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Synthesis of a hyperbranched polyamide charring agent and its flame-retarding and toughening behavior in epoxy resin

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ABSTRACT

A hyperbranched polyamide charring agent (HPCA) was synthesized by amidation of 1,2,3,4-butanetetracarboxylic acid and melamine, and its chemical structure was characterized. Such a charring agent, combined with ammonium polyphosphate (APP), was applied in epoxy resin. V-0 rating in the UL-94 vertical burning test and 32.3% of Limiting Oxygen Index were achieved with only 10% total flame retardant loading. A HPCA/APP ratio of 1/1 showed better flame retardant properties than the system with only HPCA or APP involved, indicating an apparent synergistic effect. The residual char at high temperature was analyzed by using FTIR and X-ray Photoelectron spectroscopy (XPS) to further explore the above synergistic mechanisms. Additionally, HPCA, as a co-curing agent, was grafted into the crosslinking net of epoxy resin due to the reactivity of carboxylic acids with epoxy group and hydroxyl group. The introduced hyperbranched polyamide structure effectively improved the toughness of original rigid crosslinking net of epoxy resin.

1. Introduction

Epoxy resin (EP) [1-4], owing to its low shrinkage, high electrical insulation properties and other excellent performance, has been widely applied in adhesives, coatings, construction industries and so on. However, like most polymers, a fatal flaw in epoxy resin lies in its inherent combustibility. Without fire safety, the application of epoxy resin in many fields has been restricted [5,6]. Hence, the improvement of epoxy resin in flame retardancy is important and significant [7-11].

In recent years, considering the safety problems of halogen flame retardants, halogen-free intumescent flame retardants have been developed rapidly [12-15]. Intumescent flame retardant systems are more and more paid attention due to its high efficiency, good safety and relatively low cost. A typical intumescent flame retardant system usually consists of three components: acid catalyst, blowing agent and charring agent [16,17]. Among them, conventional charring agents include pentaerythritol, starch, etc. However, due to its low decomposition temperature, poor water resistance and low flame retardant efficiency, it is difficult to meet the requirements of commercial applications. Therefore, a lot of work has been done for the exploration of high-efficiency charring agents, including piperazine derivatives [18], triazine derivatives [19] and phenolic resins [20], etc. Among them, hyperbranched charring agents have attracted much attention due to their high char-forming efficiency, high thermal stability, and good synergistic effects with other components. Wen et al [21]., synthesized a hyperbranched piperazine charring agent (HCFA) by the reaction of anhydrous piperazine and cyanuric chloride, and was used in flame retardant polypropylene combined with ammonium polyphosphate. The results showed that APP/HCFA was able to effectively improve the thermal stability and thermal oxidation stability of char residue, and reduce the heat release rate (HRR) and fire growth index of the composite. Li et al [22]., prepared another hyperbranched triazine charring agent (HTCA) through the reaction of 4,4-oxybisbenzenamine and cyanuric trichloride. The results showed that HTCA and APP had good synergistic flame-retarding effect. HTCA/APP was capable to effectively improve the char-forming capacities and flame retardant properties of acrylonitrile-butadiene-styrene (ABS). Zhang et al [23]., prepared a hyperbranched N-containing and P-containing polyurethane charring agent (HPPU). The addition of 25wt% APP/HPPU resulted in decrease in total heat release rate of 72% and peak of heat release rate of 38%.

From previous studies, a large number of papers have been published in the last years proposing hyperbranched N-containing charring agents [18,24,25]. According to the literature published, most of the hyperbranched charring agents are triazine derivatives

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with aryl rings, and they were almost alike in structure. Additionally, the reported hyperbranched charring agents were mainly used in polyolefin materials. However, the commercial applications of hyperbranched charring agents in epoxy resin were few reported in recent years, possibly due to relatively low flame retarding efficiency and caused deterioration in mechanical properties. Accordingly, developing a hyperbranched charring agent suitable in epoxy resin is significant whether in academia or industry. In this research, 1, 2, 3, 4-butanetetracarboxylic acid (BTCA) with excellent thermal stability, widely used in chemical industry to prepare high temperature resistant materials [26], is reacted with melamine (MEL) via amide-acid condensation to synthesize a hyperbranched polyamide (HPCA) charring agent. Different from the structure of the previously reported triazine hyperbranched charring agents, the triazine rings connect a polycarboxyl charring agent without aryl rings in HPCA molecule. Additionally, HPCA is also capable of acting as a curing agent grafted into the crosslinking net of epoxy resin, thus effectively improving the toughness of the epoxy resin [27]. Therefore, compared with other hyperbranched charring agents, HPCA shows the unique advantages in flame retardant epoxy resin.

2. Experimental

2.1. Materials

Epoxy resin (diglycidyl ether of bisphenol-A type, epoxy equivalent weight: 489 g per eq.) and 4,4′-diaminodiphenylmethane (DDM, 98%) were provided by Huntsman Advanced Materials Co., Ltd. MEL and 4-dimethylaminopyridine (DMAP) were bought from Chengdu Cologne Chemicals Co., LTD. Dimethylsulfoxide (DMSO) was supplied by Zhengzhou Pengni chemical Reagent Factory. 1,2,3,4-butanetetracarboxylic acid (BTCA, 99%) was obtained from Guangdong Wengjiang Chemical Reagent Co. LTD. N,N'-dicyclohexyl carbon diamine (DCC) was received from Tianhua Reagent Co. LTD.

2.2. Synthesis of hyperbranched polyamide

The synthesis route of HPCA was shown in Scheme 1. Firstly, under being stirred, BTCA (0.06 mol, 14g) was added to a three-necked flask containing 100ml DMSO at 150°C. Then, DCC (0.33mol, 7g) was added to the solution. MEL (0.08mol, 10g) and DMAP (0.16mol, 2g) were dissolved in 100ml DMSO and added to the flask drop by drop. Then, the above reaction was conducted for 15h. Finally, the obtained powder product was repeatedly washed with deionized water and dried at 100°C for 1h. The mass of final powder was 8g (yield: 40%).

Table 1
The formulations of the flame retardant epoxy resin.

Specimens	Composition(g)			
	EP	DDM	APP	HPCA
EP	100	25	-	-
EP/APP	100	25	14	-
EP/HPCA	100	25	-	14
EP/APP/HPCA	100	25	7	7

2.3. Preparation of the flame retardant epoxy resin

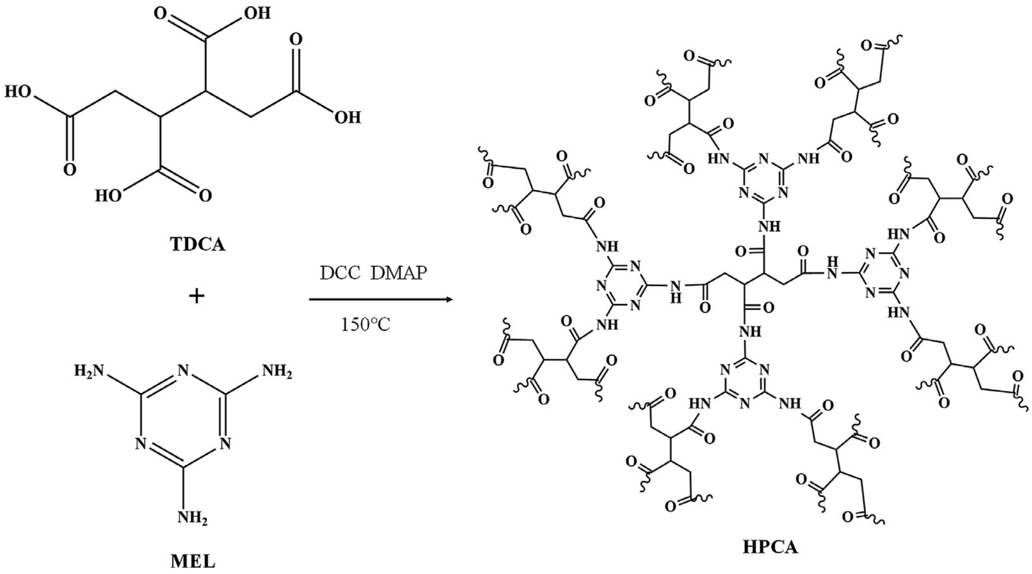
The formulations of flame retardant epoxy resin were listed in Table 1. Firstly, EP and different amount of the flame retardants (APP/HPCA) were added into the three-necked flask at 90°C. Then, the curing agent, DDM was dissolved into the above solution with constant stirring for 10 min, and finally, the obtained viscous liquid was poured into the molds, and further cured in a vacuum oven as the following procedure: 80°C for 2 h, 120°C for 2 h and 150°C for 2 h.

2.4. Characterization

Fourier transform infrared (FTIR) spectroscopy was performed on a Nicolet 6700 infrared spectrometer (Thermo Fisher Scientific, Waltham, Massachusetts, USA) in order to explore the chemical structure of HPCA. The frequency range recorded by the spectrum was between 4000 and 500 cm^{-1}.

Avance II-400 MHz NMR spectrometer was used to measure the ^{1}H NMR spectra of HPCA (dimethyl sulfoxide-d6 as a solvent, and tetramethylsilane as an internal standard).

The average molecular weight of HPCA was determined by gel permeation chromatography (GPC). The specimen was added to tetrahydrofuran (2mg/ml), dissolved overnight and filtered with a



Scheme 1. Synthesis route of HPCA.

filter head (Whatman Nylon Membrane) with a pore diameter of 0.22 micron. Finally, the above system was injected into the gel permeation chromatography instrument (PL-GPC 50, USA) for testing.

Thermal degradation behavior of all specimens were studied with TA Q50 thermal analyzer from 40 °C to 700 °C. The heating rate of the program was 10 °C/s.

Limiting oxygen index (LOI) value was obtained using an oxygen index instrument according to ASTM D 2863-77. The dimension of all specimens was 120 × 10 × 4 mm^3. Vertical burning test was performed on a JT-HVR5455 instrument (Dongguan, China) according to GB/T2408-2008, and the dimension of all specimens was 125 × 13 × 3.2 mm^3.

Cone Calorimeter (CC) tests of all specimens were carried out on an FTT0007 device (UK) according to ISO5660 with an incident flux of 50 kW/m^2, and the dimension of specimens was 100 × 100 × 4 mm^3.

Morphologies of residual chars after vertical burning test were conducted using a JSM-5610LV scanning electron microscope (SEM) at an acceleration voltage of 25 kV.

Elemental analysis of residual char were performed on an X-ray photoelectron spectroscopy meter (Shimadzu, Japan) using Al Ka excitation radiation (hv = 1486.6 eV).

The gelation time of epoxy resin was subject to GT193.6-87. The gelation disk experiment was used to determine the gelation time of resin. The time it took to go from a flowing state to a non-flowing gel state was gelation time.

Dynamic mechanical analysis (DMA) of EP thermosets were performed on a TA DMA Q800 (USA) meter from 25 °C to 160 °C at a heating rate of 3°C/min and a frequency of 1 Hz.

Mechanical performance tests of EP thermosets were conducted at room temperature with a crosshead speed of 50 mm/min (ISO527) using a Reger RG L-10 universal mechanical testing machine (Shenzhen, China). The impact properties of all specimens were tested using a JYM-17XJJ-50 impact tester according to GB/TL 043.1-2008 test standard.

3. Results and discussion

3.1. Characterization of HPCA

The chemical structure of HPCA was firstly confirmed via FTIR spectra. The FTIR spectra of BTCA, MEL and HPCA were shown in Fig. 1. The two characteristic absorption peaks at about 2928 cm^{-1} and 2856 cm^{-1} in HPCA were attributed to the stretching vibration of methylene group. The peaks at 3365 cm^{-1} and 1683 cm^{-1} were assigned to -OH- and -C=O- of carboxyl. And the existence of carboxyl group was further proved by the bending vibration peak of - OH - of carboxylic acid at 1399 cm^{-1}. Moreover, the absorption peaks at 3086 cm^{-1} and 1311cm^{-1} were caused by the -NHCO- and -C-N-, respectively, which confirmed the occurrence of the reaction between BTCA and MEL. The peaks at 3469 cm^{-1} and 3418 cm^{-1} of MEL, corresponding to the amino group, disappeared in HPCA, indicating that the amino group in MEL fully reacted with BTCA.

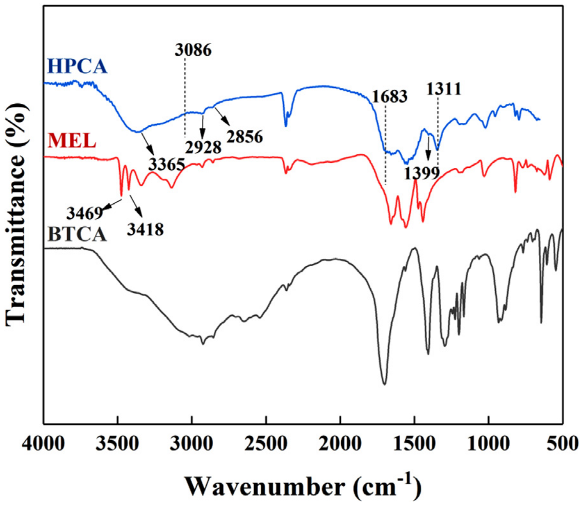


Fig. 1. FTIR spectra of BTCA, MEL and HPCA.

The ^{1}H NMR spectrum was able to further prove the chemical structure of HPCA. The resonance at about 1.05 ppm was assigned to -CH$_2$- in Fig. 2. Meanwhile, the chemical shift of -CH- appeared at 2.08 ppm. The secondary amides in DMSO-d$_6$ showed weak and broad peak signals (7.3-7.8ppm) [28-30]. According to the molecular structure of HPCA, theoretical ratio of H in -CH$_2$- to H in -CH- to H in amide bond was 1:0.5:0.38. As shown in Fig. 2, the integral area ratio of peak a to peak b to peak c was 1:0.49:0.36, which proved the successful synthesis of HPCA. Although from a structural point of view, HPCA is able to grow into a large cross-linked structure, the steric hindrance effect of the triazine rings probably limits the molecule growth to a great degree. The obtained HPCA was completely dissolved in DMSO, suggesting that HPCA was a non-crosslinked polymer. Here, GPC was adopted to measure the molecular weight of HPCA. It was found that HPCA had a wide distribution of molecular weight, and the number-average molecular weight (Mn) and weight- average molecular weight (Mw) were 898 and 1314 (Fig. 3).

Additionally, HPCA also showed entirely different thermal degradation behavior from MEL and BTCA from their TGA and DTG curves (Fig. 4a,b). Compared with one-step degradation for BTCA from 150-300 °C or one-step sublimation for MEL from 270-400°C, the degradation process of HPCA was divided into two stages. Before 300°C, HPCA mainly involved the dehydration of carboxylic acids, which promoted the production of anhydride. The second degradation stage occurred mainly from 300-400°C, due to the intra-molecular cross-linking reaction. Compared with MEL that sublimated at high temperature, the chemical bond between BTCA and MEL restrained the sublimation behavior of MEL, and made for the condensation of amino groups to form cross-linking structure. Accordingly, HPCA showed as high as 26.39% residues at 700°C, far higher than that of MEL (0%) and BTCA (15.21%) Furthermore, the FTIR spectra of HPCA at different temperatures were used to confirm the above viewpoints (Fig. 4c). Compared with the room temperature (RT), at 250°C, the FTIR spectra of HPCA showed two peaks (1650 cm^{-1} and 1560 cm^{-1}), which were attributed to the bimodal structure of anhydride. With increase of temperature, the peaks of anhydride gradually weakened, indicating the degradation of anhydride. Over 300°C, a peak appeared at 1080 cm^{-1}, belonging to typical crosslinked char (-C-O-C-) [31,32]. With increasing temperature, this peak became more and more obvious, indicating the increased amount of the char layer in the condensed phase.

3.2. Flame retardancy of HPCA/APP on EP and the corresponding synergism

The vertical burning and LOI test were used to evaluate the flame retardancy of EP thermosets. Fig. 5 and Table 2 showed the vertical combustion as well as LOI test results of the EP thermosets. When the cured EP was ignited, the flame spread rapidly and was not able to self-extinguish, so did EP/APP and EP/HPCA. The LOI of the specimens with 10% APP and HPCA increased compared with EP, however, the increased value was small, thus still failing to pass the UL-94 V-0 test (no rating). In contrast, EP/APP/HPCA showed much better flame retardant property. The V-0 rating and 32.3%

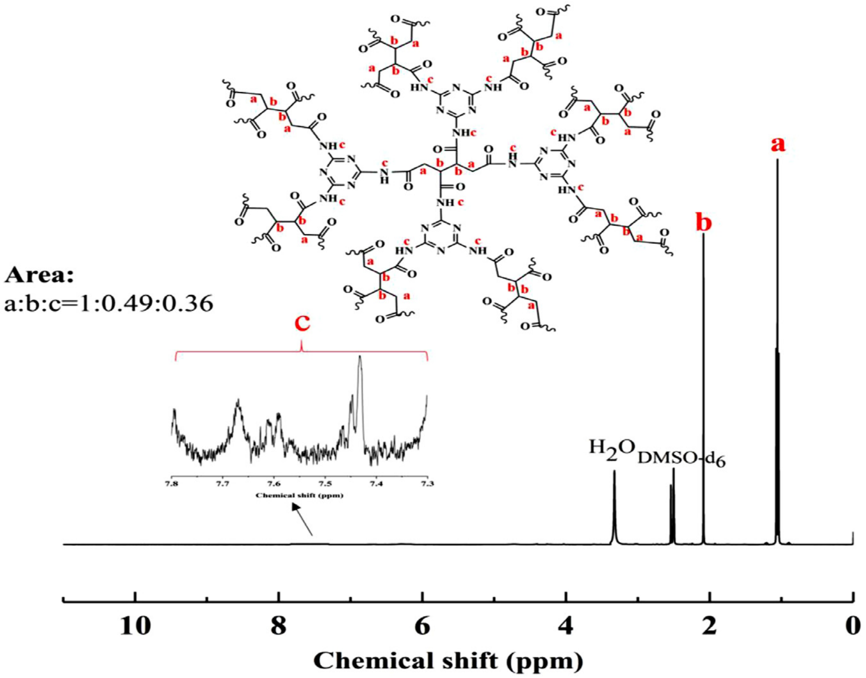


Fig. 2. ^{1}H NMR spectrum of HPCA.

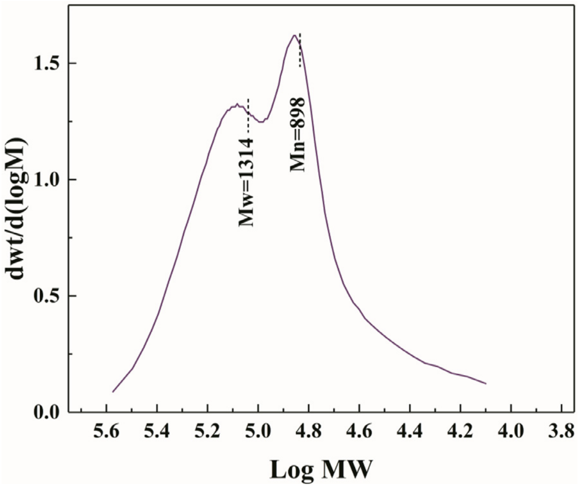


Fig. 3. Chromatogram of HPCA in GPC test.

Table 2
The limit oxygen index and vertical burning test results.

Specimens	LOI (%)	UL-94 test (3.2mm)		
		$^*t_1/t_2$(s)	Dripping	Rating
EP	19.8	-	Yes	NR
EP/APP	24.3	10/28	None	NR
EP/HPCA	22.5	12/45	None	NR
EP/APP/HPCA	32.3	0/0	None	V-0

t_1, t_2 represent the after flame time: after the first and second 10 s flame application respectively.

LOI was achieved at only 10% total flame retardant content, indicating that APP and HPCA had remarkable synergistic effect.

Cone calorimetry (CC) test was also adopted to evaluate the flame retardancy of the above materials. Fig. 6 showed the heat release rate (HRR), total heat release rate (THR), specimen mass and rate of smoke release (RSR) curves of the flame retardant EP, and the characteristic parameters were summarized in Table 3. The pk-HRR and THR of cured EP were as high as 1385kW/m^2 and 93 MJ/m^2, respectively, showing high flammability. EP/APP and EP/HPCA showed a little decrease for pk-HRR (1267 kW/m^2 and 1200 kW/m^2) and THR value (61 MJ/m^2 and 84 MJ/m^2), which suggested that APP or HPCA alone had very little impact on improvement of the flame retardancy. Similarly, EP/APP/HPCA composites greatly decreased the flammability. The pk-HRR and THR of EP/APP/HPCA were reduced by 75.5% (340 kW/m^2) and 47.3% (53 MJ/m^2) than cured EP. Furthermore, it is also significant to examine the smoke emission during combustion. Compared with the total smoke release (TSR: 4985 m^2/m^2) of cured EP, the TSR of EP/APP, EP/HPCA and EP/APP/HPCA were decreased by 29.7%, 29.5% and 56.0%, respectively. The lowest TSR (2194.1 m^2/m^2) for EP/APP/HPCA indicated the flame retardant system had best suppression effect of smoke emission. The average effective combustion heat (av-EHC) reflects the combustion of volatile gases in a flame. The great decrease of av-EHC for EP/APP/HPCA was due to more quick dehydration and deamination resulted from the synergism. Additionally, Compared with EP, EP/APP, and APP/HPCA (their char yield were 0.1 wt%, 32.5 wt%, and 12.1 wt%, respectively), the char yield of EP/APP/HPCA was increased to 39.9 wt%. EP had the longest ignition time compared other systems. The reduced time to ignition for flame retardant EP is probably ascribed to the heat release in advance because of the decomposition of EP accelerated by the flame retardants. Fig. 7 showed digital and SEM photographs of the above residues. EP retained minimal residual char after the test and there's a certain amount of residual char on EP/APP and EP/HPCA. However, there were many holes on the surface of the char layer, so it was difficult to block the release of heat and combustible gases. In contrast, the char layer of EP/APP/HPCA showed denser and more continuous, which possessed much better isolating effects.

In order to investigate the detailed synergistic mechanisms between APP and HPCA, Fig. 8 presented the experimental TGA and DTG curves of APP/HPCA system and their calculated curves. The calculation curves are composed of TGA and DTG curves of APP and HPCA in a proportion of 1/1. The obvious difference between

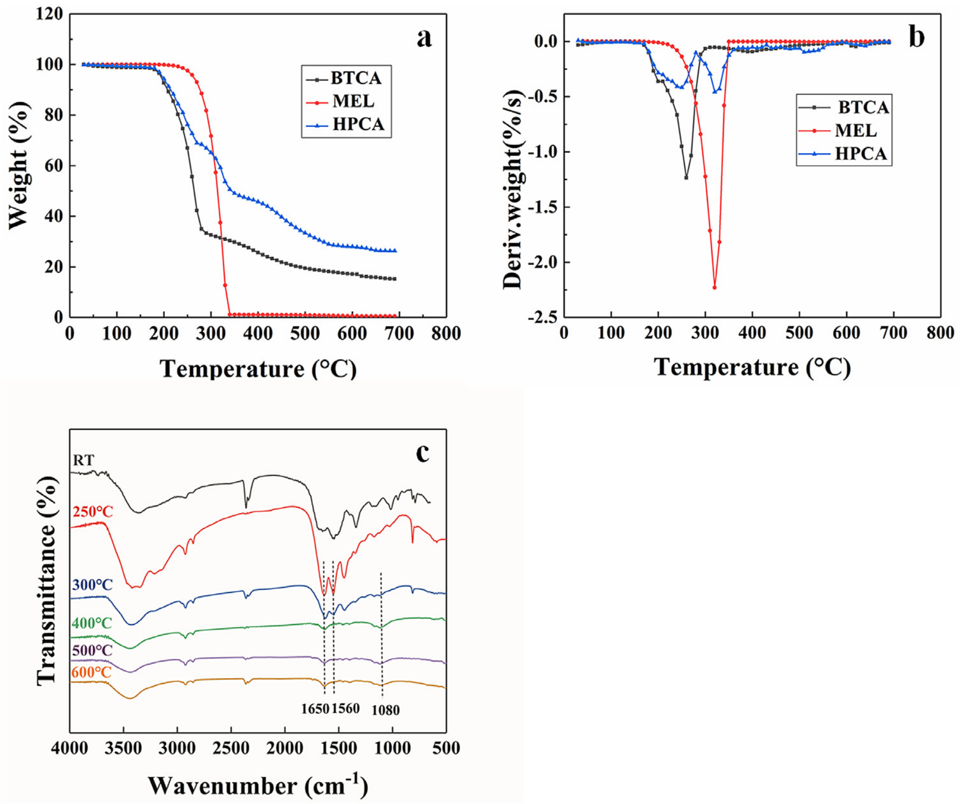


Fig. 4. . TGA and DTG spectra of BTCA, MEL and HPCA (a, b); The FTIR spectra of HPCA char residue at different temperatures (c).

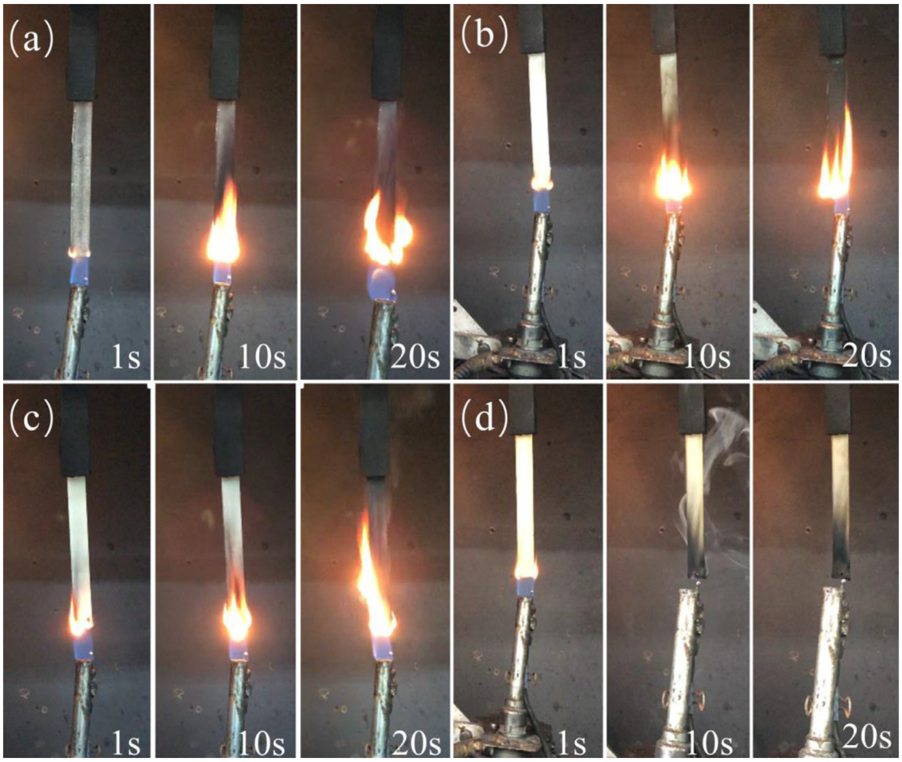


Fig. 5. Screenshots of EP (a), EP/APP (b), EP/HPCA (c) and EP/APP/HPCA (d) during vertical burning test.

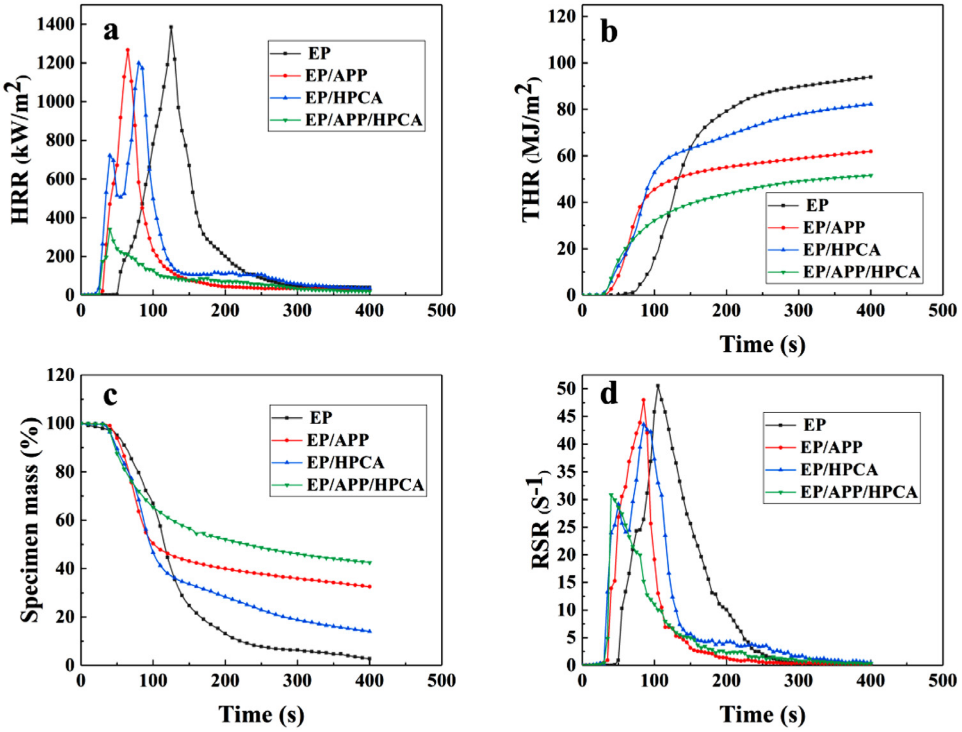


Fig. 6. HRR (a), THR (b), MASS (c) and RSR (d) curves of EP, EP/APP, EP/HPCA and EP/APP/HPCA.

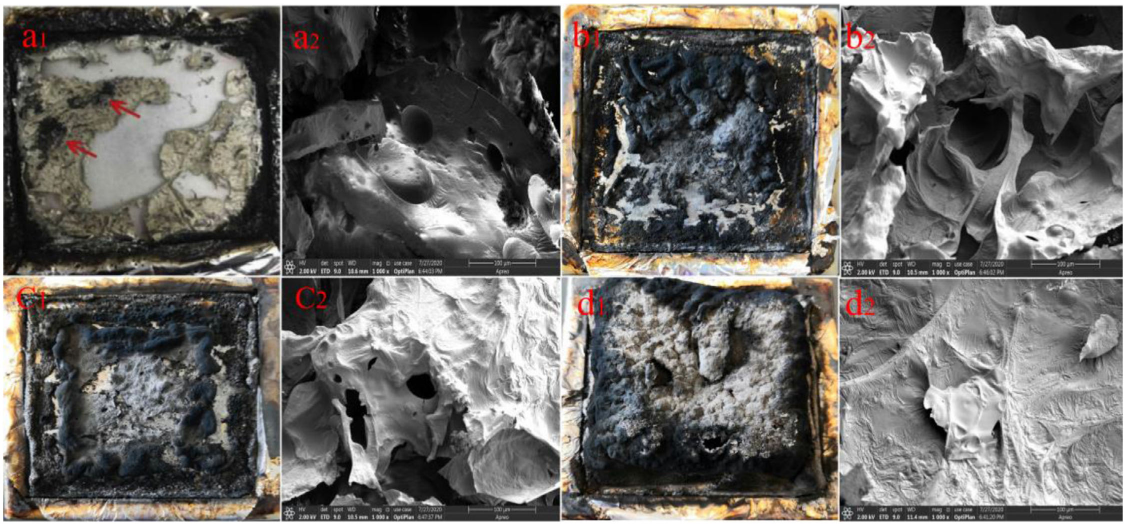


Fig. 7. Digital and SEM photographs of the residues(EP:a1,a2, EP/APP:b1,b2, EP/HPCA:c1,c2, EP/APP/HPCA:d1,d2) after cone calorimeter test.

Table 3
CC test parameters of EP, EP/APP, EP/HPCA and EP/APP/HPCA.

Specimens	pk-HRR (kW/m^2)	THR (MJ/m^2)	Residue (wt %)	TTI (s)	TSR (m^2/m^2)	Av-EHC (MJ/kg)
EP	1385±10	93±1	0.1±0.2	53±2	4985±15	22.1±1.0
EP/APP	1267±10	62±1	32.5±1.0	34±1	3501±12	20.1±0.6
EP/HPCA	1200±9	84±1	12.1±1.1	28±3	3512±13	21.7±0.7
EP/APP/HPCA	340±5	53±1	39.9±1.3	31±1	2194±10	17.7±1.0

the experimental and calculated ones, implied the remarkable interaction of HPCA and APP. According to experimental curve of APP/HPCA, the char residue at 700°C was 51.9 wt%, while the calculated APP/HPCA was only 20.9 wt%. In addition, the experimental weight loss rate of APP/HPCA was more and more obviously lower than the calculated one over 400°C. The results implied that the interactions between HPCA and APP promoted the generation of some cross-linked residues with good thermal stability. The interactions involved the acceleration of the phosphorylation and dehydration reaction.

The variation of APP/HPCA mixture at elevated temperature, also reflected the interaction of the two components. From Fig. 9,

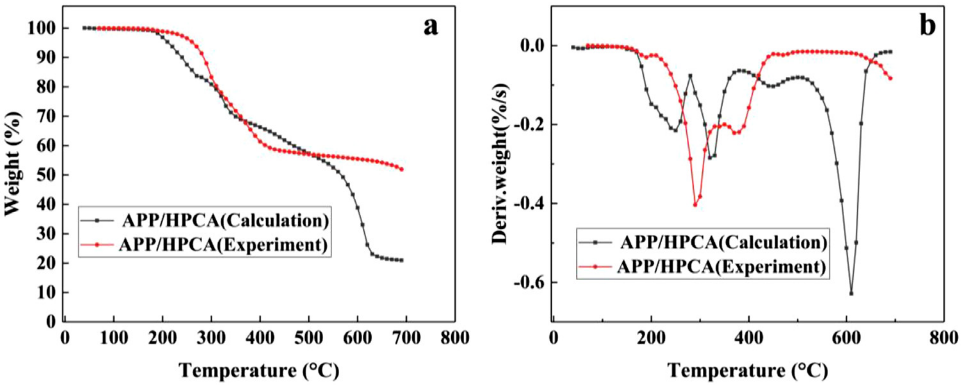


Fig. 8. TGA (a) and DTG (b) curves of APP/HPCA (calculation) and APP/HPCA (experiment) in N_2.

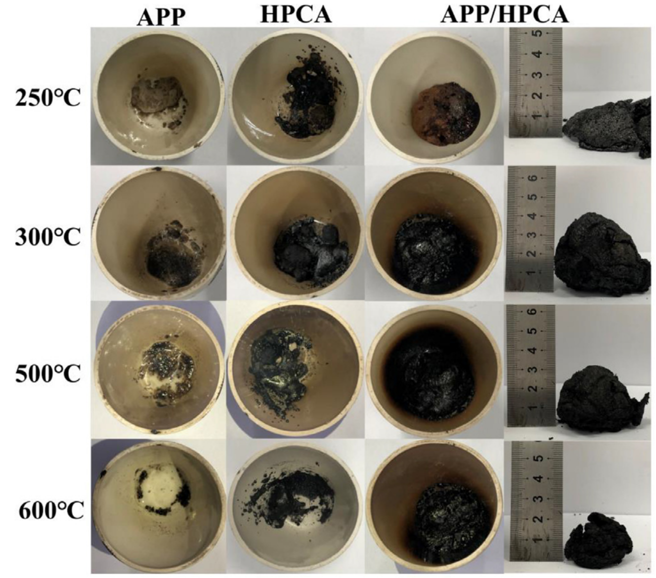


Fig. 9. Morphology of the flame retardant systems varied with elevated temperature.

the residues of only APP or only HPCA became less and less with increasing temperature, and both of them retained a little at 600°C. In comparison, APP/HPCA mixture formed obvious intumescent char [33,34]. The evolution photos of the intumescent char for APP/HPCA were also displayed as shown in Fig. 9. The char layer of APP/HPCA was at its maximum height at 300°C, showing the most intumescent morphology. The above intumescent mechanisms mainly result from the decomposition and interaction of the two components at the temperature. In fact, APP combined with HPCA constitutes a typical intumescent flame retardant system. As is well known, APP decomposes and releases both acidic and N-containing gas sources at 300°C, and in the similar temperature range, HPCA also decomposes into the BTCA and MEL. The produced phosphoric acid compounds from APP were able to catalyze the dehydration and deamination of BTCA and MEL effectively to form the condensed phase. Additionally, the generated water vapor and ammonia gas further make the condensed phase foam and expand to form highly intumescent structure.

The chemical structure of the intumescent char layer (EP/APP/HPCA) was also analyzed by FTIR and XPS (Fig. 10). In Fig. 10a, the peak at 1080 cm^{-1} and 1624 cm^{-1} were assigned to C-O-C and C=O. The absorption peaks at 1170 cm^{-1} and 981 cm^{-1} was corresponded with the P=O and P-O-C, indicated the formation of phosphorus-rich char layer. In Fig.10b, the wide-scan spectra showed the contents of various elements in the residues of EP/APP/HPCA. It showed that C and O constitute the main elements of the residues, and a small amount of P and N were involved. Moreover, the C_{1s} spectrum was deconvoluted into three main peaks at 284.5eV (C-C), 286.2eV (C-O) and 288.9eV (C=O). The N_{1s} peak at 400.0eV was attributed to -NHCO- and the peak at 401.5eV corresponded to oxynitride. The O_{1s} peaks at 531.2eV, 533.0eV and 533.7eV were assigned to P=O, P-OH and P-O-P, derived from the decomposition of APP. The O_{1s} peak centered at 532.2eV was attributed to P-O-C. The P_{2p} peaks at 134.2eV and 135.0eV was assigned to P-O-P and PO_3, resulted from polyphosphate and pyrophosphate [35].

Based on the above analysis, the flame retardant mechanism of EP/APP/HPCA was summarized as follows (Scheme 2). When the material is ignited, APP starts to release ammonia and produce phosphoric acid, pyrophosphoric and metaphosphate. These produced acidic compounds catalyzes HPCA effectively to be dehydrated and deaminated to form anhydride and melam-like structures [36], thus rapidly constructing carbon skeleton with good thermal stability. On the other hand, under the catalysis of acidic compounds and isolation of the constructed carbon skeleton, incomplete combustible EP is inclined to be converted to C-rich char layer, which further protects the underlying substrate.

3.3. Curing behavior of HPCA and toughening effect

Except high flame retardant efficiency, another advantage of HPCA is that this charring agent was acted as a co-curing agent for EP due to its reactivity [37,38]. In this way, such hyperbranched polyamide structure was successfully grafted into the three dimensional net of the EP thermoset as shown in Scheme 3. The curing behavior of the flame retardant EP was investigated by FTIR (Fig. 11a). In EP/APP/HPCA, the peak of epoxide group at 914 cm^{-1} disappeared, suggesting that the epoxide group has been consumed. Compared with pure epoxy resin, EP/APP/HPCA appeared two peaks at 1715 cm^{-1} and 1184 cm^{-1}, attributed to carbonyl and the -C-O-C- bond of ester group, indicating that HPCA was either esterified with the hydroxyl group on the side chain of the epoxy molecule or ring-opened with the epoxy group. In addition, a peak appeared at 814 cm^{-1}, which was attributed to the stretching vibration of triazine ring in HPCA. The above results indicated that HPCA was introduced into the molecular chain as a co-curing agent in the curing process of epoxy resin. In addition, HPCA also demonstrated its promoting effect on the gelation of EP (Fig. 11b, c, d). It was difficult for pure epoxy to form gelation under heating condition. On the contrary, when DDM and HPCA were added to epoxy resin, they appeared wire drawing in 5 min and 10 min respectively, suggesting that HPCA promoted the curing reaction of epoxy resin.

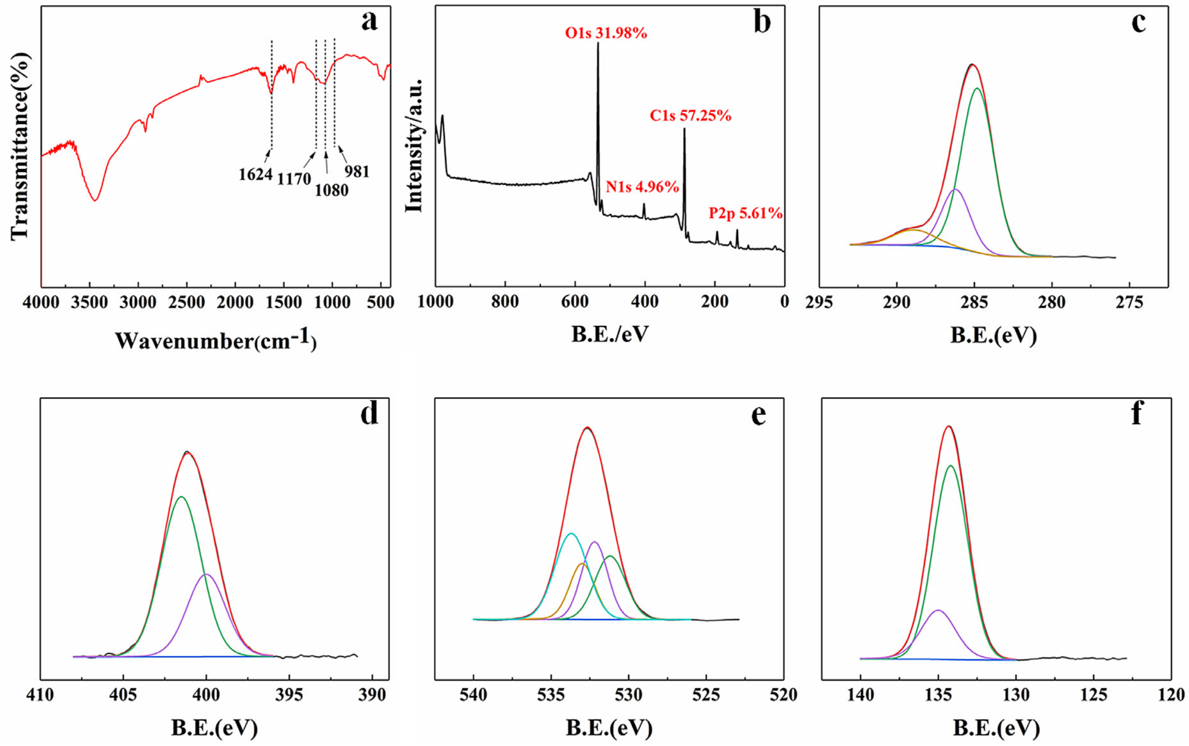
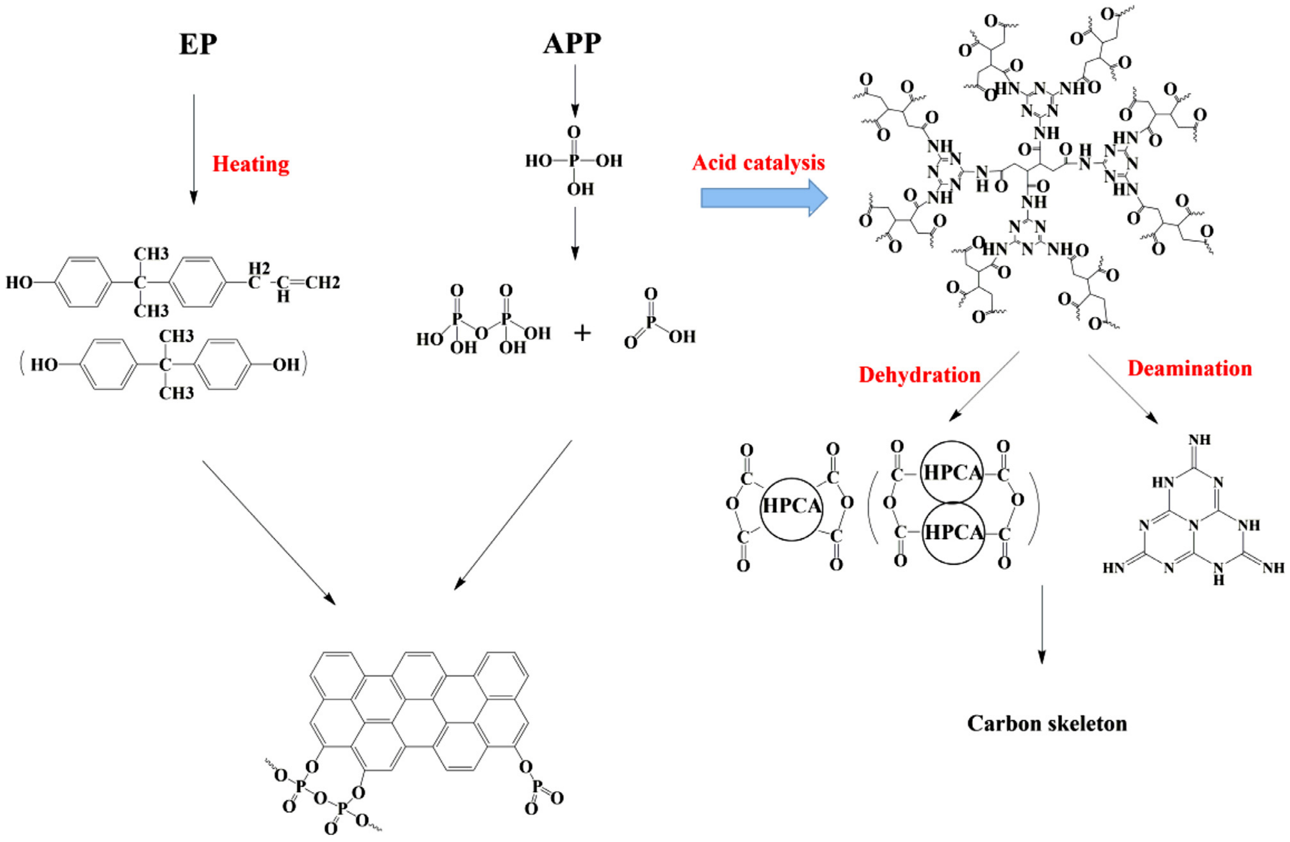
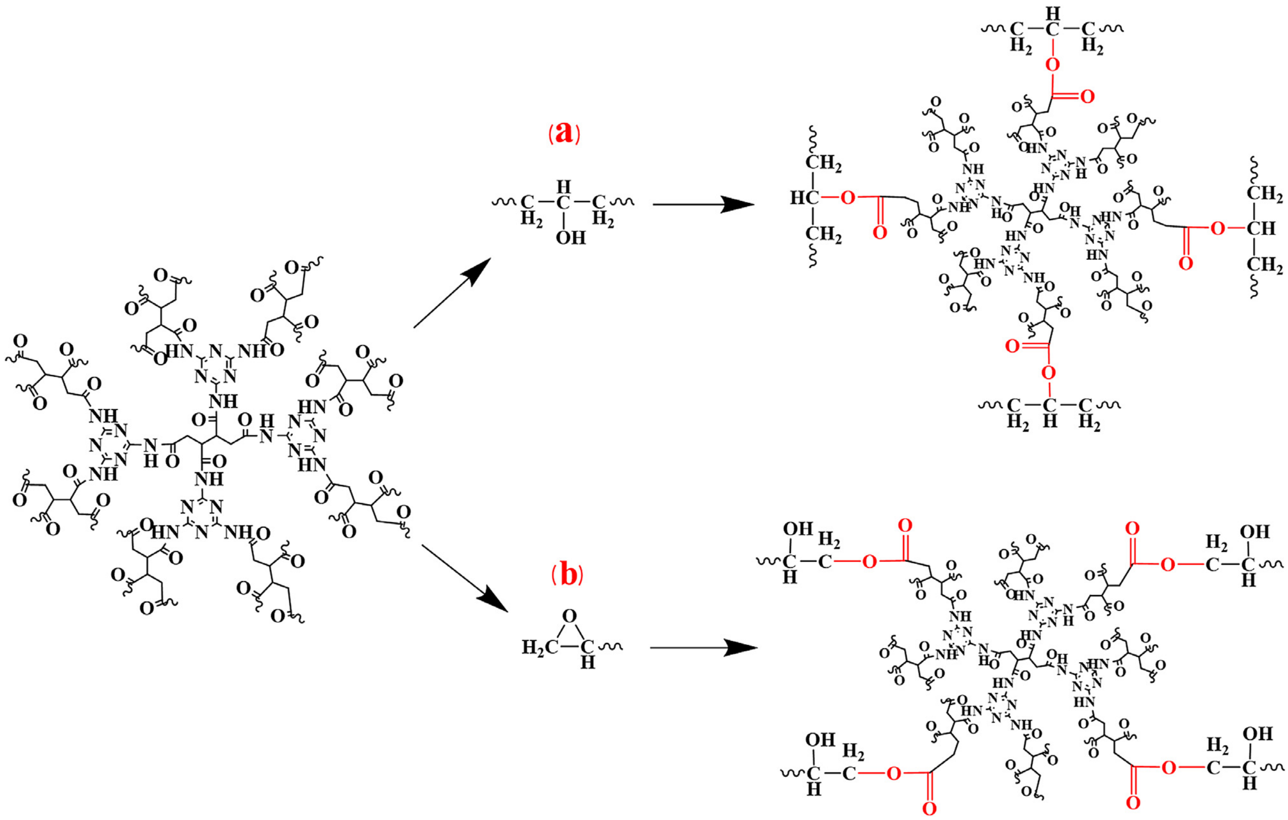


Fig. 10. FTIR spectrum of EP/APP/HPCA residues (a); XPS spectra (b. wide-scan spectra, c. C1s, d. N1s, e. O1s, f. P2p) of EP/APP/HPCA residues.



Scheme 2. Flame-retardant mechanism of EP/APP/HPCA.



Scheme 3. Curing behavior of HPCA: esterification reaction (a); ring-opening reaction (b).

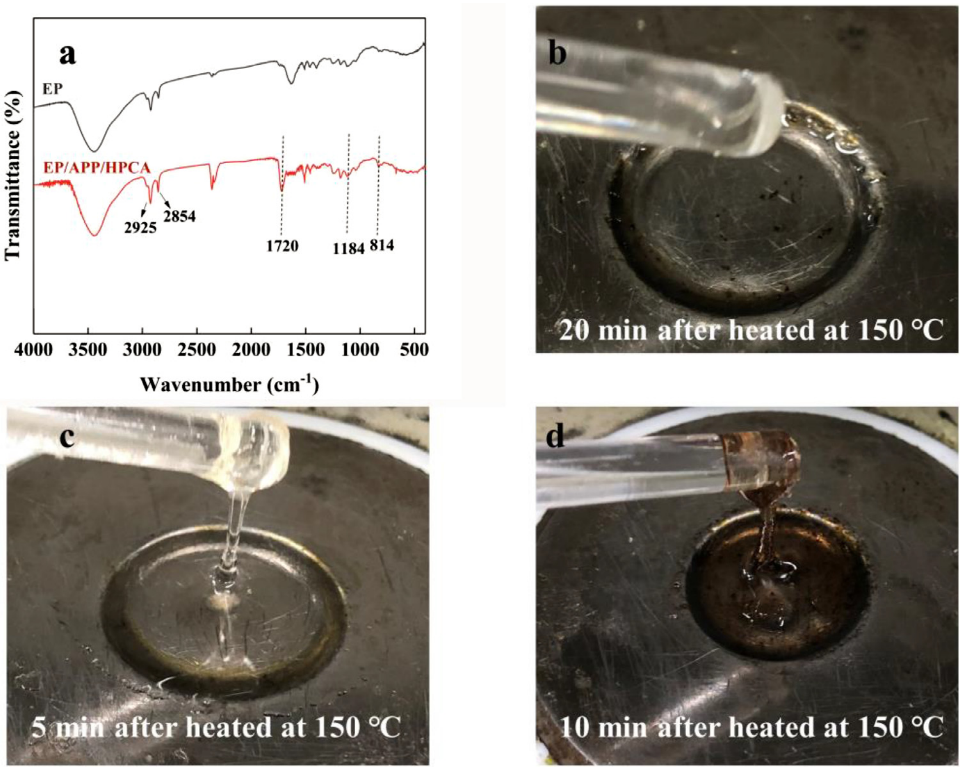


Fig. 11. FTIR spectra of cured EP and EP/APP/HPCA (a); gel state of epoxy resin under different curing agents (b: pure EP; c: DMM/EP; d: HPCA/EP).

Table 4
Mechanical property of EP, EP/APP, EP/HPCA and EP/APP/HPCA.

Specimens	Elongation at break (%)	Impact strength (KJ/m^2)	Tensile strength (MPa)
EP	4.715±0.112	7.10±0.10	41.325±0.188
EP/APP	4.012±0.102	6.23±0.22	33.895±0.263
EP/HPCA	6.015±0.085	9.94±0.12	38.462±0.326
EP/APP/HPCA	5.323±0.109	8.56±0.09	37.123±0.156

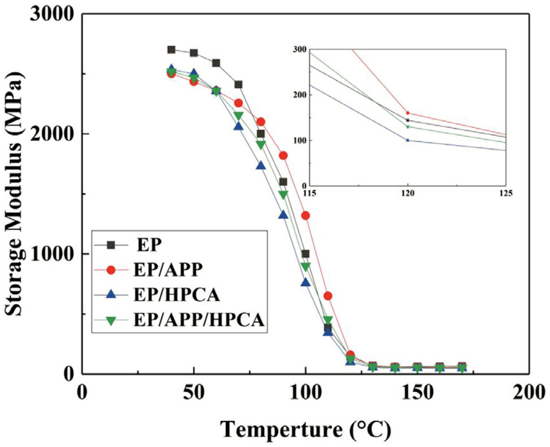


Fig. 12. Dynamic properties of EP thermosets.

As is well known, high brittleness is an acknowledged shortcoming for EP materials. Possessing flexible amide bonds and large free volume resulted from the hyperbranched macromolecular structure, the grafted HPCA endowed EP with greatly improved toughness. The static mechanical properties test of the flame retardant EP confirmed the toughening effects in Table 4. The elongation at break, impact strength and tensile strength of cured epoxy were 4.715%, 7.10kJ/m^2 and 41.325MPa, respectively. The introduction of the additive APP, made all the mechanical properties of EP decreased significantly. By contrast, the introduction of HPCA greatly increased the elongation at break (137.2% and 118.9% for EP/HPCA and EP/APP/HPCA) and impact strength (139.6% and 120.2% for EP/HPCA and EP/APP/HPCA), reflecting remarkable improvement of the tenacity of the materials [39]. Meanwhile, the tensile strength and storage modulus reflecting the rigidity, dropped slightly (Fig. 12).

4. Conclusion

In summary, a hyperbranched polyamide charring agent suitable for EP, HPCA was successfully prepared. HPCA, combined with APP, exhibited high flame retardant efficiency in EP. Their synergism resulted from the interaction of the two components to rapidly construct dense and thermal stable carbon skeleton. Additionally, HPCA also participated in the curing process of epoxy resin as a co-curing agent, thus grafting into the three dimensional net of the EP thermoset. Taking advantages of the flexible amide bonds and large free volume resulted from the hyperbranched macromolecular structure, HPCA toughen the EP effectively. Accordingly, such a polyamide charring agent is expected for preparing flame retardant EP materials with high performance.

Declaration of Competing Interest

This article does not involve any dispute of interest.

CRediT authorship contribution statement

Wei Wang: Conceptualization, Formal analysis, Project administration, Software, Visualization, Writing - original draft. **Yuan Liu:** Conceptualization, Data curation, Funding acquisition, Resources, Supervision, Validation, Writing - review & editing. **Hui Wen:** Investigation. **Qi Wang:** Methodology.

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