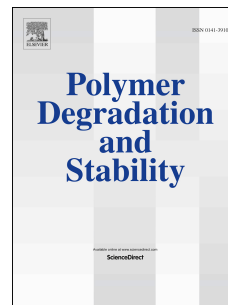


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PII: S0141-3910(18)30174-5

DOI: [10.1016/j.polyimdegradstab.2018.05.021](https://doi.org/10.1016/j.polyimdegradstab.2018.05.021)

Reference: PDST 8555

To appear in: *Polymer Degradation and Stability*

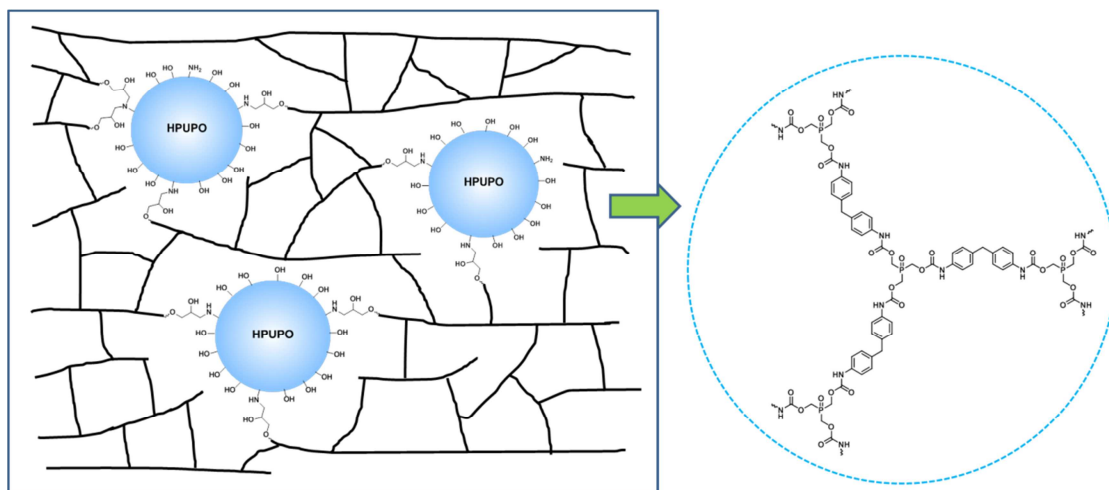
Received Date: 11 February 2018

Revised Date: 8 May 2018

Accepted Date: 20 May 2018

Please cite this article as: Ma C, Qiu S, Wang J, Sheng H, Zhang Y, Hu W, Hu Y, Facile synthesis of a novel hyperbranched poly(urethane-phosphine oxide) as an effective modifier for epoxy resin, *Polymer Degradation and Stability* (2018), doi: 10.1016/j.polyimdegradstab.2018.05.021.

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ACCEPTED MANUSCRIPT

Facile synthesis of a novel hyperbranched poly(urethane-phosphine oxide) as an effective modifier for epoxy resin

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ABSTRACT

In this work, a novel hyperbranched poly(urethane-phosphine oxide) (HPUPO) was facilely synthesized from 4,4'-diphenylmethane diisocyanate and trihydroxymethylphosphine oxide at room temperature. When HPUPO was incorporated, flame retardancy and toughness of epoxy resin are improved with maintained T_g and increased modulus and strength. The gas and condensed phase flame retardant mechanisms and toughening mechanisms are provided. The poor compatibility of epoxy resin/HPUPO hybrids determines the unchanged T_g of epoxy matrix phase. The tensile modulus and strength and storage modulus of modified epoxy thermosets are raised due to more rigid skeleton of HPUPO and hydrogen bond interaction. Moreover, the reactivity of epoxy resin curing systems containing HPUPO is elevated for the catalytic effect of its hydroxyl. The surface hydrophilicity of epoxy resin composites is decreased resulting from their increased surface roughness and the hydrophobicity of HPUPO. And the thermal decomposition temperature of epoxy resin hybrids is depressed. The epoxy resins modified by HPUPO with simple synthesis and preparation can be used for various high-performance applications in industries.

Keywords:

hyperbranched polymer; modification of epoxy resin; flame retardant

1. Introduction

Epoxy resins find their multifaceted applications including coatings, adhesives, insulating materials for electrical devices and fiber-reinforced composites in transportation sector. They are characterized by high thermal stability, chemical resistance, superior electrical properties and good adhesion to substrates. However, most epoxies are inherently accompanied by two major drawbacks: the high flammability (high contents of C and H elements) and poor toughness [1-3] (highly cross-linked rigid thermosets).

Flame retardant epoxy resins can be effectively rendered with bromine-containing compounds by incorporation of bromide additives (such as decabromodiphenyl ether) or copolymerization with brominated monomers (for example diglycidyl ether of tetrabromobisphenol A). Nevertheless, for human health and environment concern, halogenated flame retardants are banned by current legislations. Organophosphorus compounds are promising alternatives for their high efficiency and low toxicity and smoke. Among them, phosphorus-containing hyperbranched flame retardants have drawn much attention [4-8] due to their easy synthesis (in comparison to dendrimers), low leaching (oligomeric or polymeric structure), relative low intrinsic viscosity (compared to linear polymers), good miscibility with polymer matrix and abundant reactive end groups. Unfortunately, fire resistance improvement of epoxy resins by organophosphorus flame retardants always brings about the deterioration of glass transition temperature (T_g) [9-14] and mechanical properties [15-19]. Some 9,10-dihydro-9-oxa-10-phosphaphenanthrene 10-oxide (DOPO) derivative modified

epoxy resins show maintained or increased T_g [20-22] because that the bulky rigid DOPO groups hinder the mobility of chain segments.

For applications, the hydrolysis of organophosphorus flame retardants is an important factor inducing loss of their effectiveness. Generally, P-C bonds are much harder to hydrolysis than P-O-C bonds, thus, phosphine oxides consisting of sole P-C bonds are very resistant to hydrolyze. Up to now, there are only several flame retardant applications of alkyl phosphine oxides reported. Cádiz et al. synthesized isobutylbis(glycidylpropylether)phosphine oxide and UL-94 V-0 rating epoxy thermosets could be obtained when it was either used as the sole epoxy compound [23] or copolymerized with other epoxy monomers [24-25]. Sivriev et al. prepared bis(hydroxymethyl)-N,N-bis(2-hydroxyethyl)aminomethylphosphine oxide [26], bis(hydroxymethyl)-N-piperidinomethylphosphine oxide [27] and tris[N,N-bis-(2-hydroxyethyl)aminomethyl]phosphine oxide [28] and the diol or polyol were reacted into linear polyurethanes or rigid polyurethane foams to improve their resistance to combustion. With the increase of phosphorus content, the limited oxygen index (LOI) of the polyurethanes increase. Besides, Chen et al. introduced trihydroxymethylphosphine oxide (THPO) into flexible polyurethane foam and proposed that THPO mainly played a role in the condensed phase for more than 60% of phosphorus retained in the char residue after combustion [29].

With the aim of toughening epoxy resins, rubbers or thermoplastic polymers are generally added. Currently, hyperbranched polymers have been found to hold considerable promise for this purpose. Hyperbranched polymers possess high

solubility in various solvents and lower viscosity than that of linear polymers with comparable molar mass, which allows them not to reduce the processing properties of epoxy resins. Moreover, the high density terminal groups on the shell of hyperbranched polymers facilitate the formation of strong particle matrix adhesion. This is a critical requirement for providing an optimum level of toughness enhancement. However, along with toughening, hyperbranched polymers always depress T_g [30-34] and modulus [30,35-37] of epoxy resins due to the incorporation of flexible chains. Some papers reported no sacrificed T_g for the small residual miscibility between epoxy-functionalized hyperbranched polymer phase and epoxy resin matrix phase [38-39], and the increase of cross-linking density by multifunctional hyperbranched curing agent [40-41] or the introduction of hyperbranched monomers with rigid backbone [42-45] in homogeneous systems. Jin et al. reported toughening of aliphatic hyperbranched epoxide with increased tensile and compressive modulus of epoxy resin and ascribed the moduli improvement to the strong hydrogen-bonding interaction formed by the hydroxyl-rich hyperbranched epoxide [31]. The epoxy resins modified by a stiff hyperbranched polyimide curing agent show unchanged flexural modulus and T_g at low loadings [45].

In our previous work [41], we reported simultaneous improvement of flame retardancy and toughness of epoxy resin without deteriorated T_g . The hyperbranched poly(aminomethylphosphine oxide-amine) modified epoxy resins form homogeneous morphology. However, the steric hindrance of its secondary amino groups decreases the curing reactivity and its flexible aliphatic chains depress modulus and strength of

epoxy resin. In this work, a novel hyperbranched poly(urethane-phosphine oxide) (HPUPO) was facilely synthesized from 4,4'-diphenylmethane diisocyanate (MDI) and trihydroxymethylphosphine oxide (THPO) at room temperature. The epoxy resins modified by HPUPO are heterogeneous and they achieve the above goal with different mechanisms. The catalytic effect of hydroxyl groups of HPUPO improves the curing reactivity and the more rigid skeleton of HPUPO and hydrogen bond interaction raise modulus and strength of epoxy resin. Additionally, we investigated the surface hydrophilicity of epoxy resin and it is decreased in the presence of HPUPO.

2. Experimental

2.1. Materials

Dibutyltin dilaurate (DBTDL), 4,4'-diaminodiphenylmethane (DDM), N,N-dimethylformamide (DMF), methanol, acetone and barium oxide were supplied by Sinopharm Chemical Reagent Co. Ltd., China. MDI was purchased from Aladdin Chemistry Co. Ltd., China. Diglycidyl ether of bisphenol A (DGEBA, E-44, epoxy value = 0.44 mol/100 g) was obtained from Nantong Xingchen Synthetic Material Co. Ltd., China. DMF was purified before use to remove water by treatment with barium oxide followed by distillation in vacuo. All other chemical reagents were used as received. THPO was prepared according to our previous procedure [46].

2.2. Synthesis of HPUPO

THPO (24.1 g, 0.172 mol) and DBTDL (0.48 g, 0.76 mmol) were first dissolved

in 250 mL anhydrous DMF under nitrogen. Then MDI (38.0 g, 0.152 mol) was slowly added in portions. After MDI was dissolved, the mixture was agitated under nitrogen at room temperature for 48h. A small amount of solution was taken out and evaporated for ^{31}P NMR test to calculate the conversion of THPO. The spectrum is depicted in Fig. S1 and the conversion is 94% as shown in in the Supplementary material file. Then the solution was poured into 2.5 L methanol with agitation. The precipitate was filtered and washed with methanol. After drying at 100 °C under vacuum for 24 h, a white solid was obtained at 72.6% yield. The dried product was grinded into fine powders before use.

2.3. Preparation of epoxy thermosets

HPUPO (0, 1, 2, 3 and 4 percent of total weight of epoxy thermoset) was added into DGEBA and the mixture was heated to 100 °C. It was stirred until HPUPO was homogeneously dispersed. Then DDM of equivalent amount to DGEBA was added. After it was dissolved, the mixture was degassed for 3 min in a vacuum oven at 100 °C and poured into a mold. All samples were cured at 120 °C for 2 h, 150 °C for 2 h and 180 °C for another 2 h. Then the thermoset was cooled naturally to room temperature to prevent stress cracking. The neat epoxy resin was represented as EP. The epoxy resin hybrid with X wt % HPUPO incorporated was labeled as EPX.

2.4. Characterization

Nuclear magnetic resonance (NMR) spectrum was acquired on a Bruker AV400 NMR spectrometer (400 MHz). Tetramethylsilane was used as an internal standard for ^1H NMR and 85% H_3PO_4 as an external standard for ^{31}P NMR.

Fourier transform infrared (FTIR) spectroscopy was obtained on a Nicolet 6700 spectrometer (Nicolet Instrument Company, USA). The sample was mixed with KBr and pressed into pellet.

Gel permeation chromatography (GPC) was performed with an instrument equipped with a G1310B ISO pump, a G1316A PLgel column, and a G1362A differential refractive index detector. DMF with 1.0 g/L LiBr was used as eluent and the flow rate was 1.0 mL/min. A series of polystyrene standards with low polydispersity were employed for calibration.

Differential scanning calorimetry (DSC) was conducted on a DSC Q2000 (TA Instruments Inc., USA) under nitrogen. T_g was measured at a heating rate of 10 °C/min and it was recorded at the mid-point of the inflexion curve from the second heating run. To study the curing kinetics, DGEBA, HPUPO and DDM were added in a minor amount of acetone with agitation under room temperature. After DGEBA and DDM were dissolved and HPUPO was well dispersed, nitrogen purge was applied to remove the solvent. Then the mixture was put in a vacuum oven at room temperature to further remove the residual trace solvent. The freshly prepared samples were subjected to DSC scans at 5, 10, 15 and 20 °C/min.

Thermogravimetric analysis (TGA) was performed on Q5000 thermal analyzer (TA Co., USA) under nitrogen and air at a heating rate of 20 °C/min.

Limited oxygen index (LOI) was measured according to ASTM D 2863 with a HC-2 oxygen index meter (Jiangning Analysis Instrument Company, China). The dimension of testing specimens was 100×6.5×3.0 mm³. The minimum oxygen

concentration required to support the candle-like combustion of samples was recorded.

Vertical burning test (UL-94) was conducted with a CFZ-2 type instrument (Jiangning Analysis Instrument Co., China). The dimension of samples was $130 \times 13 \times 3$ mm³. In the test, the specimens were subjected to two 10 s ignitions, and the self-extinguish times were recorded as t_1 and t_2 . A sample achieves UL-94 V-0 flammability rating if each t_1 and t_2 of five specimens did not exceed 10 s and the total burning time of five specimens did not exceed 50 s without any dropping.

Cone calorimetry was carried out on a Fire Testing Technology apparatus according to ISO 5660 with the sample of $100 \times 100 \times 3$ mm³ under an external heat flux of 35 kW/m². Triplicate measurements were conducted for each sample.

The pyrolysis photoionization time-of-flight mass spectrometry (PY-PI-TOFMS) was described elsewhere [47-48].

Dynamic mechanical analysis (DMA) was measured on TA DMA Q800. Specimens were tested in a three point bending mode at a heating rate of 5 °C/min and a fixed frequency of 10 Hz.

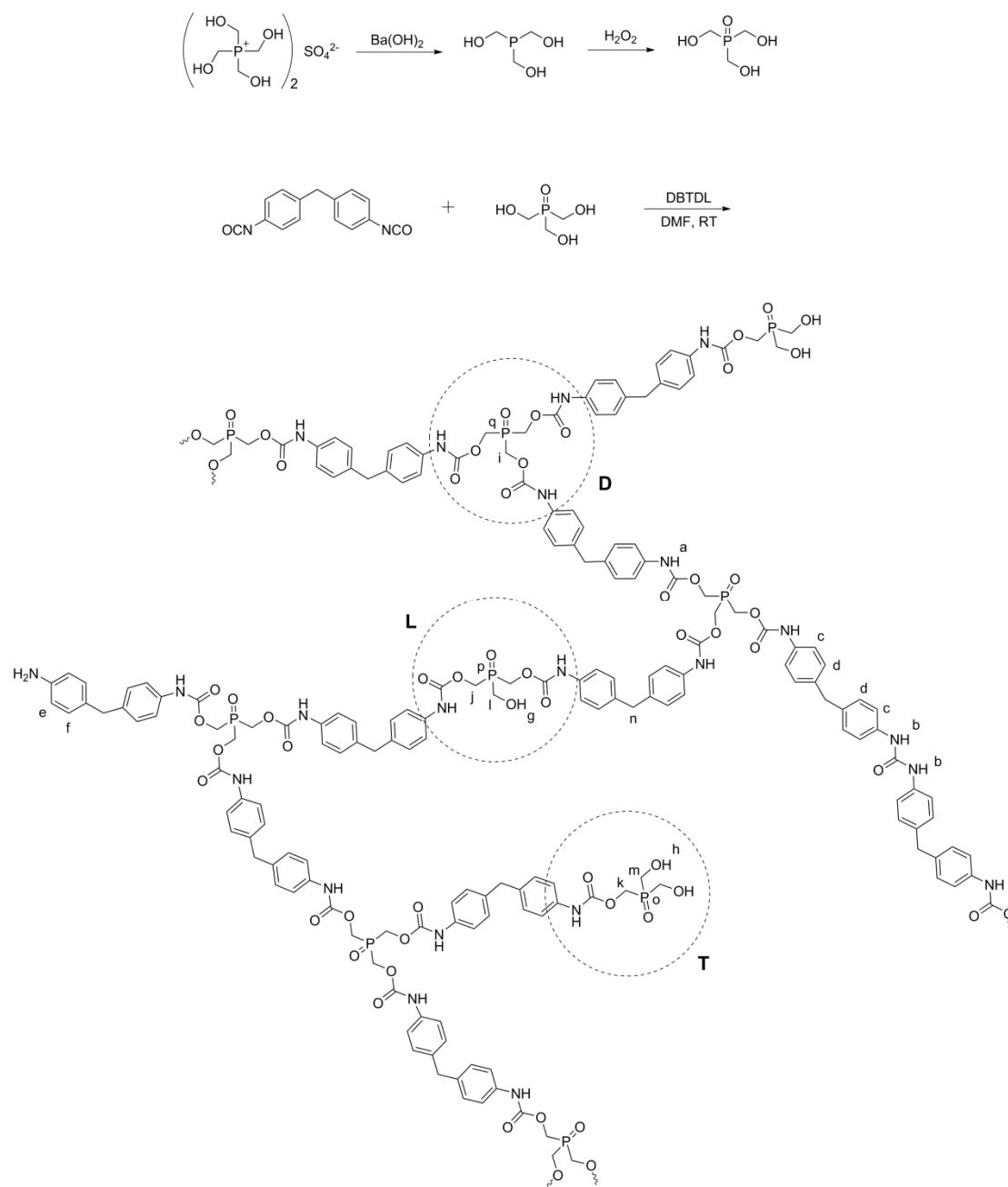
Tensile test was performed on a CMT6104 universal testing machine (MTS Systems Co., Ltd., China) at room temperature. The dumb-bell shaped tensile specimens were tested according to ASTM D638. The unnotched Izod impact strength test was carried out with a ZBC1400-A impact tester (MTS Systems Co., Ltd., China) as per ASTM D256. Results are presented as energy absorbed per cross-sectional area. For mechanical property tests, an average of five specimens was taken for each

sample.

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

Static water contact angle was measured on Contact Angle Meter SL200B (Solon Tech. Co., Ltd.). A droplet of doubly distilled water with a surface tension of 72 mN/m was dropped onto the surface of epoxy thermoset or HPUPO film (from DMF solution). The mean contact angle value on three different points for each sample was taken as the final result.

3. Results and discussion



Scheme 1. Synthetic route of HPUPO.

3.1. Synthesis and structure characterization of HPUPO

HPUPO was synthesized from MDI and THPO in the presence of DBTDL as the catalyst at room temperature. The synthetic route is shown in Scheme 1 and Fig. 1 illustrates ^1H and ^{31}P NMR spectra of HPUPO. In the ^1H NMR spectrum, the peak at

9.82 ppm is ascribed to the hydrogen of $-NH-(C=O)-O-$ and that at 8.52 the proton of $-NH-(C=O)-NH-$. The chemical shift at 7.34 and 7.10 ppm are attributed to the hydrogen of benzene rings adjacent to urethane and urea bonds, while the neighboring weak peaks at 6.98 and 6.66 ppm are assigned to those adjacent to amino groups. Without electron-withdrawing carbonyl, the chemical shift of proton on $H_2N-C_6H_4-$ is lower. Due to the hydrolysis of isocyanate groups with trace water, the structures of $H_2N-C_6H_4-$ and $-NH-(C=O)-NH-$ exist in HPUPO. The chemical shift at 5.65 and 5.43 ppm correspond to the hydrogen of residual hydroxyls on $(-NHCOO-CH_2)_2P(=O)-CH_2-OH$ and $-NHCOO-CH_2-P(=O)(-CH_2-OH)_2$. The signal between 4.83 and 4.35 ppm are attributed to the methylene protons adjacent to urethane bonds (4.77 ppm for $(-NHCOO-CH_2)_3P=O$, 4.56 ppm for $(-NHCOO-CH_2)_2(P=O)-CH_2-OH$ and 4.45 ppm for $-NHCOO-CH_2-(P=O)(-CH_2-OH)_2$). The resonance at 3.98 and 3.89 ppm are due to the methylene proton of hydroxymethyls on $(-NHCOO-CH_2)_2P(=O)-CH_2-OH$ and $-NHCOO-CH_2-P(=O)(-CH_2-OH)_2$. The peak at 3.80 ppm reveals the contribution of the hydrogen on $-Ph-CH_2-Ph-$. The appearance of chemical shift of a, i, j and k verifies the successful reaction between MDI and THPO to form urethane. In the ^{31}P NMR spectrum, three singlets located at 42.0, 39.1 and 36.1 ppm can be clearly seen and they are ascribed to the phosphorus of $-NHCOO-CH_2-(P=O)(-CH_2-OH)_2$, $(-NHCOO-CH_2)_2(P=O)-CH_2-OH$ and $(-NHCOO-CH_2)_3P=O$ respectively. These three kinds of structures are distinguished as terminal (*T*), linear (*L*) and dendritic (*D*) units of a hyperbranched polymer respectively. In addition, the structural perfection of hyperbranched polymers

is always expressed as degree of branching (DB) and it is calculated according to the following equation:

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

where D, T, and L refer to the numbers of dendritic, terminal, and linear units respectively. From the integral intensities of peak o, p and q in the ^{31}P NMR spectrum, DB of HPUPO is calculated to be 0.52.

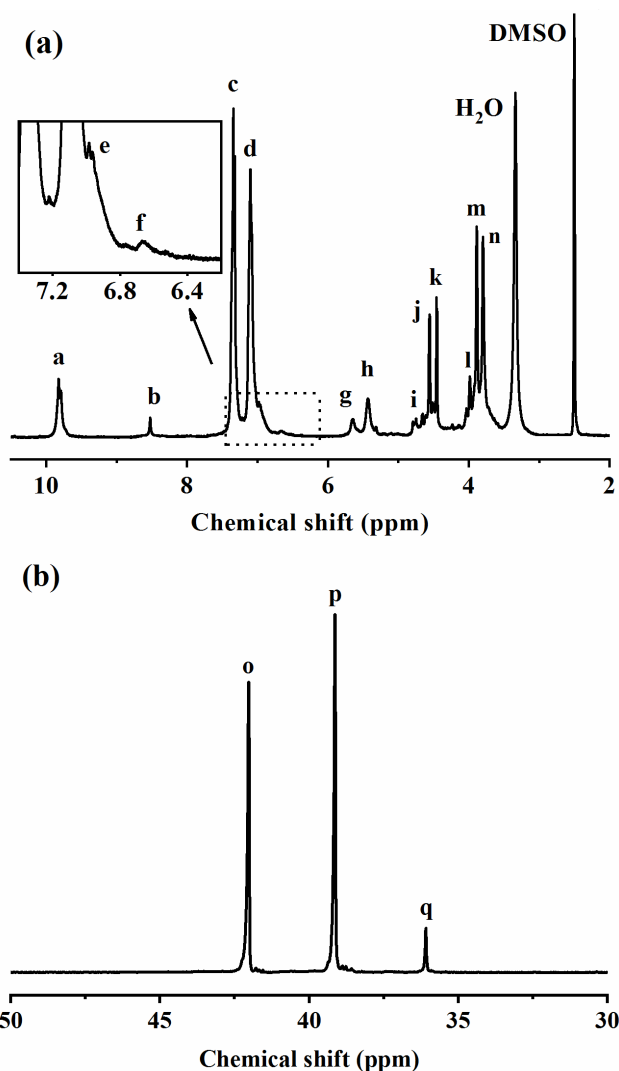


Fig. 1. ^1H (a) and ^{31}P (b) NMR spectra of HPUPO in $\text{DMSO-}d_6$.

Fig. 2 depicts FTIR spectroscopy of HPUPO. The absorption around 3372 cm^{-1} corresponds to the stretch vibration of O–H and N–H. The band at 3020 cm^{-1} is

assigned to the stretch mode of C–H on benzene rings while those at 2895 and 2837 cm^{-1} C–H of methylene groups. The stretch vibration of C=O in urethane bonds occurred at 1712 cm^{-1} . The intense peaks at 1610 and 1510 cm^{-1} are attributed to the skeletal vibration of benzene rings. The band at 1420 cm^{-1} is ascribed to the bending mode of C–H on methylene groups and that at 1308 cm^{-1} O–H. Furthermore, the absorbance at 1510 (amide II band) and 1308 cm^{-1} (amide III band) also characterizes the coupling of N–H bending and C–N stretching vibration [49]. The peak at 1235 cm^{-1} is due to P=O stretching mode and that at 1153 cm^{-1} reveals the contribution of stretching vibration of C–O–C in urethane linkages and C–P. The vibration band at 1041 cm^{-1} is relative to the stretching of C–O in hydroxymethyl groups. And the absorption at 806 cm^{-1} is attributed to C–H out of plane bending mode of 1,4-disubstitued benzene rings. The peaks corresponding to C=O and C–O–C in urethane linkages demonstrate that urethane bonds were formed in HPUPO.

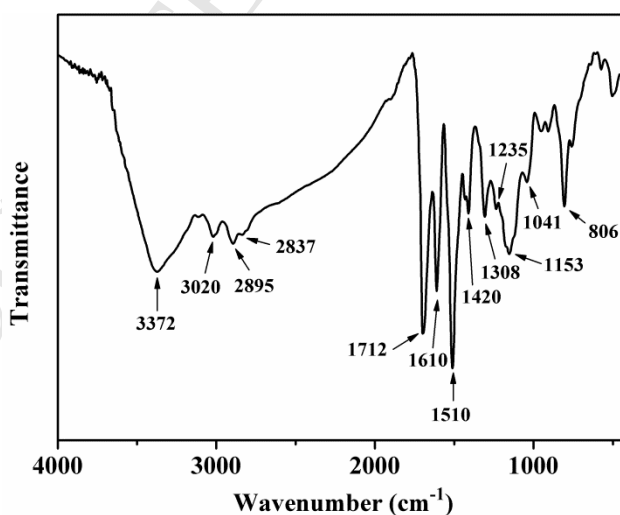


Fig. 2. FTIR spectrum of HPUPO.

The molecular weight of HPUPO was measured by GPC and the GPC trace is shown in Fig. S2. Its number-average molecular weight is 7500 g/mol and the

polydispersity index is 1.73. Thus, the polymeric structure of HPUPO is proven.

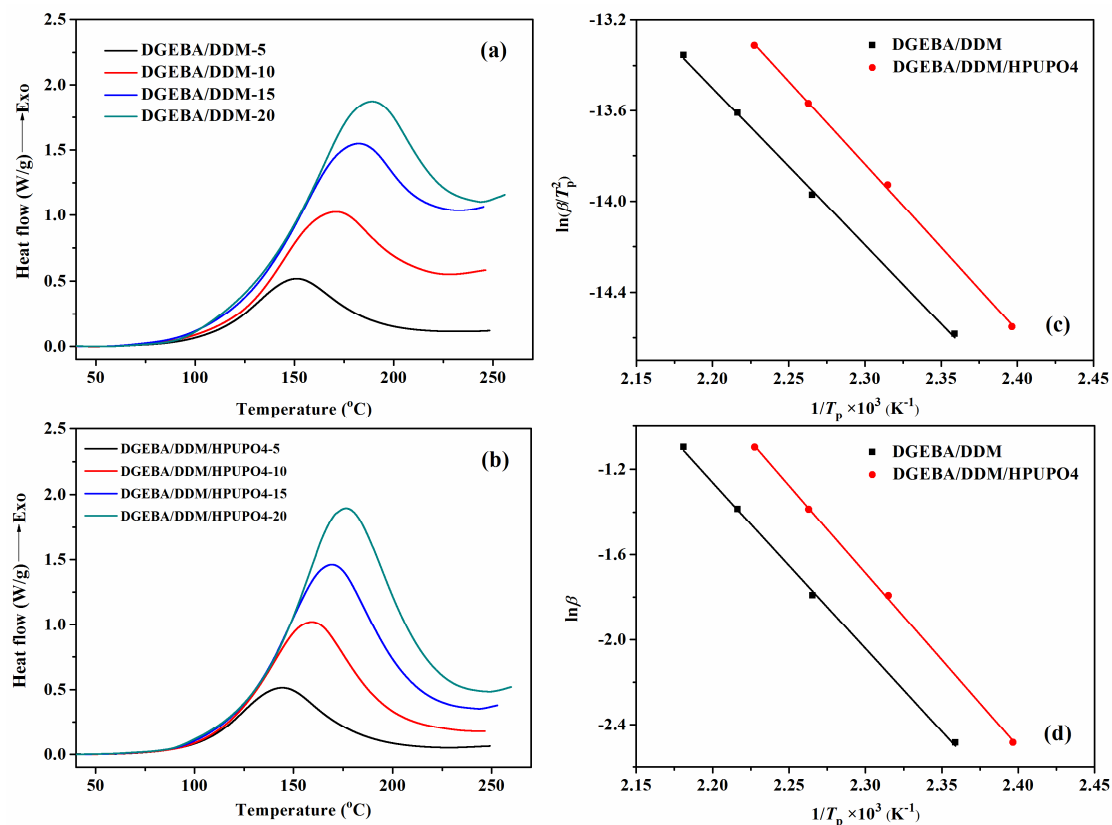


Fig. 3. DSC thermograms of DGEBA/DDM (a) and DGEBA/DDM/HPUPO4 (b) curing systems at different heating rates and their plots of $\ln(\beta/T_p^2)$ (c) and $\ln\beta$ (d) against $1/T_p$.

3.2. Nonisothermal curing behaviors and apparent reaction activation energy

The nonisothermal curing processes of DGEBA/DDM and DGEBA/DDM/HPUPOX (the number X represents the weight percent of HPUPO) systems were traced by dynamic DSC scans at heating rates of 5, 10, 15 and 20 °C/min. The DSC curves of DGEBA/DDM and DGEBA/DDM/HPUPO4 curing systems are shown in Fig. 3a and b as representatives. DSC curves of all the curing systems exhibit single exothermic peak. The exothermic peak temperature (T_p) was directly obtained from them. The onset exothermic temperature (T_{onset}) was recorded

by extrapolation of the steepest portion of the upward curve and the area of the exothermic curve was integrated as curing heat (ΔH). These data are listed in Table 1. At a given heating rate, the lower T_p indicates the higher curing reactivity. For the above epoxy curing systems, T_p shows non-monotonic variation with the increase of HPUPO content. The reactivity change can be attributed to two opposite factors: catalytic effect and steric hindrance. The residual hydroxyl of HPUPO catalyzed epoxy-amine reaction through the formation of termolecular hydrogen-bonded transition state [50], which enhanced the curing reactivity. The amino groups in HPUPO can be involved into the curing reaction, thus, the steric hindrance of hyperbranched polymer restricted the diffusion of functional groups and diminished reactivity [51-52]. Even though its variation is complex, T_p of DGEBA/DDM/HPUPO curing systems are all lower than that of DGEBA/DDM at the same heating rate. Therefore, HPUPO improves the reactivity of epoxy resin curing reaction due to the dominated catalytic effect of its hydroxyl.

For every curing system, T_p increase with the increase of heating rate, which is because of the less prompt respond of reaction mixture to faster heating rate. This systematic peak evolution depends on the apparent reaction activation energy and frequency factor as expressed by the well-known Kissinger's [53] and Ozawa's [54] equations:

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

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

where β , R , A and E are heating rate, ideal gas constant, frequency factor and activation energy, respectively. According to the above equations, the plots of $\ln(\beta/T_p^2)$ and $\ln\beta$ versus $1/T_p$ should be linear and activation energy can be calculated from the slope of the straight line. These two linear relationships were observed for all the curing systems and Fig. 3c and d illustrate those of DGEBA/DDM and DGEBA/DDM/HPUPO4 curing systems. The activation energy derived from Eqs. (2) and (3) are listed in Table 1 as E_k and E_o respectively. For the same curing system, E_o is higher than E_k . However, good consistence between them was found that they both decrease first and increase later as HPUPO content increases. The catalytic effect of hydroxyl depresses activation energy while the steric hindrance of hyperbranched polymer raises it. Ultimately, activation energy of DGEBA/DDM/HPUPO4 curing system is higher than that of DGEBA/DDM.

Table 1

Nonisothermal curing parameters obtained from DSC analysis.

curing system	β (°C/min)	T_{onset} (°C)	T_p (°C)	ΔH (J/g)	E_k (kJ/mol)	E_o (kJ/mol)
DGEBA/DDM	5	109.31	150.78	303.4	57.54	61.65
	10	123.73	168.25	237.6		
	15	129.62	178.00	220.3		
	20	133.08	185.32	214.0		
DGEBA/DDM/ HPUPO1	5	90.11	138.37	241.7	57.27	61.18
	10	102.17	155.34	227.7		
	15	107.76	164.40	206.8		
	20	110.64	170.98	186.1		
DGEBA/DDM/ HPUPO2	5	100.31	140.28	298.7	48.43	52.86
	10	110.50	158.45	293.2		
	15	124.49	170.46	281.8		
	20	131.76	178.93	260.4		
DGEBA/DDM/ HPUPO3	5	102.11	143.28	321.8	55.03	59.15
	10	114.27	158.86	314.9		
	15	122.71	170.11	294.8		
	20	131.72	177.97	277.8		
DGEBA/DDM/ HPUPO4	5	102.76	144.11	328.5	60.82	64.64
	10	114.33	158.92	321.6		
	15	120.59	168.77	301.3		
	20	129.38	175.80	284.9		

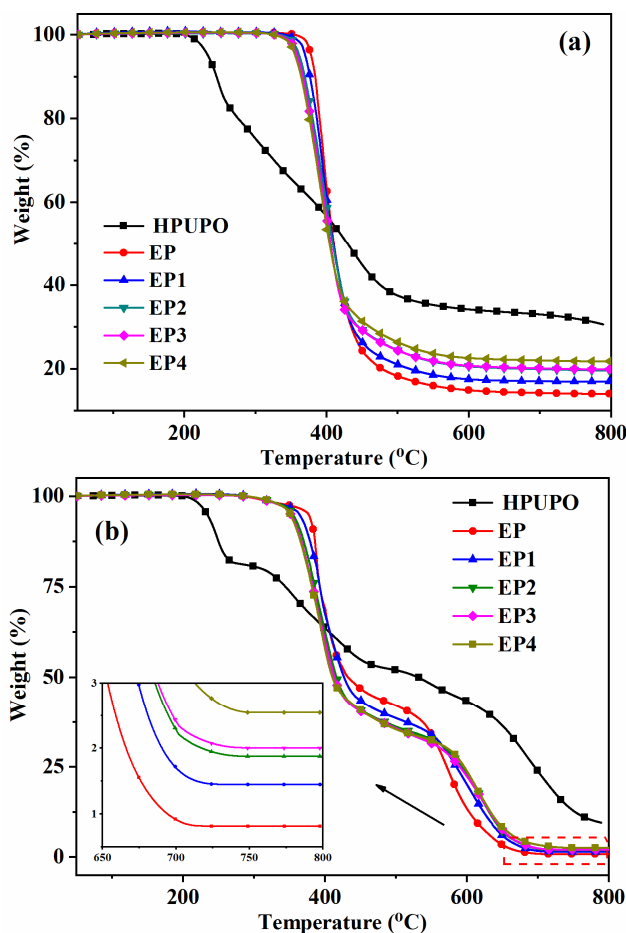


Fig. 4. TGA curves of HPUPO and epoxy thermostets under nitrogen (a) and air (b).

3.3. Thermal properties of HPUPO and cured epoxy resins

TGA was used to assess the thermal stability of HPUPO and epoxy thermostets. TGA curves under nitrogen and air are shown in Fig. 4 and the related parameters include the decomposition temperature at 5% weight loss (T_d), the temperature at maximum weight loss rate (T_{max}) and the char yield at 750 °C (CY) are listed in Table 2. When HPUPO was added into epoxy thermostets, their T_d values decrease both under nitrogen and air. The depressed thermal stability may be attributed to the less thermostable P(=O)–CH₂–OH structure in HPUPO, which releases formaldehyde to form P–H bonds. In the second-stage degradation of epoxy resin hybrids under air, the T_{max} values obviously shift to higher temperatures. And the CY values are elevated

with increasing HPUPO content both under nitrogen and air. These results indicate that HPUPO improves the thermal and thermal-oxidative stability of char residue at high temperature, which is beneficial for the increment of flame retardancy.

Table 2

Thermal properties of HPUPO and epoxy thermosets.

sample	nitrogen			air			T_g^a (°C)	T_g^b (°C)
	T_d (°C)	T_{max} (°C)	CY (%)	T_d (°C)	T_{max} (°C)	CY (%)		
HPUPO	234	248, 435	32.0	234	248, 353, 683	12.8	133.5	-
EP	378	396	14.1	377	388, 573	0.82	156.8	177.9
EP1	370	394	17.0	364	393, 602	1.45	157.0	178.7
EP2	362	401	19.7	355	383, 622	1.89	157.7	179.5
EP3	359	403	20.0	352	386, 623	2.01	156.8	178.3
EP4	356	394	21.9	352	396, 617	2.54	156.9	178.4

^a T_g measured from DSC.

^b T_g measured from DMA.

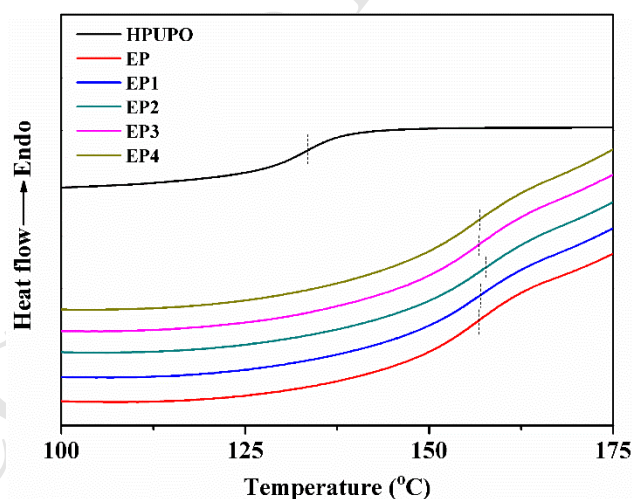


Fig. 5. DSC curves of HPUPO and epoxy thermosets.

The glass transition temperatures of HPUPO and epoxy thermosets were obtained from DSC. Fig. 5 presents their DSC thermograms and the T_g values are listed in Table 2. From the DSC profile of HPUPO, a T_g of 133.5 °C can be determined, which indicates the formation of macromolecular structure. The T_g of EP is 156.8 °C and

those of HPUPO modified epoxy thermosets are nearly unchanged (the differences are small enough to be within experimental error).

3.4. Combustion behaviors of cured epoxy resins

The combustion behaviors of epoxy thermosets were initially investigated by LOI and UL-94 testing and their results are shown in Table 3. The pure epoxy resin is flammable with an LOI value of 24.5% and no UL-94 rating. As HPUPO content increases, the LOI value and UL-94 rating of epoxy resin hybrids are improved. With 4 wt% HPUPO loaded, EP4 reached V-0 rating with the LOI value of 30.5%. Therefore, increased flame retardancy is obtained for HPUPO modified epoxy resins.

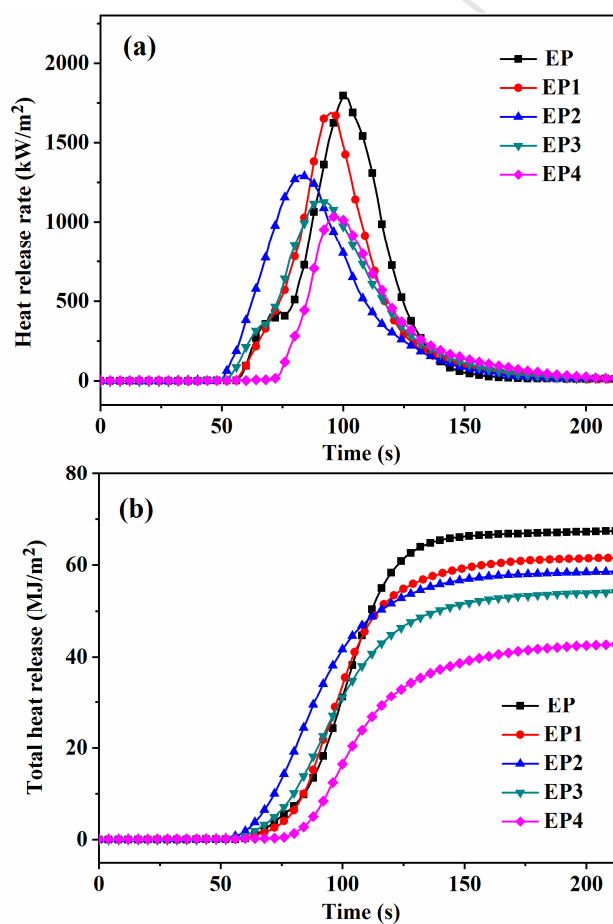


Fig. 6. HRR (a) and THR (b) curves of cured epoxy resins.

Table 3

Combustion parameters of epoxy thermosets.

sample	LOI (%)	UL-94 rating	TTI (s)	p-HRR (kW/m ²)	THR (MJ/m ²)	CY (%)	av-EHC (MJ/kg)
EP	24.5	NR ^a	58	1795	67.5	9.1	22.5
EP1	26.8	V-1	57	1690	61.6	14.9	21.9
EP2	28.3	V-1	51	1291	58.7	17.0	21.2
EP3	29.7	V-1	54	1129	54.1	17.6	19.6
EP4	30.5	V-0	73	1035	42.7	19.8	15.7

^a No rating.

Cone calorimetry provides abundant information about combustion behaviors and flame retardant mechanisms. The plots of heat release rate (HRR) and total heat release (THR) versus time of epoxy thermosets are depicted in Fig. 6. And the concerned combustion parameters include time to ignition (TTI), peak of heat release rate (p-HRR), THR, char yield (CY) and average effective heat of combustion (av-EHC) are listed in Table 3.

The TTI value of EP is 58 s and it decreases first and increases afterwards with the increase of HPUPO fraction. On the one hand, more combustible gases produced in the initial decomposed stage of HPUPO modified epoxy resins as shown in Fig. 4 rendered earlier ignition. On the other hand, TTI was prolonged due to the active H and OH radicals quenched by PO type radicals produced from HPUPO and/or the release of nonflammable gases [11]. This factor is dominated for EP4, therefore, its TTI is delayed by 15 s in contrast with that of EP, which implies decreased flammability of EP4.

The p-HRR and THR values of EP are 1795 kW/m² and 67.5 MJ/m², respectively. When HPUPO was incorporated, they both decrease as HPUPO content increases.

P-HRR of EP4 is reduced by 42.3% and THR 36.7%. Therefore, HPUPO improves the flame retardancy of epoxy resins. The depressed av-EHC values indicate gas phase flame retardant mechanism of HPUPO in epoxy resin, which will be discussed in Section 3.5. The condensed phase flame retardant mechanisms can be verified via the yield and morphology of char residue after cone test. In Table 3, the CY values of flame retardant epoxy resins are obviously higher than that of EP, which means that less volatiles were released during their combustion. The digital photographs of char residue are presented in Fig. 7. The char residue of EP is fragmentary, loose and fragile. However, continuous, compact and rigid char residue is observed for HPUPO modified epoxy resins. This kind of char residue can effectively insulate decomposed volatiles from heat and oxygen and slow down their release to flaming zone while that of EP can't provide such protective and barrier effect. As a result, condensed phase flame retardant mechanisms of HPUPO in epoxy resins are increased char yield and protective and barrier effect of char residue.

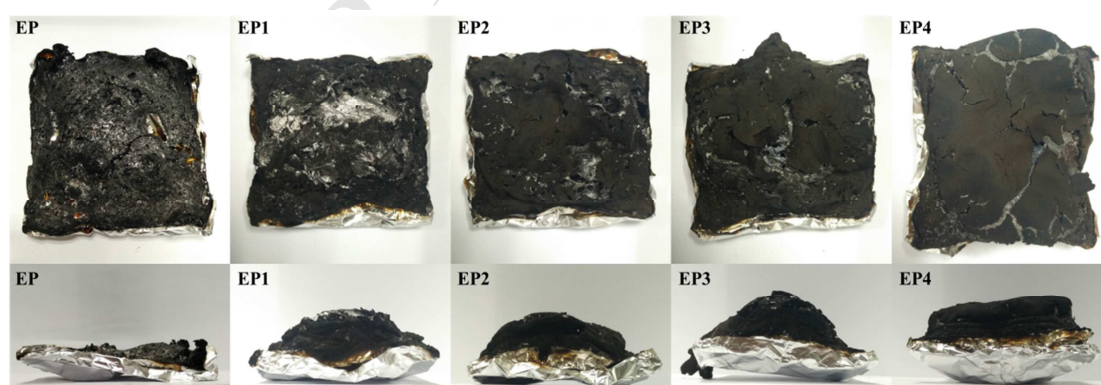


Fig. 7. Char residue of epoxy thermosets after cone test from front and side view.

To further elucidate the protective and barrier effect, char residue was subjected to SEM measurement. Fig. 8 shows the SEM micrographs of exterior and interior char

residue of EP and EP4. The exterior char residue of EP is loose and fluffy while that of EP4 is continuous and compact. EP4 exterior char residue can effectively seal the pyrolytic gases and prevent oxygen and heat supply. Accordingly, it exhibits protective and barrier effect. Moreover, the interior char residue of EP is flat while numerous closed pores can be seen in that of EP4. This honeycomb-like interior char residue further enhances the protective and barrier effect [55-56].

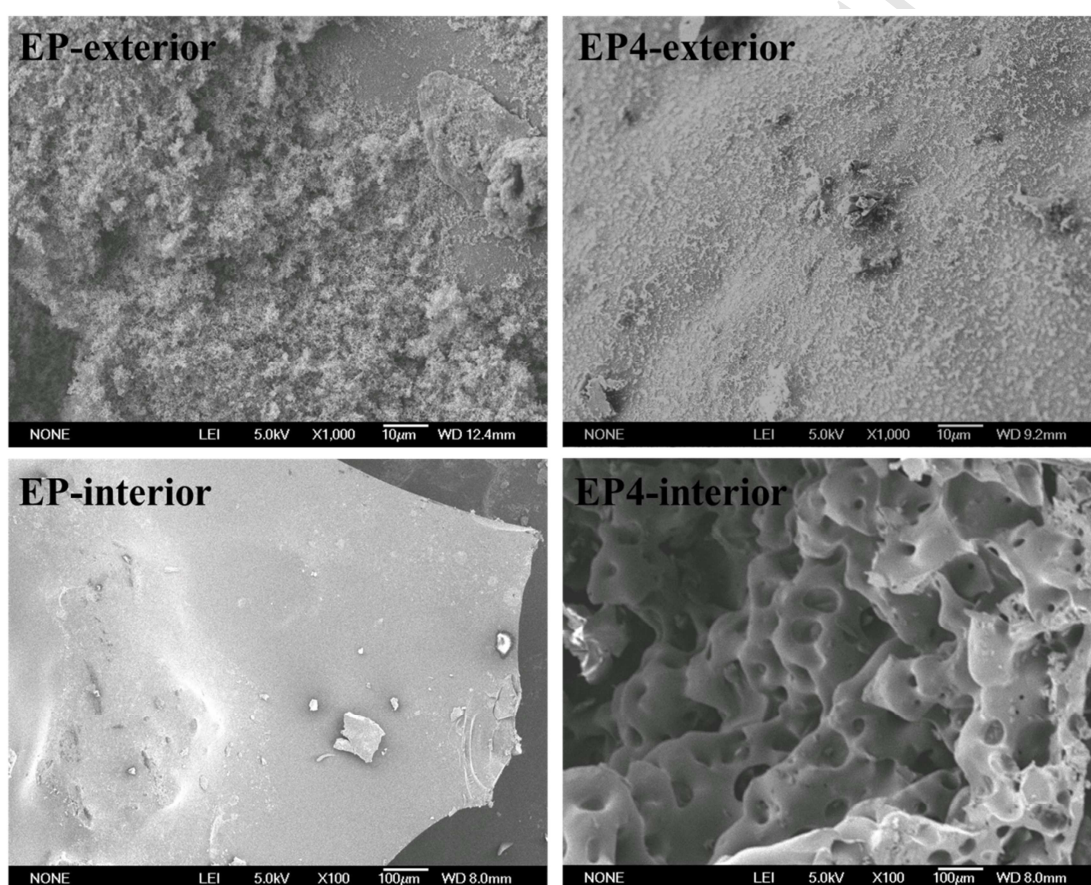


Fig. 8. SEM images of exterior and interior char residue of EP and EP4.

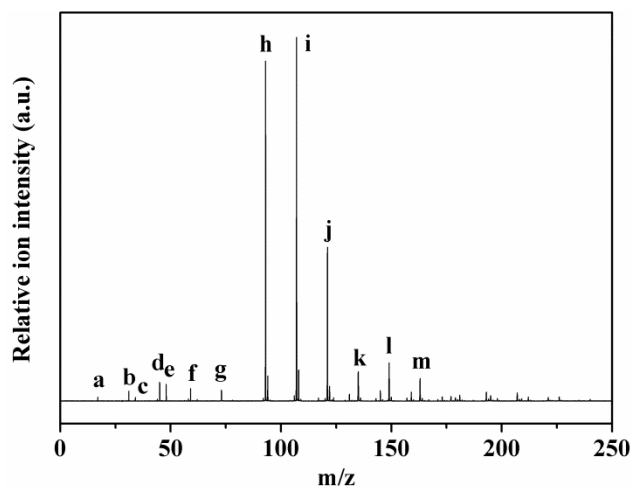


Fig. 9. PY-PI-TOFMS of HPUPO.

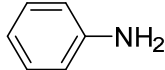
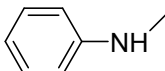
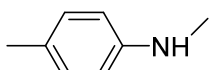

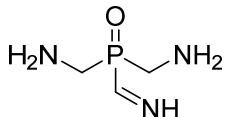
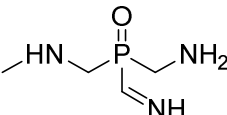

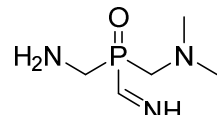

3.5. Pyrolysis of HPUPO

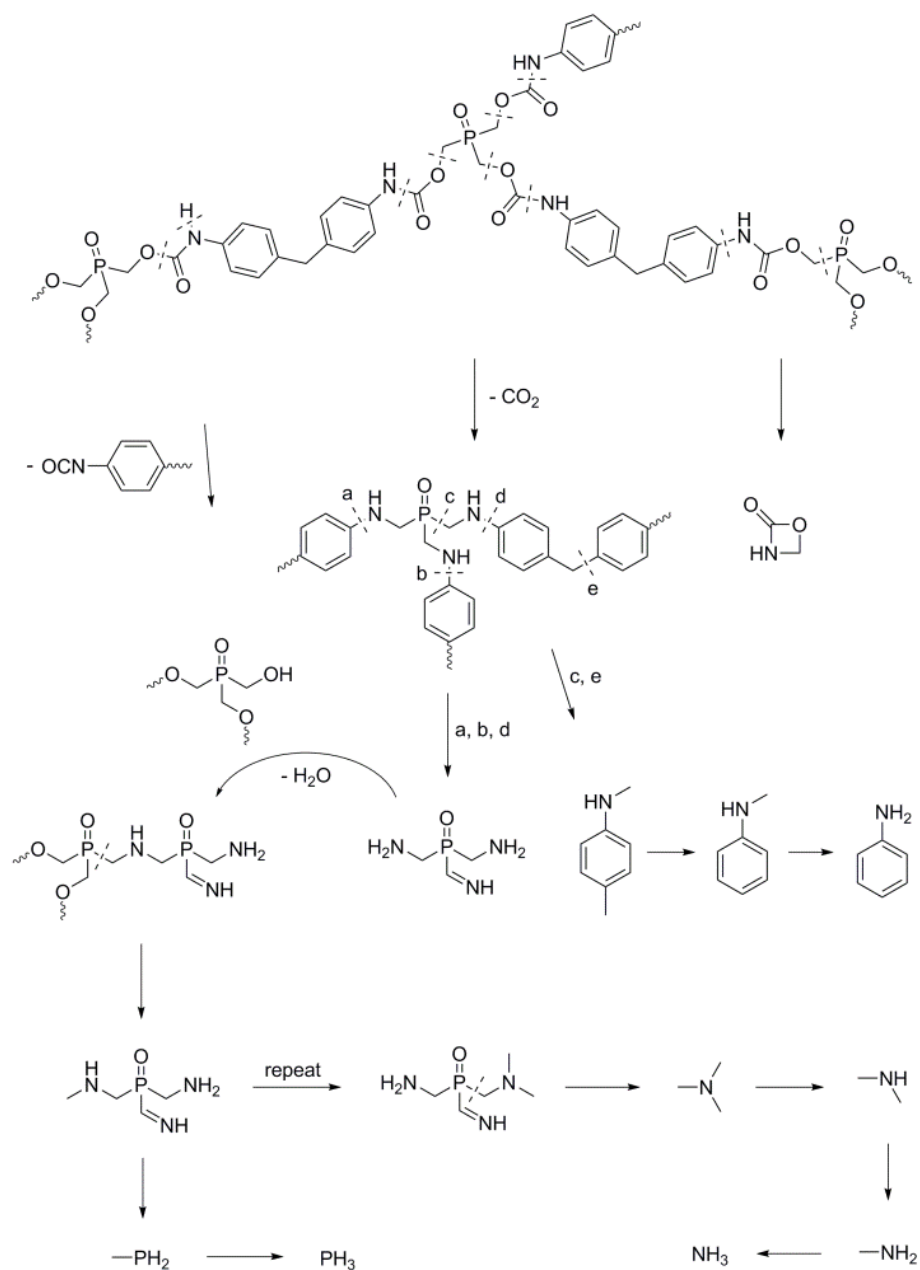
The gaseous pyrolytic products of HPUPO were detected by PY-PI-TOFMS. 20.0 mg HPUPO was put into a tubular furnace preset at 500 °C and nitrogen was used as the carrier gas. The accumulated signal was recorded until pyrolysis was complete. Fig. 9 depicts the mass spectrum of HPUPO. Thanks to the near-threshold “soft” photoionization, nearly all mass peaks can be assigned as fragment-free parent ions [47-48]. Table 4 presents their assignments. The pyrolytic volatiles of HPUPO mainly contain aromatic amines and bis(aminomethyl)(iminomethyl)phosphine oxides. The proposed pyrolytic pathway is shown in Scheme 2. Aminomethylphosphine oxide structure was first formed via the elimination of carbon dioxide from urethane linkage. Then it decomposed to produce bis(aminomethyl)(iminomethyl)phosphine oxide and aromatic amines. After the dehydration reaction between amino group of bis(aminomethyl)(iminomethyl)phosphine oxide and hydroxymethyl (produced or residual), the product further decomposed to generate methyl substituted bis(aminomethyl)(iminomethyl)phosphine oxide. On the other hand, the

phosphorus-containing pyrolytic volatiles, phosphine and phosphine oxide, are speculated to produce PO type radicals during combustion, which would effectively scavenge the active H and OH radicals and interrupt the chain reactions of combustion. Therefore, the gas phase flame retardant mechanism of HPUPO in epoxy resins is proposed as the flame inhibition effect of the released phosphine and phosphine oxide.

Table 4

Assignments of mass peaks in PY-PI-TOFMS of HPUPO.

peak	m/z	structure	peak	m/z	structure
a	17	NH_3	h	93	
b	31	$-\text{NH}_2$	i	107	
c	34	PH_3	j	121	
d	45		k	135	
e	48	$-\text{PH}_2$	l	149	
f	59		m	163	
g	73				



Scheme 2. Possible pyrolytic pathway of HPUPO.

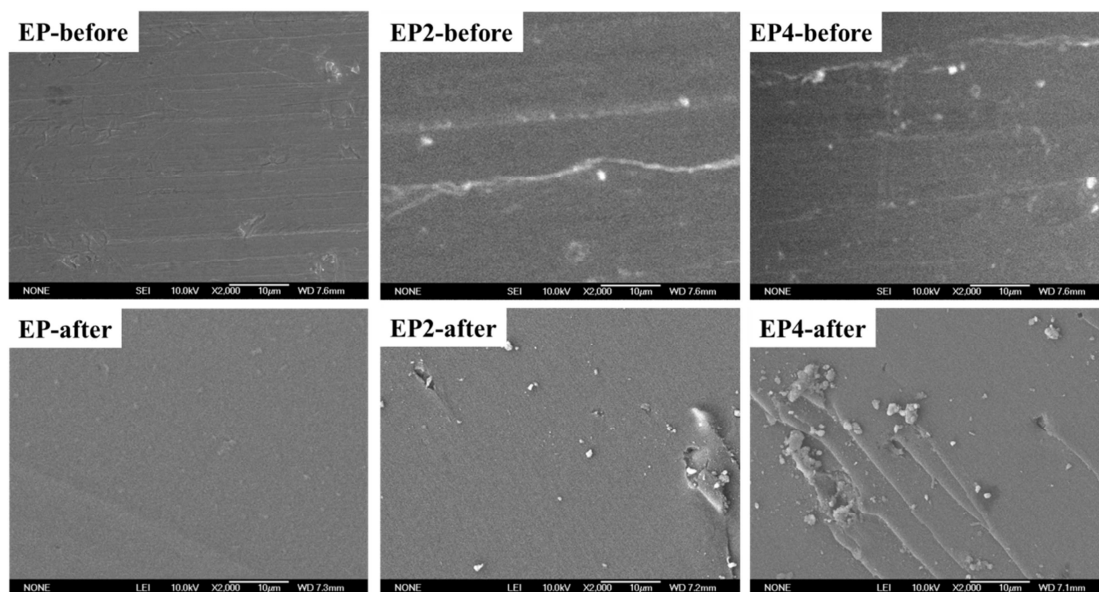


Fig. 10. SEM micrographs of cryogenically fractured surfaces of EP, EP2 and EP4 before and after etching.

3.6. Morphological analysis of epoxy thermosets

To investigate the morphology of epoxy thermosets, they were fractured under cryogenic condition using liquid nitrogen and then etched in DMF for 12 h and dried. Fig. 10 depicts SEM images of cryogen fracture surfaces of EP, EP2 and EP4 before and after etching as representatives. From those before etching, the neat EP shows a completely homogeneous morphology while heterogeneous morphology is observed for epoxy resin/HPUPO hybrids. The discrete HPUPO particles with diameter of 1-3 μm are dispersed in continuous epoxy matrix. After etching, HPUPO was removed and the cured epoxy resin remained unaffected (EP-after). The SEM images of hybrids after etching display some discrete vacant holes in epoxy matrix and their diameter is similar with that of the particles before etching. Thus, the two-phase microstructure of epoxy resin/HPUPO hybrids is further proved. Moreover, with the increase of the percentage of HPUPO, there is an increase in the number of the

particles and holes while there is no coarsening of them.

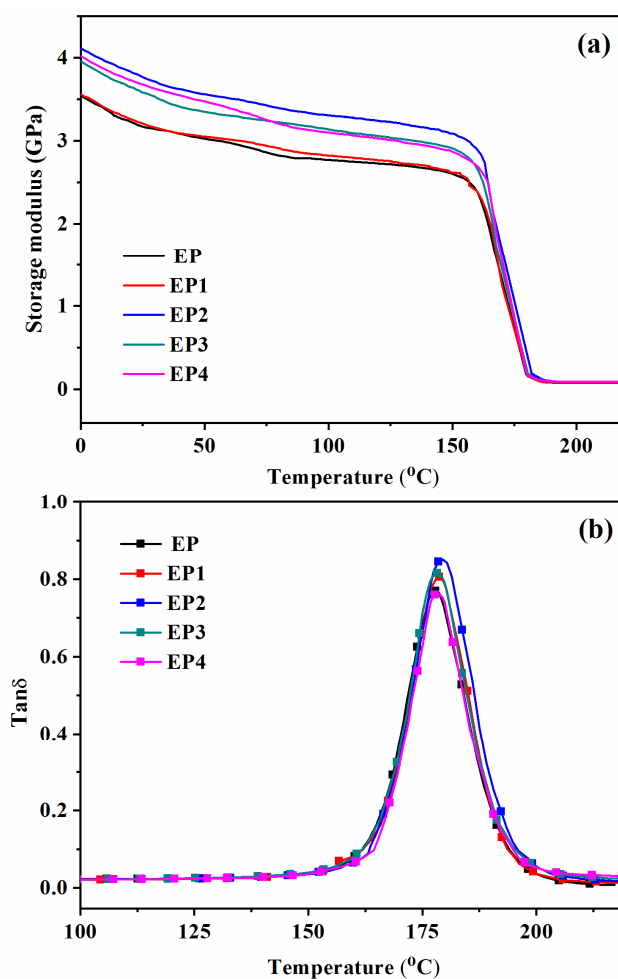


Fig. 11. Storage modulus (a) and loss tangent (b) versus temperature plots of epoxy thermosets.

3.7. Dynamic mechanical analysis

DMA technique was used to study the viscoelastic behavior of epoxy thermosets. Fig. 11 shows the dependence of storage modulus and loss tangent on temperature. In $\tan\delta$ curve, the temperature at the maximum value of α relaxation peak is identified as T_g , which is listed in Table 2. Even though two-phase microstructure is observed for epoxy resin/HPUPO blend, only one T_g of epoxy matrix phase can be appreciated in both DSC and DMA measurements. The expected glass transition of HPUPO phase

is not discernible due to its low content [57-58] (and for DSC, its technique is less sensitive than DMA for T_g measurement). Moreover, with the addition of HPUPO, T_g of epoxy matrix is maintained compared to that of the neat epoxy resin (the DMA and DSC results are in accordance) for the small miscibility of HPUPO within it.

As for the storage modulus of epoxy thermosets, their values in the glassy state show a non-monotonic increment as HPUPO content increases. This can be interpreted by competing factors: the more rigid skeleton of HPUPO (higher content of aromatic rings) and hydrogen bonds [59] formed by HPUPO improve modulus; molecule-scale cavities arising from hyperbranched polymer [35] provide room for segments to move when subjected to external force [44] and decrease modulus; the additional internal defects in heterogeneous system depress modulus.

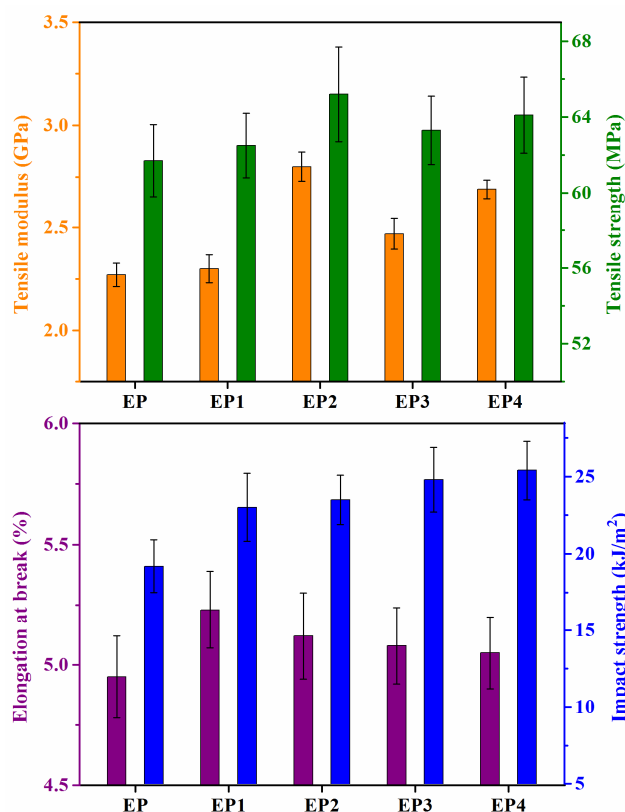


Fig. 12. Tensile modulus and strength, elongation at break and impact strength of epoxy thermosets.

3.8. Mechanical properties of cured epoxy resins

The effect of HPUPO content on mechanical properties of epoxy thermosets is shown in Fig. 12. The tensile modulus and strength increase in the order: EP < EP1 < EP3 < EP4 < EP2. Their improvement upon the incorporation of HPUPO is consistent with that of storage modulus at room temperature in DMA measurement. In the case of failure strain, it increases first and decreases afterwards as HPUPO ratio increases, which can be interpreted as follows. The presence of free volume from intra-molecular and inter-molecular cavities within and between hyperbranched molecules provides room for chain segment movement and raises the percent elongation [35,43]. However, the more rigid skeleton of HPUPO and hydrogen bond

interaction have adverse effect on it. And the additional internal defects in heterogeneous system can bring about the early failure of sample. Moreover, the elongation at break of modified epoxy resins are all higher than that of the neat one, which indicates the ductility of epoxy resin is enhanced by HPUPO.

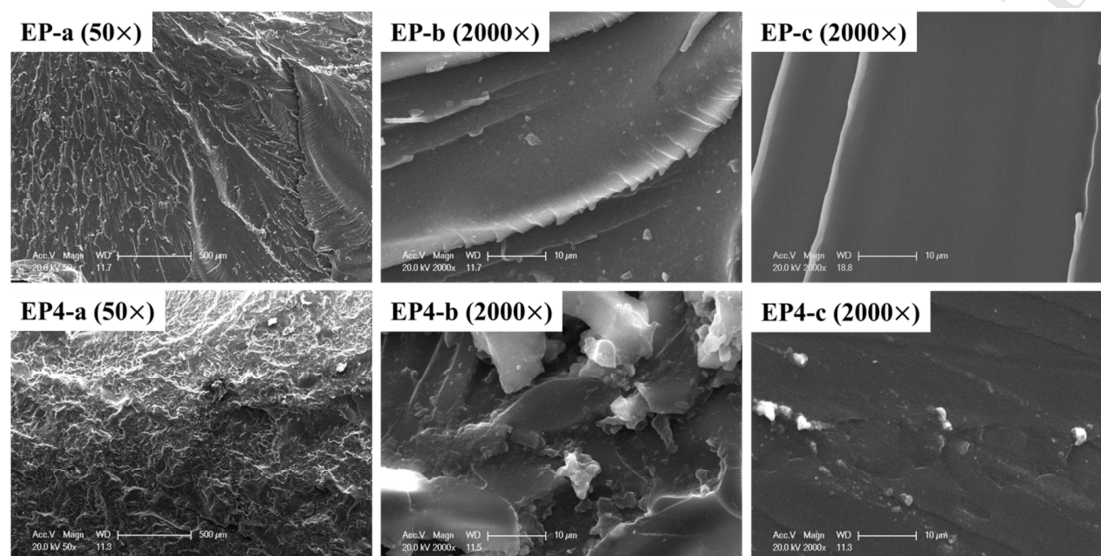


Fig. 13. SEM photographs of fracture surfaces of EP and EP4 after impact test.

The impact strength of cured epoxy resin is raised with an increase of HPUPO concentration and EP4 shows a 32.3% improvement compared to EP. The impact behavior can be elucidated according to the morphology of fracture surface after impact testing. Fig. 13 displays the SEM micrographs of the cross-sectional surfaces of EP and EP4. As can be seen, that of EP shows large amount of smooth glassy surfaces on it (EP-a and EP-b), indicative of the poor toughness of EP. However, the fracture surface of EP4 is obviously more rugged and irregular (EP4-a and EP4-b). The presence of abundant plastic deformation gives rise to more energy absorbed during impact testing, thus, enhanced toughness is acquired for EP4. Besides, the graph EP4-c in Fig. 13 shows that HPUPO particles with size of 1-3 μm are

dispersed in epoxy resin matrix, which is consistent with the above morphological analysis results.

The toughening mechanisms of HPUPO for epoxy resin are proposed. The introduction of intra-molecular and inter-molecular cavities arising from hyperbranched polymer can provide motion space for chain segments and absorb much energy during impacting [35,42-43]. The particulate toughening mechanism also works. HPUPO particles with different stiffness compared to epoxy resin matrix can act as stress concentrators, leading to shear deformation of matrix. Additionally, the strong interfacial adhesion derived from chemical bonding and hydrogen bonding interaction facilitates stress transfer between HPUPO particles and epoxy resin matrix, which contributes to the effective toughening.

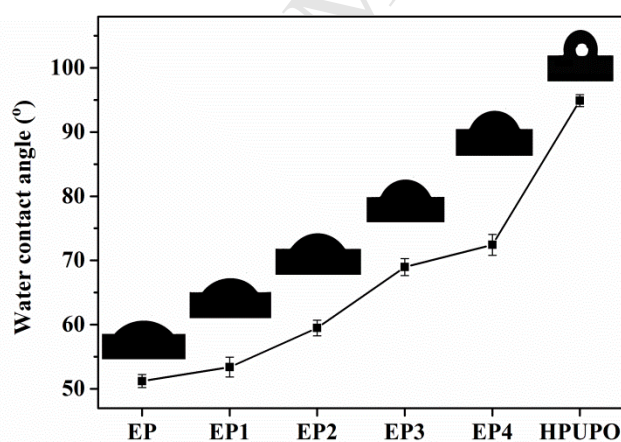


Fig. 14. The static water contact angles of epoxy thermosets and HPUPO and the shapes of water droplets on their surfaces.

3.9. Water contact angles of epoxy thermosets

Fig. 14 depicts the static water contact angles of cured epoxy resins and HPUPO film. The contact angle of EP is 51.2° , which indicates its hydrophilic surface. The surface hydrophilicity of EP is attributed to its hydrophilic hydroxyl and amino

groups. With HPUPO addition, a continuous increase of contact angles of epoxy thermosets is induced and the value of EP4 is 72.4° , which is 21.2° higher than that of EP. Thus, the surface hydrophilicity of epoxy resin is diminished by HPUPO. This phenomenon can be explained by two factors: the hydrophobic nature of HPUPO and the increased surface roughness of HPUPO modified epoxy resins. The hydrophobic units (phenylene, urethane and urea groups) of high content determine the hydrophobicity of HPUPO, which is verified by its contact angle of 94.9° . HPUPO particles in epoxy resin hybrids cause their elevated surface roughness.

4. Conclusions

A novel hyperbranched poly(urethane-phosphine oxide) was facilely prepared via the polycondensation reaction of MDI and THPO at room temperature. Its structure is characterized by NMR, FTIR and GPC. When HPUPO was added, the reactivity of epoxy resin curing reaction is improved due to the catalytic effect of its hydroxyl and the activation energy decreases first and increases later. The cured epoxy resins modified by HPUPO show depressed T_d and increased CY. With 4 wt% HPUPO incorporated, the epoxy thermoset receives UL-94 V-0 rating and its LOI value is 30.5%. Cone calorimetry results indicate decreased p-HRR and THR of epoxy resin hybrids. The condensed phase flame retardant mechanisms are increased char yield and protective and barrier effect of char residue. The gas phase flame retardant mechanism is speculated as the flame inhibition effect of the released phosphine and phosphine oxide from HPUPO. The tensile modulus and strength and storage modulus

of modified epoxy thermosets are elevated for more rigid skeleton of HPUPO and hydrogen bond interaction. The impact strength is also improved and the toughening mechanisms are proposed. The poor compatibility of epoxy resin/HPUPO hybrids determines the nearly unchanged T_g of epoxy matrix phase. The surface hydrophilicity of epoxy thermosets is diminished by HPUPO, as illustrated by their increased water contact angles, which results from their raised surface roughness and the hydrophobicity of HPUPO. In summary, HPUPO improves flame retardancy, tensile modulus and strength and toughness of epoxy resin with maintained T_g , increased curing reactivity, decrease surface hydrophilicity and depressed thermal decomposition temperature.

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Acknowledgement

The authors would like to acknowledge the support from National Key Research and Development Program of China (2016YFB0302104), National Natural Science Foundation of China (21374111, 51603200), and Fundamental Research Funds for the Central Universities (WK2320000037).

Appendix A. Supplementary data

Supplementary data related to this article can be found at

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A novel hyperbranched poly(urethane-phosphine oxide) was prepared from MDI and THPO.

Flame retardancy, mechanical properties, curing reactivity and hydrophobicity of EP are improved with maintained T_g .

Mechanisms for property enhancement are provided.