for an epoxy/amine system, *Polymer* 60 (2015) 88-95.
- [36] T. Liu, Y.X. Nie, R.S. Chen, L.D. Zhang, Y. Meng, X.Y. Li, Hyperbranched polyether as an all-purpose epoxy modifier: controlled synthesis and toughening mechanisms, *J. Mater. Chem. A* 3 (2015) 1188-1198.
- [37] M. Grayson, Phosphonium compounds. III. mechanism of hydroxide cleavage of tetrakis(hydroxymethyl)phosphonium chloride, *J. Am. Chem. Soc.* 85 (1963) 79-83.
- [38] J.W. Ellis, K.N. Harrison, P.A. Hoye, A.G. Orpen, P.G. Pringle, M.B. Smith, Water-soluble tris(hydroxymethyl)phosphine complexes with nickel, palladium, and platinum. crystal structure of $[\text{Pd}\{\text{P}(\text{CH}_2\text{OH})_3\}_4]\cdot\text{CH}_3\text{OH}$, *Inorg. Chem.* 31 (1992) 3026-3033.
- [39] W.J. Vullo, Studies concerning the neutralization of tetrakis(hydroxymethyl)phosphonium chloride and the reaction of tris(hydroxymethyl)phosphine with formaldehyde, *J. Org. Chem.* 33 (1968) 3665-3667.
- [40] Y.N. Zhu, X.M. Chen, Y.Z. Wang, W. Wen, Y. Wang, J.Z. Yang, Z.Y. Zhou, L.D.

- Zhang, Y. Pan, F. Qi, Online study on the catalytic pyrolysis of bituminous coal over the HUSY and HZSM-5 with photoionization time-of-flight mass spectrometry, *Energy Fuels* 30 (2016) 1598-1604.
- [41] Y. Wang, Q. Huang, Z.Y. Zhou, J.Z. Yang, F. Qi, Y. Pan, Online study on the pyrolysis of polypropylene over the HZSM-5 zeolite with photoionization time-of-flight mass spectrometry, *Energy Fuels* 29 (2015) 1090-1098.
- [42] A.W. Frank, G.L. Drake Jr, Displacement of tertiary phosphines from methylolphosphonium salts by tributylphosphine, *J. Org. Chem.* 36 (1971) 549-552.
- [43] S.S. Mahapatra, N. Karak, Silver nanoparticle in hyperbranched polyamine: synthesis, characterization and antibacterial activity, *Mater. Chem. Phys.* 112 (2008) 1114-1119.
- [44] S.E. Ellzey Jr, W.J. Connick Jr, G.J. Boudreaux, H. Klapper, Nuclear magnetic resonance study of the formaldehyde-induced exchange of methylol groups in tetrakis(hydroxymethyl) phosphonium chloride and tris(hydroxymethyl)phosphine, *J. Org. Chem.* 37 (1972) 3453-3457.
- [45] H.E. Kissinger, Reaction kinetics in differential thermal analysis, *Anal. Chem.* 29 (1957) 1702-1706.
- [46] T. Ozawa, A new method of analyzing thermogravimetric data, *Bull. Chem. Soc. Jpn.* 38 (1965) 1881-1886.
- [47] J.T. Wan, B. Gan, C. Li, J. Molina-Aldareguia, Z. Li, X. Wang, D.Y. Wang, A novel biobased epoxy resin with high mechanical stiffness and low flammability:

- synthesis, characterization and properties. *J. Mater. Chem. A* 3 (2015) 21907-21921.
- [48] Q.Q. Luo, Y.C. Yuan, C.L. Dong, S.M. Liu, J.Q. Zhao, Intumescent flame retardancy of a DGEBA epoxy resin based on 5,10-dihydro-phenophosphazine-10-oxide. *RSC Adv.* 5 (2015) 68476-68484.
- [49] Q.Q. Luo, Y.C. Yuan, C.L. Dong, S.M. Liu, J.Q. Zhao, High performance fire-retarded epoxy imparted by a novel phenophosphazine-containing antflaming compound at ultra-low loading, *Mater. Lett.* 169 (2016) 103-106.
- [50] W.C. Zhang, X.M. Li, R.J. Yang, Blowing-out effect in epoxy composites flame retarded by DOPO-POSS and its correlation with amide curing agents, *Polym. Degrad. Stab.* 97 (2012) 1314-1324.
- [51] W.C. Zhang, X.D. He, T.L. Song, Q.J. Jiao, R.J. Yang, The influence of the phosphorus-based flame retardant on the flame retardancy of the epoxy resins, *Polym. Degrad. Stab.* 109 (2014) 209-217.
- [52] T.T. Cao, L. Yuan, A.J. Gu, G.Z. Liang, Fabrication and origin of new flame retarding bismaleimide resin system with low dielectric constant and loss based on microencapsulated hexaphenoxycyclotriphosphazene in low phosphorus content, *Polym. Degrad. Stab.* 121 (2015) 157-170.
- [53] J.Y. Wang, L.J. Qian, B. Xu, W. Xi, X.X. Liu, Synthesis and characterization of aluminum poly-hexamethylenephosphinate and its flame-retardant application in epoxy resin, *Polym. Degrad. Stab.* 122 (2015) 8-17.
- [54] C. Ma, B. Yu, N.N. Hong, Y. Pan, W.Z. 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.

[55] P.J. Flory, Molecular theory of rubber elasticity, *Polymer* 20 (1979) 1317-1320.

ACCEPTED MANUSCRIPT

HIGHLIGHTS

Hyperbranched polymer was synthesized from α -aminomethylation reaction of THP.

A novel poly(aminomethylphosphine oxide-amine) was prepared without organic solvent.

Fire safety, T_g and toughness of epoxy resins were concurrently enhanced.

ACCEPTED MANUSCRIPT

GRAPHICAL ABSTRACT

