



The non-halogen flame retardant epoxy resin based on a novel compound with phosphaphenanthrene and cyclotriphosphazene double functional groups

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ABSTRACT

A novel flame retardant additive hexa-(phosphaphenanthrene -hydroxyl-methyl-phenoxy)-cyclotriphosphazene (HAP–DOPO) with phosphazene and phosphaphenanthrene double functional groups has been synthesized from hexa-chloro-cyclotriphosphazene, 4-hydroxy-benzaldehyde and 9,10-dihydro-9-oxa-10- phosphaphenanthrene 10-oxide(DOPO). The structure of HAP–DOPO was characterized by Fourier transformed infrared (FT-IR) spectroscopy and ^1H nuclear magnetic resonance (^1H NMR) and ^{31}P nuclear magnetic resonance (^{31}P NMR). The additive HAP–DOPO was blended into diglycidyl ether of bisphenol-A (DGEBA) to prepare flame retardant epoxy resins. The flame retardant properties and thermal properties of the epoxy resins cured by 4, 4'-Diamino-diphenyl sulfone (DDS) were investigated from the differential scanning calorimeter (DSC), the thermogravimetric analysis (TGA), UL94 test, the limiting oxygen index (LOI) test and Cone calorimeter. Compared to traditional DOPO–DGEBA and ODOPB–DGEBA thermosets, the HAP–DOPO/DGEBA thermosets have higher T_g s at the same UL94 V-0 flammability rating for their higher crosslinking density and have higher char yield and lower pk-HRR at same 1.2 wt.% phosphorus content which confirm that HAP–DOPO has higher flame retardant efficiency on thermosets. The scanning electron microscopy (SEM) results shows that HAP–DOPO in DGEBA/DDS system obviously accelerate formation of the sealing, stronger and phosphorus-rich char layer to improve flame retardant properties of matrix during combustion.

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1. Introduction

The non-halogen flame retardant epoxy resins containing 9,10-dihydro-9-oxa-10- phosphaphenanthrene-10-oxide (DOPO) have been widely researched and a few have been applied in semiconductor encapsulants, fiber reinforced composites and printed circuit boards for its excellent flame retardancy [1–5]. Most of them is based on diglycidyl ether of bisphenol-A (DGEBA) owing to its remarkable adhering, low shrinkage on cure, good electrical and mechanical properties, and especially ease of handling and processability [6–11]. Usually, the epoxy resins containing DOPO group are prepared by the methods that P–H bond of DOPO react with epoxide group of epoxy resins by addition reaction or that DOPO derivatives react with epoxide group [11–14].

But the functionality of the flame retardant epoxy resins prepared by above methods is obviously decreased for the addition reaction of DOPO and its derivatives with epoxide groups. Consequently, it directly leads to a less crosslinking density in the cured

epoxy resins and the low T_g s of thermosets [15]. Further, the flame retardant epoxy resins based on DOPO reach UL94 V-0 flammability rating still need a higher adding ratio of DOPO or its derivatives for their phosphorus content below 14.4 wt.% [16,17]. For more convenient application, more excellent flame retardant performance and more outstanding physical–mechanical properties, it is necessary to explore an unreactive way of utilizing DOPO which can preserve the functionality of resins for more excellent physical–mechanical properties. The cyclotriphosphazene compounds, which have been attention for its excellent thermal and charring properties, can provide improved flame retardant properties to polymers and their composites [18–22]. We tend to integrate phosphaphenanthrene and cyclotriphosphazene groups into one molecule as flame retardant additive instead of reactive DOPO and its derivatives in epoxy resin thermosets.

In this work, we synthesized a novel-structure additive hexa-(phosphaphenanthrene- hydroxyl-methyl-phenoxy)-cyclotriphosphazene (HAP–DOPO) derived from DOPO, 4-hydroxy-benzaldehyde and hexa-chloro-cyclotriphosphazene. The additive is also mixed into DGEBA to prepare non-halogen flame retardant epoxy resins and then the flame retardant properties and mechanism of cured epoxy resins are characterized and disclosed. We also explore

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the difference of flame retardant behaviors between HAP–DOPO resins and DOPO–DGEBA resins and ODOPB–DGEBA resins.

2. Experimental

2.1. Materials

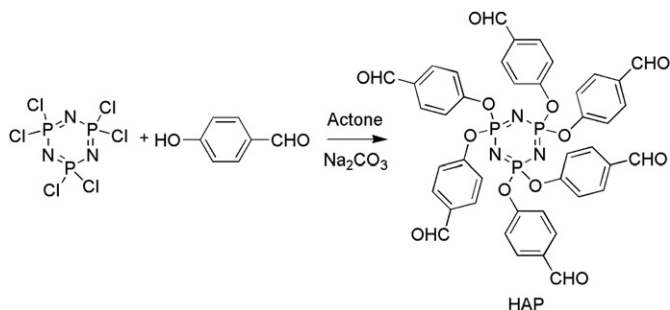
Hexa-chloro-cyclotriphosphazene (HCP) was purchased from Zibo Lanyin Chemical Co. Ltd., China. 4-Hydroxy-benzaldehyde was purchased from Kunshan Keyida Chemical Co. Ltd., China. The epoxy resin (DGEBA) with an epoxide equivalent weight (EEW) of 184–194 g/eq was kindly supplied by Wuxi Bluestar Co. Ltd., China. 4,4'-Diamino-diphenyl sulfone (DDS) was supplied by Shanghai SSS Reagent Co. Ltd., China. DOPO and 2-(6-oxide-6H-dibenz<c,e>-1,2>oxaphos-phorin-6-yl)-dihydroxyphenylene (ODOPB) were provided by Shanghai Eutec Chemical Co., China. Acetone, potassium carbonate, chlorobenzene and ethanol were purchased from Beijing Chemical reagent Co. Ltd., China. All the solvents were used after dried.

2.2. Synthesis of hexa-(4-aldehyde-phenoxy)-cyclotriphosphazene(HAP) [23]

Anhydrous potassium carbonate (42 g, 304.35 mmol) and 4-hydroxy-benzaldehyde (37.5 g, 307.38 mmol) were stirred and dissolved in 150 mL acetone at room temperature. Then HCP (15 g, 43.1 mmol) was added into the mixture. The mixture was stirred at 56 °C for 14 h. Then the precipitate was filtrated and washed twice by water to remove potassium chloride. The light-yellow powder of hexa-(4- aldehyde-phenoxy)-cyclotriphosphazene was collected after recrystallization with ethyl acetate. The reaction formula is shown in Scheme 1. Yield: 31.7 g (85.5%). m.p.: 158–159 °C; IR(KBr,cm⁻¹): 1706 (C=O), 1159, 1181, 1208 (P=N), 962 and 745 (P–O–Ph); ¹H NMR (CDCl₃, ppm): δ = 9.94 (s, 6H), δ = 7.75 (d, 12H), δ = 7.12 (d, 12H).

2.3. Synthesis of hexa-(phosphaphenanthrene-hydroxyl-methyl-phenoxy)-cyclotriphosphazene (HAP–DOPO)

HAP (3 g, 3.48 mmol) and DOPO (7.00 g, 32.4 mmol) were melted and stirred for 4 h at 140 °C. Then the mixture was washed with toluene for three times. The products were obtained and dried at 110 °C for 2 h. The reaction formula is shown in Scheme 2. Yield: 6.1 g (82%). m.p.185–186 °C. IR (KBr, cm⁻¹): 3383 (–OH), 1238 (P=O), 962 and 745 (P–O–Ph), 1203, 1184, 1162 (P=N); ¹H NMR (DMSO-d₆, ppm): δ = 7.56–8.17 (m, 8H), δ = 6.49–7.33 (m, 16H), δ = 6.30 and 6.34 (d, 2H), δ = 5.19 and 5.38 (d, 2H); ³¹P NMR (DMSO-d₆, ppm): δ = 30.99, 9.32.



Scheme 1. Synthesis of HAP.

2.4. Preparation of flame retardant epoxy resin based on HAP–DOPO

Epoxy resin (DGEBA), HAP–DOPO and DDS were heated to 185 °C and then blended together. The mixture was kept in a vacuum oven at 185 °C for 3 min for degassing. Then the mixture was poured into the molds. The mixture was cured at 150 °C for 3 h and at 180 °C for 5 h. The feeding ratio of DGEBA, DDS and HAP–DOPO in samples F1–F5 is listed in Table 1.

2.5. Preparation of the comparing samples of DOPO–DGEBA/DDS and ODOPB–DGEBA/DDS thermosets

The flame retardant epoxy resins include DOPO–DGEBA and ODOPB–DGEBA are two kinds of typical DOPO series resins which have been widely researched till now. For comparing the flame retardant behaviors of HAP–DOPO, DOPO and ODOPB on thermosets, we prepared DOPO–DGEBA/DDS (sample F6) and ODOPB–DGEBA/DDS (sample F7) thermosets containing 1.2 wt.% phosphorus content according to the literature [1,24].

2.6. Characterizations

FT-IR spectra were detected on a Nicolet iN10MX type spectrometer with KBr pellets. ¹H NMR and ³¹P NMR spectra were obtained on Bruker AV300MB. The chemical shifts of ³¹P NMR spectra are downfield relative to 85% D₃PO₄. The T_gs of the cured samples were performed with TA instrument Q100 differential scanning calorimeter (DSC) under N₂ atmosphere at a heating rate of 10 °C/min. Thermo gravimetric analysis (TGA) was recorded on TA instrument Q5000 IR thermal gravimetric analyzer with a heating rate of 20 °C/min from 50 to 700 °C under N₂ atmosphere. Scanning electron microscopy (SEM) was detected on TESCAN VEGAII for the surface morphology of residues of epoxy resin. Elementary content of the char residues were performed with energy-dispersive X-ray spectroscopy (EDX) by EDAX Genesis XM2.

The limiting oxygen index (LOI) values were performed on an FTT (Fire Testing Technology, UK) Dynisco LOI instrument according to ASTM D2863-97, with sheet dimensions 130 × 6.5 × 3.2 mm³.

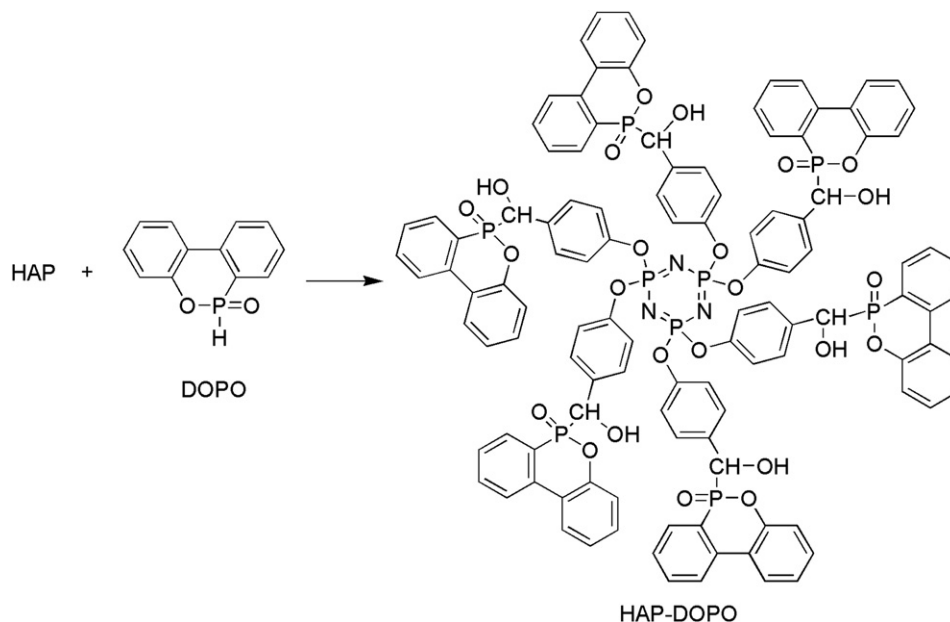
The vertical burning test (UL94) was performed on FTT0082 instrument according to ASTM D 3801 testing procedure with sheet dimensions of 125 × 12.7 × 3.2 mm³.

The fire behaviour was characterized on an FTT cone calorimeter according to ISO5660 under an external heat flux of 50 kW/m². The dimension of samples was 100 × 100 × 3 mm³. Heat release rate (HRR), time to ignition (TTI) and other parameters were recorded simultaneously.

3. Results and discussion

3.1. Synthesis of HAP–DOPO

As an intermediate of HAP–DOPO, HAP firstly was prepared by elimination reaction between HAP and 4-Hydroxy-benzaldehyde. Then the flame retardant additive HAP–DOPO was synthesized through the addition reaction of HAP and DOPO. The chemical structure of HAP–DOPO is confirmed by FT-IR in S1 in Supplementary data, ¹H NMR in Fig. 1 and ³¹P NMR in Fig. 2. The absorption peak at 3383 cm⁻¹ of HAP–DOPO indicates the formation of –OH, and correspondingly the disappeared >C=O absorption peak at 1700 cm⁻¹ of HAP confirms that the reaction between the >C=O group in HAP and P–H in DOPO has happened. The structure of HAP–DOPO can be further confirmed by the other absorption peaks at 935 cm⁻¹ and 755 cm⁻¹ (P–O–Ph) for



Scheme 2. Synthesis of HAP–DOPO.

phosphaphenanthrene group, and 1203 cm^{-1} , 1184 cm^{-1} , 1162 cm^{-1} ($\text{P}=\text{N}$) for cyclotriphosphazene groups.

As shown in Fig. 1, the ^1H NMR spectrum of HAP–DOPO shows the chemical shifts of chiral tert-methyl protons at 5.19 and 5.38 ppm, hydroxyl groups at 6.30 and 6.34 ppm and aromatic hydrogen include benzene ring and phosphaphenanthrene group at 6.49–8.17 ppm. Although the hydrogen in benzene ring and phosphaphenanthrene group is hard to be discriminated, it can be calculated that the ratio of three kinds of hydrogen ($\text{C}-\text{H}:-\text{OH}:\text{Ar}-\text{H}$) is 1:1:12 in ^1H NMR spectrum of HAP–DOPO. The result is consistent with the ratio in HAP–DOPO formula, which confirms that HAP–DOPO has been synthesized.

Fig. 2 shows the ^{31}P NMR spectrum of HAP–DOPO. Two single peaks at chemical shift 30.99 and 9.32 ppm correspond respectively to the phosphorus atoms in cyclic phosphaphenanthrene and cyclotriphosphazene structure.

3.2. Thermal analysis of the cured epoxy resins

T_g is an important parameter for application of epoxy resin thermosets. The T_g s of the control and the phosphorus-containing epoxy resins cured with DDS have been measured by DSC. The results are listed in Fig. 3. The T_g s of cured HAP–DOPO flame retardant epoxy resins gradually decrease from $193\text{ }^\circ\text{C}$ to $153\text{ }^\circ\text{C}$ with the phosphorus content increasing from 1% to 2%. As an

additive, obviously, HAP–DOPO will decrease T_g s of epoxy resins for that the bulky and non-coplanar phosphaphenanthrene group can increase the intermolecular distance [25] and that cyclotriphosphazene group is not rigid conjugate structure but rather a flexible structure [22,23] which is convenient to molecular motion and formation of T_g . Therefore, HAP–DOPO in epoxy resin thermosets can provide motion space to groups of epoxy resin and make T_g s of the thermosets decrease when the additive is added. But if HAP–DOPO is added with a less ratio, the T_g s of thermosets just slightly reduce. Typically, the T_g of F3 is just decrease $6\text{ }^\circ\text{C}$ than that of F1, whereas its flame retardant classification has reached the UL94 V-0 flammability rating.

The comparing samples F6 and F7 disclose that the T_g s of DOPO–DGEBA/DDS and ODOPB–DGEBA/DDS are $172\text{ }^\circ\text{C}$ and $182\text{ }^\circ\text{C}$. As an additive, HAP–DOPO flame retardant epoxy resin thermosets obtain higher T_g than that of DOPO or its derivatives flame retardant epoxy resins. It is attributed to the less adding ratio and preserving more epoxide groups for higher crosslinking density. Usually, the higher crosslinking density of thermosets after cured result in higher T_g . The T_g above $190\text{ }^\circ\text{C}$ and excellent flame retardancy imply that it has prospect to be applied more widely as flame retardant materials [15,26].

The TGA curves of F1–F5 in Fig. 4 show the behaviors of the thermal degradation of epoxy thermosets containing HAP–DOPO,

Table 1
The formula of the phosphorous-containing epoxy resins cured with DDS^a.

Samples	E-51/g	DDS/g	HAP–DOPO/g	P (wt.%)
F1	100.0	31.6	0	0
F2	100.0	31.6	11.0	1.0%
F3	100.0	31.6	13.5	1.2%
F4	100.0	31.6	17.3	1.5%
F5	100.0	31.6	24.1	2.0%
F6 ^b	100.0	28.2	–	1.2%
F7 ^c	100.0	28.0	–	1.2%

^a Epoxy equivalent/amino equivalent of F1–F7 = 1:1.

^b The amount of DOPO 11.7 g.

^c The amount of ODOPB 18.9 g.

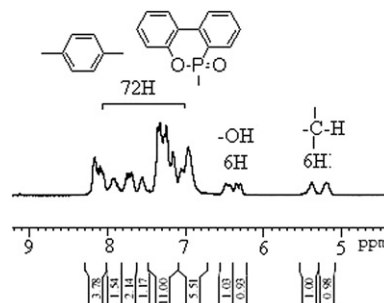


Fig. 1. ^1H NMR spectra HAP–DOPO.

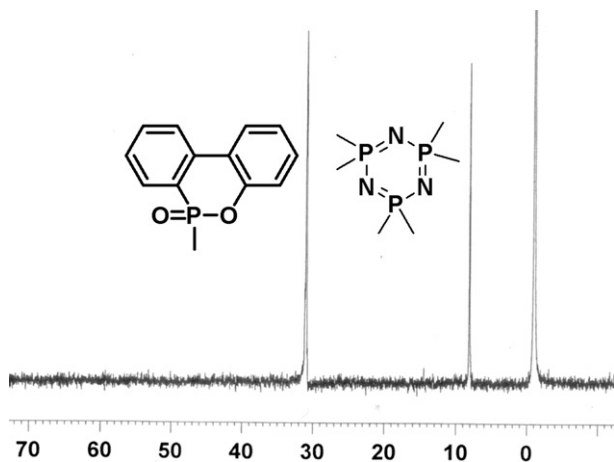


Fig. 2. ^{31}P NMR spectra HAP–DOPO.

and the obtained results are summarized in Table 2. It exhibits a major mass loss via a single largely decrease of approximately 65 wt.% from 350 °C to 430 °C, and then the rate of mass loss decreases very slowly. Compared with the onset degradation temperature (T_d) 372 °C of the control sample F1, the T_d s of F2–F6 drop to 326 °C–284 °C for the onset degradation of the HAP–DOPO ($T_{\text{onset}} = 200$ °C, mass loss 19 wt.% at 300 °C) at relatively low temperature. But it wouldn't influence on its application in cured epoxy resins for that the T_d of thermosets still can meet the demand of processing and application temperature. However, it is noticed that the residual char yields of F2–F5 have an over 100% increase than that of the control sample F1. Further, the char yield of F3 with 1.2% phosphorus content exceeds 15% and 40% than that of F6 and F7 whose phosphorus content also are 1.2%. It means that the additive HAP–DOPO in thermosets can enhance resins' charring properties during combustion. The result is deduced that the cyclotriphosphazene and phosphaphenanthrene structure in additive have a synergistic effect in condensed phase to promote charring of thermosets. Moreover, the yield of residual char of F2–F5 increases slightly from 25.5% to 27.0% with the increase of phosphorus content from 1% to 2%. It means that more additive HAP–DOPO added into DGEBA probably may not bring more remarkable flame retardant behavior of HAP–DOPO epoxy resins. The flame retardant behaviors will be further discussed by other characterization later.

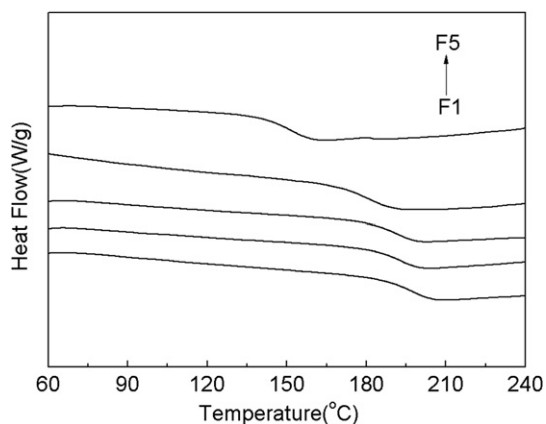


Fig. 3. DSC curves of the F1–F5 epoxy thermosets containing HAP–DOPO.

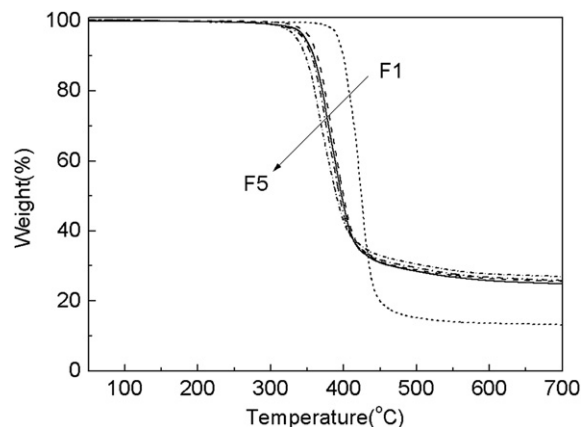


Fig. 4. The TGA curves of the F1–F5 epoxy thermosets.

3.3. Flame retardant properties

3.3.1. LOI measurement and UL94 test

The flame retardant properties of all samples have been examined by LOI and UL94 vertical measurement, and the data are summarized in Table 3. It can be seen that the LOI values of HAP–DOPO/DGEBA/DDS system significantly increase from 22.5% to 35.2% when the phosphorus content increase from 1% to 1.5% and then the LOI value turn to decrease when the phosphorus content continually increase with more HAP–DOPO added. The results can be related with P/N/C–Ar ratio in thermosets and an optimal P/N/C–Ar ratio will bring better flame retardant performance of thermosets instead of higher phosphorus content. Obviously, the higher phosphorus content from HAP–DOPO can't bring more advantages on flame retardancy to epoxy resins thermosets according to the LOI results.

The UL94 test exhibits that the thermosets with just 1.2 wt.% phosphorus content can reach UL94 V-0 flammability rating. It has the same flammability rating as that of DOPO–DGEBA/DDS epoxy resins with 1.6 wt.% phosphorus content [27], which means that the additive has higher flame retardant efficiency on DGEBA/DDS system than DOPO applied separately. We can deduce that the excellent charring interaction of cyclotriphosphazene group enhance the flame retardant efficiency of the additive and that the cyclotriphosphazene group integrate phosphaphenanthrene group jointly to exert the synergistic flame retardant function on thermosets. Moreover, the HAP–DOPO/DGEBA/DDS system hasn't dripping. The reason is that the HAP–DOPO additive with outstanding charring property can promote materials to forming stronger char layer. The char layer reduce the exothermicity caused by the pyrolysis reactions and the thermal conductivity of the surface radiated from flame, and thus, keep the samples no dripping and improve the flame retardancy of the epoxy resins thermosets [23].

Table 2
The thermal properties of the F1–F7 epoxy thermosets.

Samples	T_g	$T_{d,1\%}$ (°C)	$T_{d,10\%}$ (°C)	Char yields at 700 °C (wt.%)
F1	197	372	399	13.2
F2	193	326	364	25.5
F3	191	300	359	24.9
F4	181	298	356	25.8
F5	153	301	348	27.0
F6	172	338	363	21.6
F7	182	379	396	17.8

Table 3
The LOI value and results of UL94 test.

Samples	P (wt.%)	N (wt.%)	LOI	Dripping	UL94 rating
F1	0	2.70	22.5	Yes	unrated
F2	1.0	2.65	30.1	No	V-1
F3	1.2	2.63	31.0	No	V-0
F4	1.5	2.62	35.2	No	V-0
F5	2.0	2.59	30.8	No	V-0
F6	1.2	2.40	31.1	No	V-1
F7	1.2	2.15	34.0	No	V-1

3.3.2. Cone calorimetry

Cone calorimetry is used to research the fire behavior and burning law and evaluate the flammability and potential fire safety of polymer materials under well-ventilated conditions [28]. The samples F1–F7 have been detected by Cone calorimetry and the heat release rate (HRR), total heat release rate (THRR) and time to ignition (TTI) are listed in Table 4, respectively. The results reveal that both the HRR and pk-HRR of F2–F5 are reduced significantly owing to feeding of HAP–DOPO in Fig. 5. The pk-HRR of F3–F5 is decreased by 33%–57% compared to that of F1. Further, as phosphorus content increase, the total heat release also gradually decreased. It is confirmed that HAP–DOPO can promote thermosets to char, which prevents the transfer of heat during the ignition process from the samples, thus degrading the intensity of combustion pyrolysis reactions and decreasing release of the quantity of heat.

The results of F6 and F7 show that the pk-HRR of DOPO–DGEBA and ODOPB–DGEBA are also decreased by 19% and 33% in Fig. 6. The HAP–DOPO/DGEBA sample F3 has same phosphorus content as that of DOPO–DGEBA and ODOPB–DGEBA. But remarkably, the pk-HRR of F3 is decreased by 57% compared to that of F1. It is obvious that HAP–DOPO can bring down the heat release intensity with higher efficiency during combustion than that no matter DOPO–DGEBA or ODOPB–DGEBA resins do. The pk-HRR result is consistent with the UL94 test and char yields and they all confirm that HAP–DOPO containing two functional groups have higher flame retardant efficiency.

The times to ignition (TTI) of F2–F7 have a decrease to some extent because that the flame retardant content not only decompose ahead of time themselves but also promote resin matrix to degrade at lower temperature. At the point, all the HAP–DOPO/DGEBA, DOPO–DGEBA and ODOPB–DGEBA resins exhibit similar behaviors under cone test. Of course, in certain conditions the degradation behaviors ahead of time contribute to charring earlier during combustion and bring the thermosets better flame retardancy.

3.3.3. Morphology of the residue

The morphologies of residues after cone calorimetry and ignition by alcohol burner were investigated by SEM in Fig. 7. It displays the morphology of residues from F1 and F3. The other

Table 4
Combustion parameters obtained from cone calorimeter F1–F7.

Samples	TTI (s)	Peak of HRR (Kw/m ²)	Av-HRR (Kw/m ²)
F1	66	893	282
F2	55	593	247
F3	51	383	247
F4	63	483	233
F5	43	303	173
F6	42	721	260
F7	54	599	251

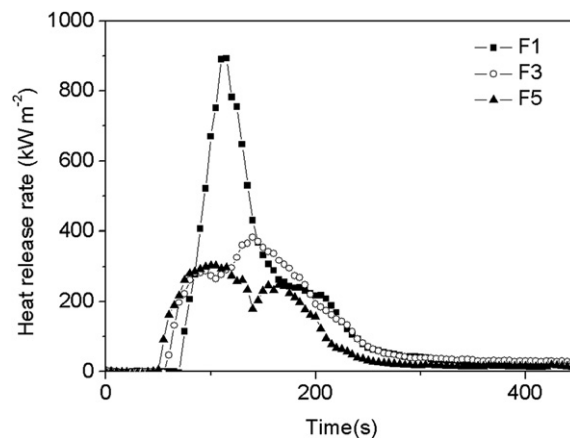


Fig. 5. Heat release rates and of F1, F3, F5 tested by cone calorimeter with 50 Kw/m².

residues of F2–F5 have similar morphology as that of F3. It is noteworthy that the combustion in cone calorimetry shrinks the sample F1 and makes it become a char flake, which has continuous surface under SEM in Fig. 7a. Differently, F3 after cone calorimetry forms slightly expanding, lacunaris and rigid-skeletal-structure char residues under SEM in Fig. 7b. The exhaustive combustion in cone calorimetry make F3 just leave the residual char skeleton, whereas F3 after ignition by alcohol burner shows a slightly expanding char layer with sealing surface under SEM in Fig. 7c and d. The results show that HAP–DOPO makes thermosets form slightly expanding and sealing char layer with stronger char skeleton. The char skeleton can sustain the expanding and thicker char layer covering on the surface of thermosets. The char layer can inhibit the transmission of heat during combustion effectively. Thus the thermosets containing HAP–DOPO obtain excellent flame retardancy.

Moreover, the elementary contents of the residue char are detected by energy-dispersive X-ray spectroscopy (EDX), and the data are listed in Table 5. The phosphorus content of F3 residue at upper surface reach to 10.00 wt.% of residues mass which shows agreement with previous opinion that phosphorus-containing epoxy resins can form phosphorus-rich residue char after thermal degradation and therefore the flame retardancy of materials also are improved accordingly [15,23,29]. Obviously, the high phosphorus content in residues can't just source from the cyclo-triphosphazene group. It can be confirmed that nearly all

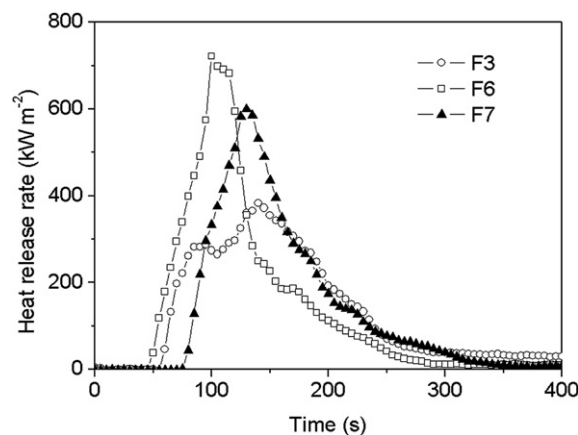


Fig. 6. Heat release rates and of F3, F6, F7 tested by cone calorimeter with 50 Kw/m².

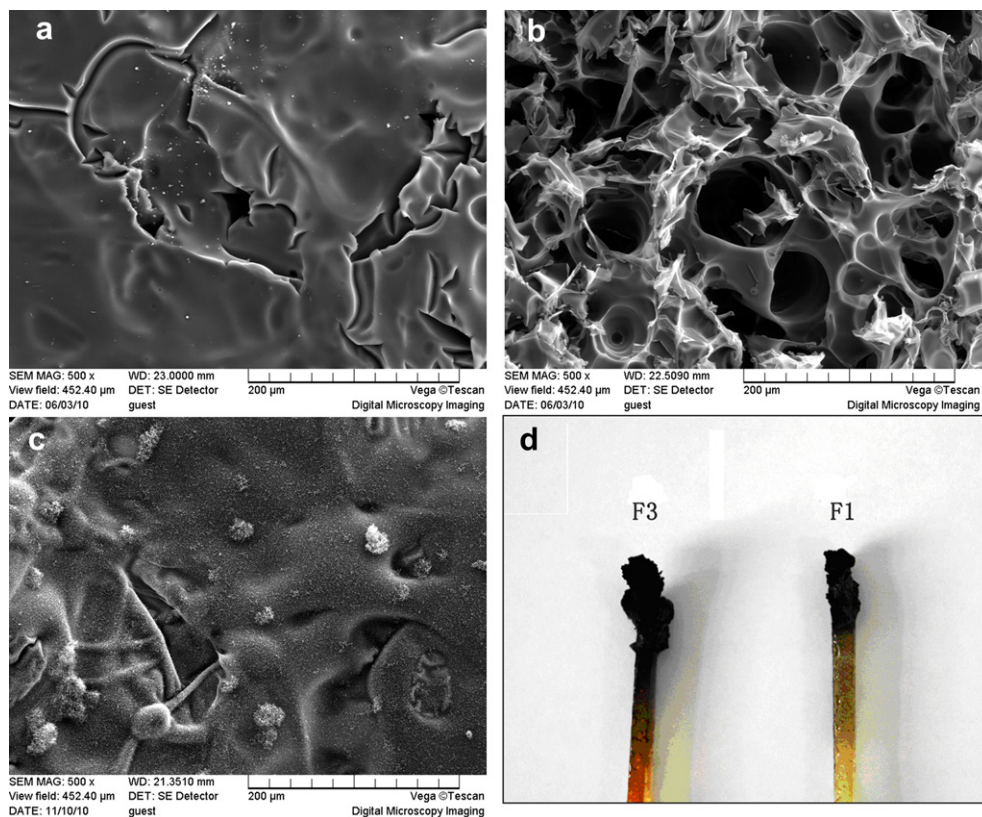


Fig. 7. SEM morphologies of the residues of F1 (a), F3 (b) from Cone and F3 (c) from ignition by alcohol burner and (d) digital photo by camera of residues of F3 from ignition by alcohol burner.

Table 5
EDX data of surface of F1 and F3 residues.

Sample	Element analysis (Wt.%)			
	C	O	N	P
F1	84.17	7.26	8.34	0.023
F3	72.86	12.20	4.95	10.00

phosphorus content from HAP–DOPO has been enriched in the surface of residues during thermal degrading. Therefore, we are sure that phosphaphenanthrene and cyclotriphosphazene groups jointly exert flame retardant interaction in condense phase during combustion of thermosets.

4. Conclusion

A novel flame retardant additive HAP–DOPO with phosphazene and phosphaphenanthrene double functional groups has been successfully synthesized from hexa-chloro-cyclotriphosphazene, 4-hydroxybenzaldehyde and DOPO. The HAP–DOPO/DGEBA/DDS thermosets with just 1.2 wt.% phosphorus content in thermosets has the LOI value 31% and reach UL94 V-0 flammability rating. Comparing with traditional DOPO–DGEBA and ODOPB–DGEBA epoxy resin, HAP–DOPO/DGEBA thermosets has higher T_g at the same UL94 V-0 flammability rating and has higher char yields and lower pk-HRR at same 1.2 wt.% phosphorus content. Obviously, phosphaphenanthrene/phosphazene synergistic flame retardant system brings higher flame retardant efficiency to thermosets. By forming slightly expanding, sealing, stronger and phosphorus-rich char layer, the thermosets containing HAP–DOPO reduce the heat transmission and the rate of heat release during combustion.

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Appendix. Supplementary data

Figures showing the FT-IR spectra of HAP–DOPO and HAP, total heat release of F1, F3, F5 tested by cone calorimeter with 50 kW/m². Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.polyimdeggradstab.2011.03.001.

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