The Flame Retardant Group-Synergistic-Effect of a Phosphaphenanthrene and Triazine Double-Group Compound in Epoxy Resin

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ABSTRACT: A flame retardant tri-(phosphaphenanthrene-(hydroxyl-methylene)-phenoxyl)-1, 3, 5-triazine (Trif-DOPO) and its control samples are incorporated into diglycidyl ether of bisphenol-A (DGEBA) and 4, 4′-diamino-diphenyl sulfone (DDS) to prepare flame retardant thermosets, respectively. According to the results of limited oxygen index (LOI), UL94 vertical burning test and cone calorimeter test, the Trif-DOPO/DGEBA/DDS thermoset with 1.2 wt % phosphorus possesses the LOI value of 36% and UL94 V-0 flammability rating, and Trif-DOPO can decrease the peak of heat release rate (pk-HRR) and reduce the total heat release (THR) of thermosets. All these prove better flame retardant performance of Trif-DOPO than that of 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide(DOPO). The residue photos of thermosets after cone calorimetry test disclose that Trif-DOPO can promote the formation of thick and tough melting char layer for combined action of the flame retardant groups of Trif-DOPO. The results from thermo gravimetric analysis (TGA) and pyrolysis-gas chromatography-mass spectrometry(Py-GC/MS) show that the groups in Trif-DOPO can be decomposed and produce PO_2 fragments, phosphaphenanthrene and phenoxy fragments, which can jointly quench the free radical chain reaction during combustion. Therefore, the excellent flame retardancy of Trif-DOPO is attributed to its flame retardant group-synergic-effect. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 39709.

INTRODUCTION

Epoxy resins are widely used as adhesive and electrical encapsulation material due to their remarkable adhesion to many substrates, excellent mechanical performance, chemical and electrical resistances, and low shrinkage on cure.[1,2] But most of the ordinary epoxy resins are easy to burn and hard to extinguish. When they are used in electronic or electrical equipment, some flame retardants are incorporated into epoxy resins to prevent fire.

Besides the traditional brominated epoxy resin,[3] the researchers have investigated several kinds of non-halogen flame retardant epoxy resins, such as 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) epoxy resin and phosphazine epoxy resin. A few researches have been done on DOPO epoxy resin from the late 1990s.[4,5] Most of them can effectively enhance the limited oxygen index (LOI) and decrease the heat release rate (HRR), and their flammability rating can reach UL94V-0 when the phosphorus content of the thermosets with DOPO is above 1.5%.[6–8] The phosphazene compounds, especially the cyclotriphosphazene compounds with different substituent groups,[9–11] have been recently reported to increase the LOI value of epoxy thermosets to above 30%, enable the epoxy resins to reach UL94V-0 or UL94V-1 flammability rating with different curing agents,[9] and especially contribute to the high yield of residual char of matrix.[9–11]

Even so, considerable attention has been paid to the development of more efficient flame retardant in epoxy resins. An effective way used is to compound the additives containing different flame retardant functional groups or design novel molecular structure with different flame retardant functional groups, which include phosphaphenanthrene,[12–14] phosphazene,[15] triazine,[16,17] phosphate,[18,19] organic silicon[20,21] etc. Some of the flame retardants containing different structures with higher flame retardancy have been reported for their flame retardant groups' synergistic effects.[22,23] But the effects are still necessary to be further explored their essences, which are not disclosed sufficiently currently.

Recently, the work carried out by Tang et al.[24] has disclosed that the molecule tri-(phosphaphenanthrene-(hydroxyl-methyl-ene)-phenoxyl)-1, 3, 5-triazine (Trif-DOPO) containing phosphaphenanthrene, hydroxyl-methylene and tri-phenoxyl-triazine groups shows excellent flame retardant effect in the thermoset epoxy resins. But the high-efficiency flame retardant mechanism of the molecule has not yet been clarified. In this work, the flame retardant thermosets containing Trif-DOPO, triphenoxy-1, 3, 5-triazine (TPT) or DOPO were prepared, respectively. After their flame retardant properties were characterized, the high-efficiency flame retardant mechanism of Trif-DOPO was studied particularly.

EXPERIMENTAL

Materials

Cyanuric chloride was purchased from Hebei Chengxin Chemical, China. p-Hydroxybenzaldehyde was purchased from Qingdao Hanbing Chem., China. 9, 10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) was provided by Shanghai Eutec Chemical, China. The epoxy resin diglycidyl ether of bisphenol-A (DGEBA) with an epoxide equivalent weight (EEW) of 184–194 g/equiv was supplied by Blue Star New Chemical material, China. 4, 4′-Diamino-diphenyl sulfone (DDS) was purchased from Sinopharm Chemical Reagent Co. Ltd., China. Acetone, 1,2-dichloroethane, and anhydrous sodium carbonate were purchased from Beijing Chemical reagent Co. Ltd., China.

Instrumentation

The Fourier transform infrared (FT-IR) spectra were obtained from a Nicolet iN10MX type spectrometer with KBr pellets. Hydrogen^{-1} nuclear magnetic resonance (^{1}H NMR) and Phosphorous^{-31} nuclear magnetic resonance (^{31}P NMR) were performed on Bruker AV300MB, and the chemical shifts of ^{31}P NMR spectra used 85% D_3PO_4 as external standards.

The melt point (T_m) of the products and the glass-transition temperature (T_g) of cured samples were detected with a TA instrument Q100 differential scanning calorimeter (DSC) in N_2 atmosphere with a heating rate of 10°C/min. Thermo gravimetric analysis (TGA) was performed on a TA instrument Q5000 IR thermal gravimetric analyzer under N_2 atmosphere. The samples were heated from 50°C to 700°C at a heating rate of 20°C/min. The typical results from TGA were reproducible within 1%, and the reported data are average value based on three measurements.

Pyrolysis-gas chromatography-mass spectrometry (Py-GC/MS) analysis was carried out with Shimadzu GC/MS-QP5050A. The injector temperature was 250°C, 1 min at 50°C, temperature increase to 280°C at a rate of 8°C/min. The temperature of GC/MS interface was 280°C, and the cracker temperature was 350°C.

The LOI values were obtained from FTT (Fire Testing Technology, UK) Dynisco LOI instrument according to ASTM D2863-97 (sample size of 100 × 6.5 × 3.2 mm^3). The UL94 vertical burning test was made on an FTT0082 instrument according to ASTM D 3801 (sample size of 125 × 12.7 × 3.2 mm^3). The cone calorimeter test was carried out with an FTT0007 cone calorimeter according to ISO5660 under an external heat flux of 50 kW/m^2 (sample size of 100 × 100 × 3 mm^3). The specimens were
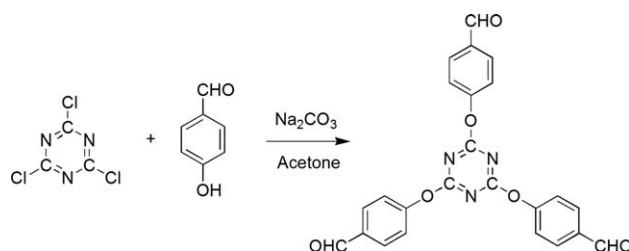
measured horizontally without any grids. Typical results from the cone calorimeter tests are reproducible within ±10%, and the reported parameters are the average from three measurements.

The surface morphology of residues of epoxy resin with a conductive gold layer was observed with a FP 2032/14 Quanta 250 FEG scanning electron microscopy (SEM) under high vacuum with voltage of 20 kV.

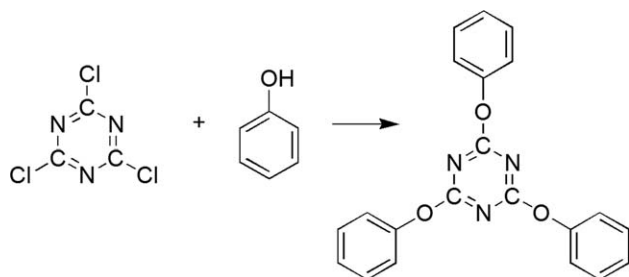### Synthesis of Tri-(4-formacylphenoxy)-1,3,5-triazine (Trif)

Anhydrous sodium carbonate (145.5 g, 1.37 mol) and p-hydroxybenzaldehyde (167.4 g, 1.37 mol) were dissolved in 400 mL acetone in a three-neck flask, and stirred at room temperature for 1 h. Then cyanuric chloride (83.0 g, 0.45 mol) was added and the mixture was stirred at 60°C for 6 h. After cooled to the room temperature, the precipitate was filtered and washed three times by water (80°C, 30 min) to remove impurities. The white powder of tri-(4-formacylphenoxy)-1, 3, 5-triazine was collected after dried at 105°C for 4 h. The reaction formula is shown in Scheme 1. Yield: 185.7 g (93.55%); m.p.: 183–184°C; FT-IR (KBr, cm^{-1}): 1701.45 (C═O), 1567.40 and 1592.20 (C$_3$N$_3$), 1361.53 (C─N), 1211.37 and 1161.73 (C─O─Ph); ^{1}H NMR (Acetone-d$_6$, ppm): δ = 9.98 (s, 3H), δ = 7.98 and 7.95 (d, 6H), δ = 7.49 and 7.46 (d, 6H).

Synthesis of Tri-(phosphaphenanthrene-hydroxyl-methyl-phenoxyl)-1,3,5-triazine (Trif-DOPO)

DOPO(21.6 g, 0.10 mol) was dissolved in 100 mL 1,2-dichloro-ethane in a three-neck flask at 85°C. Then Trif (11.0 g, 0.025 mol) was added and the mixture was stirred with a mechanical agitation for 4 h at 85°C. The precipitate was rapidly filtered above 80°C. Then it was washed twice with 1,2-dichloroethane (85°C, 30 min) and filtered to remove excess DOPO. The light-yellow powder of Trif-DOPO was collected after dried at 110°C. The reaction formula is shown in Scheme 2. Yield : 20.8 g

Scheme 1. The synthesis of Trif.
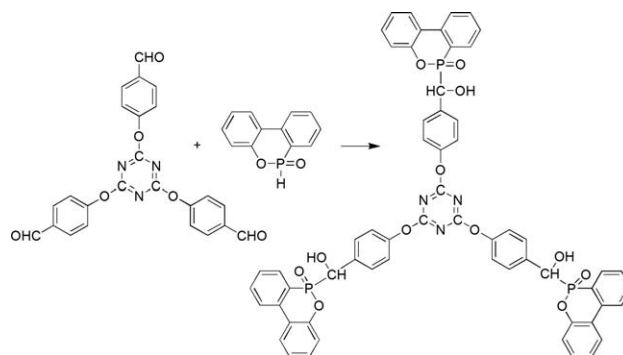
Scheme 2. The synthesis of Trif–DOPO.

Scheme 3. The synthesis of TPT.

(76.37%); m.p.: 182–183°C; FT-IR (KBr, cm^{-1}): 3381.77 (OH), 928.10, 752.12 (P—O—Ph), 1370.49 (C—N), 1568.64 (C$_3$N$_3$), ^{1}H NMR (DMSO-d_6, ppm): δ = 7.14–8.24 (m, 36H), δ = 6.37 and 6.31 (d, 3H), δ = 5.40 and 5.12 (d, 3H); ^{31}P NMR (DMSO-d$_6$, ppm): δ = 31.00.

Synthesis of Triphenoxy-1,3,5-triazine (TPT)

Anhydrous sodium carbonate (147.9 g, 1.40 mol) and phenol (131.3 g, 1.40 mol) were dissolved in 400 mL acetone with a mechanical stirring in a three-neck flask at 40°C for 1 h. Then cyanuric chloride (83.0 g, 0.45 mol) was added and the mixture was stirred at 60°C for 9 h till the end of the reaction. After cooled to the room temperature, the precipitate was filtered and washed three times by water (80°C, 30min) to remove impurities. At last, the white powders of TPT were obtained after dried at 105°C for 4 h. The reaction formula is shown in Scheme 3. Yield: 133.5 g (83%); m.p.: 118.36°C; FT-IR (KBr, cm^{-1}): 3058.69 (Ar—H), 1599.35 and 1568.36 (C$_3$N$_3$), 1493.43 (C$_6$H$_6$), 1376.60 and 1359.35 (C—N), 1206.99(Ph—O—C); ^{1}H NMR (Acetone-d_6, ppm): δ = 7.41 and 7.38 (meta position, 6H), δ = 7.28, 7.24 and 7.21 (ortho and para position, 9H).

Preparation of Flame Retardant Epoxy Resin and Control Samples

After epoxy resin (DGEBA) was heated to 185°C, Trif-DOPO and DDS were successively added and dissolved completely to form a well-blended mixture, which was kept in a vacuum oven at 185°C for 3.5 min for degassing. Rapidly, it was poured into preheated molds and cured at 150°C for 3 h and then at 180°C for 5 h. According to the different adding amount of Trif-DOPO, the samples were named Trif-DOPO/DGEBA/DDS-1.0 and Trif-DOPO/DGEBA/DDS-1.2, respectively.

The TPT/DGEBA/DDS sample with TPT instead of Trif-DOPO was also prepared with the same method. The DGEBA/DDS control sample was also made in the same way without flame retardant. The sample DOPO-DGEBA/DDS was prepared with

the method reported in the literature.[23] All the details of formula are listed in Table I.

RESULTS AND DISCUSSION

LOI Measurement and UL94 Test

The flame retardant epoxy resins Trif-DOPO/DGEBA/DDS-1.2, Trif-DOPO/DGEBA/DDS-1.0, DGEBA-DOPO/DDS, TPT/DGEBA/DDS and the neat DGEBA/DDS were prepared to explore the structure–properties relation of flame retardant. Their flame retardant data from LOI measurement and UL94 test are shown in Table II.

Compared with the data of other samples, the LOI value and flammability rating of Trif-DOPO/DGEBA/DDS-1.2 is obviously higher than those of the other samples. Trif-DOPO/DGEBA/DDS-1.2 and DOPO-DGEBA/DDS show remarkably difference in flame retardancy though they have the same phosphorus content 1.2%, the same phosphorus-containing structure and the same mole quantity of phosphaphenanthrene group. The LOI value of Trif-DOPO/DGEBA/DDS-1.2 is 36.0%, while that of DOPO-DGEBA/DDS is 31.7%, and the flammability rating of Trif-DOPO/DGEBA/DDS-1.2 is UL94V-0, while that of DOPO-DGEBA/DDS is UL94V-1. It is important to disclose why and how the flame retardant Trif-DOPO obtains the higher flame retardancy. In comparison with the chemical structures of DOPO, Trif-DOPO is composed of the phosphaphenanthrene group, hydroxyl-methylene, phenoxyl and triazine group, whereas the phosphaphenanthrene group in DOPO-DGEBA/DDS is directly connected with epoxy group of DGEBA. Although the DOPO-DGEBA/DDS sample show better flame retardant effect, the single phosphaphenanthrene group in matrix can't bring so excellent flame retardant effect as Trif-DOPO do. In addition, the excellent flame retardant effect can't be mainly contributed by the other single group of Trif-DOPO either, because TPT in TPT/DGEBA/DDS sample, which is the core structure of Trif-DOPO, has worse flame retardant performance, such as the LOI value of 24.5% and no flammability rating of thermoset. Therefore, it can be concluded that the phosphaphenanthrene group, hydroxyl-methylene, phenoxyl and triazine group in Trif-DOPO can work jointly to inhibit combustion and lead to better flame retardant effect. Further, the higher LOI value of Trif-DOPO/DGEBA/DDS-1.2 implies that Trif-DOPO reduces the release of flammable gas or has stronger ability to inhibit the chain reaction during combustion compared to the other samples.

Trif-DOPO was reduced in content to prepare sample Trif-DOPO/DGEBA/DDS-1.0 so as to further testify its flame

Table I. The Formula of the Phosphorous-Containing Epoxy Resins Cured by DDS

Samples	E-51/g	DDS/g	Trif-DOPO/g	DOPO/g	TPT/g	P/wt %
DGEBA/DDS	100	31.6	0	–	–	0.0%
Trif-DOPO/DGEBA/DDS-1.0	100	31.6	17.5	–	–	1.0%
Trif-DOPO/DGEBA/DDS-1.2	100	31.6	21.5	–	–	1.2%
DGEBA-DOPO/DDS	100	31.6	–	12.0	–	1.2%
TPT/DGEBA/DDS	100	31.6	–	–	21.5	0

Table II. The LOI Measurement and UL-94 Test of the Cured Epoxy Resins

Samples	P/wt %	LOI/%	Dripping	UL94 rate
DGEBA/DDS	0	22.5	Yes	Unrated
Trif-DOPO/DGEBA/DDS-1.0	1.0	33.9	No	Unrated
Trif-DOPO/DGEBA/DDS-1.2	1.2	36.0	No	V-0
DOPO-DGEBA/DDS	1.2	31.7	No	V-1
TPT/DGEBA/DDS	0	24.5	Yes	Unrated

retardant efficiency. The flame retardant test result is that the LOI value of Trif-DOPO/DGEBA/DDS-1.0 is 33.9%, obviously higher than that of DOPO-DGEBA/DDS, but its flammability is not able to be rated. It can be attributed to the weakening flame retardant effect in condensed phase due to the reduction of flame retardant.

TGA Analysis

For explaining the flame retardant mechanism of Trif-DOPO, the thermal degradation behaviors of Trif-DOPO and all the thermoset epoxy resins were detected. Their TGA curves are shown in Figure 1.

As shown in Figure 1, Trif-DOPO has two degradation processes: the first one is from 180°C to 350°C and it has about 170°C temperature range and 27.8% weight loss; the second one is from 350°C to 600°C and it has about 250°C temperature range and 40.4% weight loss. The released substance from the first degradation process should be some inert gas or molecular fragments according to the chemical structure of Trif-DOPO. The early degradation at the lower temperature and the released inert substance all lead to the high LOI value of its flame retardant epoxy resin. The second degradation process will lead to the formation of phosphorus-rich residual char and it may promote the charring of matrix. In addition, the process can strongly contributes to the higher flammability rating of the flame retardant thermosets.

Furthermore, the sample Trif-DOPO/DGEBA/DDS has lower onset degradation temperature due to the onset temperature 180°C of Trif-DOPO compared to that of the samples DOPO-DGEBA/DDS and TPT/DGEBA/DDS. In fact, the two chemical
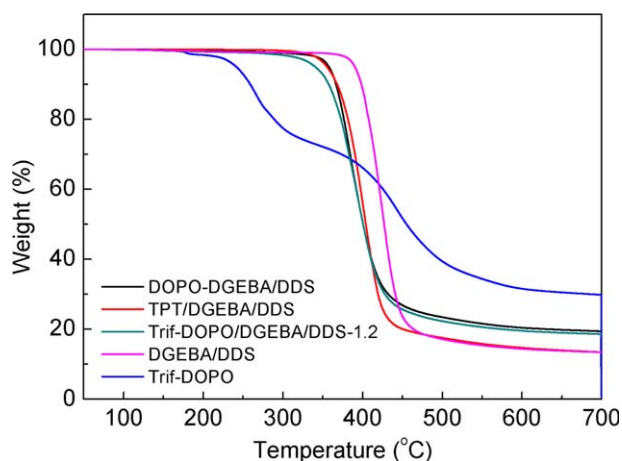
fragments phosphaphenanthrene and tri-phenoxy-triazine in Trif-DOPO won't lead to the early degradation while the hydroxyl-methylene pieces easily lead to condensation reaction and elimination reaction and can promote Trif-DOPO to decompose at a lower temperature. It can be concluded that the products from early degradation of Trif-DOPO are the inert gas or the organic molecular fragments with quenching effect on free radical chain reaction of combustion due to the remarkable LOI value of Trif-DOPO/DGEBA/DDS. Of course, the details of degradation need to be further investigated by the Py-GC-Mass.

From Figure 1, the TPT/DGEBA/DDS sample has the same residual char yield as DGEBA/DDS does. It discloses that TPT can't produce more residual char and can't promote charring of matrix either. But when TPT structure is part of Trif-DOPO, it will be incorporated into the residue and become part of it. Moreover, although TPT structure in Trif-DOPO will become part of the residue, the residual char yield of Trif-DOPO/DGEBA/DDS still has a slight decrease than that of DOPO-DGEBA/DDS. The reason is that some phosphaphenanthrene fragments from Trif-DOPO are released to gas phase at the early decomposition, which leads to reduction of polyphosphate, the main constituent of residue.

Analysis of Py-GC/MS

The Py-GC/MS test can disclose the details of decomposition of samples, and thus Trif-DOPO and the thermosets were investigated by the instrument to find the onset degradation process and the reason for high LOI value of thermosets containing Trif-DOPO. The Mass analysis of main GC peaks of Trif-DOPO's pyrolysis at 350°C is illustrated in Figure 2.
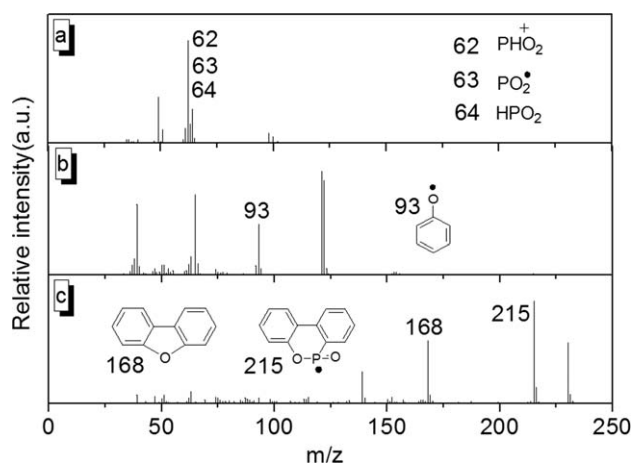

Figure 1. The TGA curves of the thermosets. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 2. The mass spectra of main GC peaks of Trif–DOPO's pyrolysis products at 350°C.

According to the previous discussion on TGA, it is clear that the first degradation process of Trif-DOPO ends in 350°C. Therefore, the pyrolysis temperature at 350°C can help us to distinguish the molecular pieces of onset degradation and further explore the flame retardant mechanism of Trif-DOPO.

As shown in Figure 2, the typical mass data of three main peaks in GC have been marked. In Figure 2(a), the outstanding m/z values are 62, 63, and 64, which represent typical PO_2^+ fragment and relevant fragments PO_2 and HPO_2. The phosphorus element only exists in phosphaphenanthrene group of Trif-DOPO, accordingly the fragments containing phosphorus are released from phosphaphenanthrene group. In Figure 2(b), the considerable m/z value is 93, which confirms the existence of phenoxyl free radical. Undoubtedly, they are from the pyrolysis of phenoxyl structure of Trif-DOPO; in Figure 2(c), the notable m/z values are 215 and 168, which correspond with phosphaphenanthrene free radical and dibenzofuran pieces, respectively. It is direct evidence that phosphaphenanthrene fragments will be released to the gas phase at a lower temperature when Trif-DOPO is heated.

Therefore, it can be confirmed that the onset degradation products from Trif-DOPO include some PO_2 fragments, phosphaphenanthrene and phenoxyl fragments in gas phase, and it also can be concluded that the polyether and phosphate left in condensed phase. The PO_2 fragments, phosphaphenanthrene and phenoxy fragments all can quench the free radical chain reaction during combustion; they will hinder the matrix from burning in gas phase due to their appearance around the matrix. All the effects will lead the higher LOI value of matrix which has been mentioned in the previous discussion. It can be deduced that the products in condensation phase from the early decomposition are produced by the reaction between Trif-DOPO and matrix due to the higher residual charring yield of thermoset. The phosphaphenanthrene group left will decompose to phosphoric acid or polyphosphoric acid compounds and react with the matrix to form thick phosphorus-rich residue, which can prevent the release of flammable gas and hinder the heat transmitting to the inner matrix.

Cone Calorimetry of the Thermosets

The curves of HRR tested by cone calorimetry are shown in Figure 3 and relevant data are listed in Table III including the peak of heat release rate (pk-HRR), the total heat release (THR), the time to ignition (TTI), the average CO yield (Av-COY), and the average CO_2 yield (Av-CO_2Y).

First, the TTI values of thermosets containing Trif-DOPO have an obvious decrease. It means the thermosets have flammable
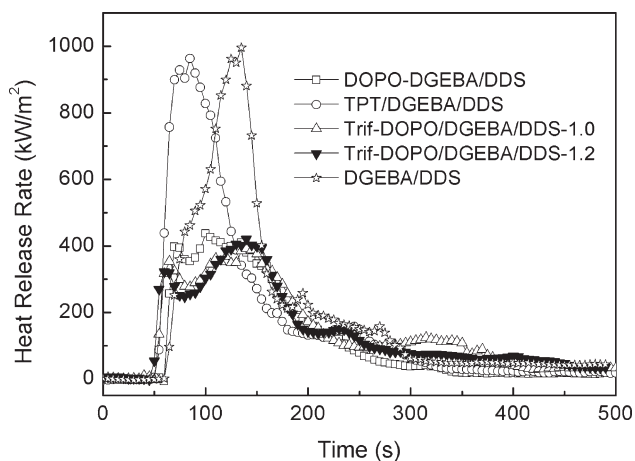

Figure 3. The HRR curves of the thermosets.

gas released early and then ignited by the electric spark. It is consistent with the result of TGA. Namely, the unstable hydroxyl-methylene group of Trif-DOPO leads to a lower degradation temperature and promotes the matrix to decompose to produce the flammable gas. For this reason, Trif-DOPO/DGEBA/DDS thermosets have smaller TTI values. Although the Trif-DOPO/DGEBA/DDS thermosets are ignited in a shorter time, their HRRs are rapidly reduced to a lower level, which lead to the lower peaks of HRR. In contrast, TTI of DOPO-DGEBA/DDS has a slight increase because DOPO-DGEBA own a more stable structure in which phosphaphenanthrene group is directly bonded with methylene and the bond won't be broken below 280°C.

After the early degradation of Trif-DOPO/DGEBA/DDS-1.2, the residue containing phosphaphenanthrene, triazine and aromatic structure prevent heat spreading to the inner of matrix from cone calorimetry. As a result, it causes the decrease of the subsequent HRR value of Trif-DOPO/DGEBA/DDS-1.2. Compared to it, the TPT/DGEBA/DDS control sample also shows the early and rapid decomposition but the reduction of the pk-HRR and THR haven't been observed. It means that the structure of triphenoxy-triazine, the core structure of Trif-DOPO, can't bring outstanding flame retardant effect alone without phosphaphenanthrene and hydroxyl-methylene groups. These further testify three main groups of Trif-DOPO jointly contribute to better flame retardant properties of Trif-DOPO/DGEBA/DDS thermosets.

The THR value of Trif-DOPO/DGEBA/DDS-1.2 is slightly higher than that of DOPO-DGEBA/DDS in Table III. According

Table III. The Data from Cone Calorimetry of the Thermosets

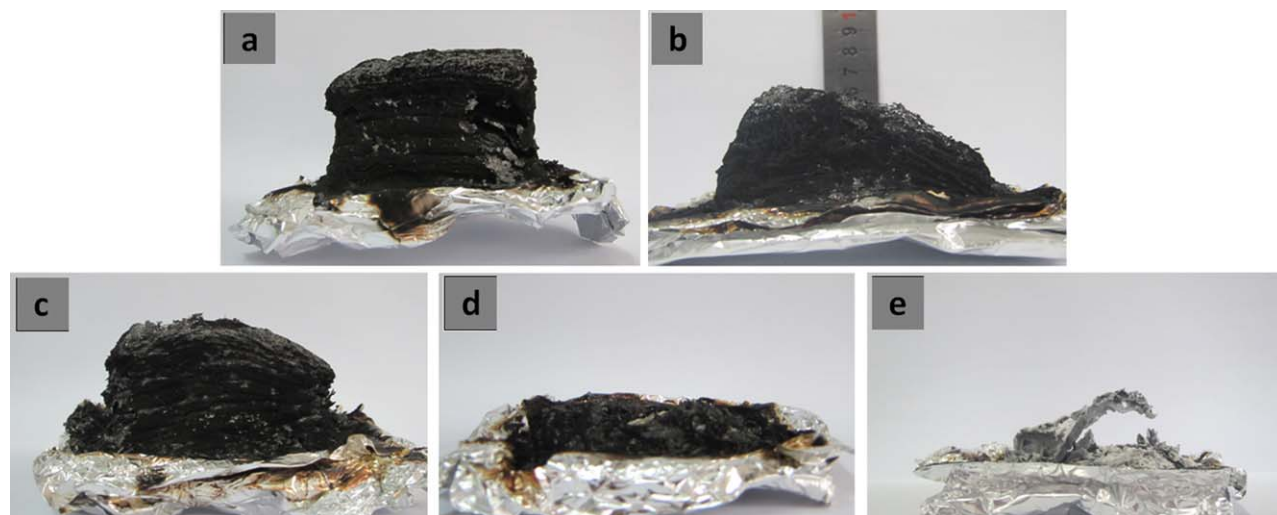| Samples	TTI (s)	pk-HRR (kW/m^2)	THR (MJ/m^2)	Av-COY (kg/kg)	Av-CO_2Y (kg/kg)
DGEBA/DDS	52	995.0	93.3	0.079	1.529
Trif-DOPO/DGEBA/DDS-1.0	48	390.8	70.4	0.143	1.540
Trif-DOPO/DGEBA/DDS-1.2	44	420.7	67.9	0.154	1.536
DOPO-DGEBA/DDS	57	437.2	60.6	0.127	1.164
TPT/DGEBA/DDS	48	963.5	88.7	0.081	2.107

Figure 4. The photos of the thermosets' residues. The height of char: (a) Trif–DOPO/DGEBA/DDS-1.2, 7.1 cm; (b) DOPO–DGEBA/DDS, 6.5 cm; (c) Trif–DOPO/DGEBA/DDS-1.0, 6.7 cm; (d) DGEBA/DDS, thin slice; (e) TPT/DGEBA/DD, thin slice. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

to the previous discussion, Trif-DOPO release some phospha-phenanthrene groups to gas phase to enhance its gas flame retardant effect, which lead to slightly weak charring ability and increase of flammable gas. The increase of Av-COY and Av-CO_2Y is also the reason. The increase of flammable gas causes the increase of products CO and CO_2 of combustion.

Residue Morphology and Analysis

Figure 4 exhibits the photos of the residues from cone calorimetry. It is noteworthy that the residue of Trif-DOPO/DGEBA/DDS-1.2 shows the swelling morphology and forms a cubic residue, which sustains the square shape of the raw cone calorimetry sample at horizontal direction. It is different with that of DOPO-DGEBA/DDS for its twisted residue shape. In addition, the height of the residue of Trif-DOPO/DGEBA/DDS-1.2 is 7.1cm, which is higher than 6.5 cm of DOPO-DGEBA/DDS. These testify that the residue from Trif-DOPO/DGEBA/DDS-1.2 is more rigid than that of DOPO-DGEBA/DDS so that it can support the weight of residue without deformation during swelling. It can be concluded that the rigid character of residue is obtained from the rigid structure tri-phenoxy-triazine of core aromatic structure in Trif-DOPO. But when the tri-phenoxy-triazine structure of TPT compounds alone appear in matrix, it won't lead to the increase of residue yields and also won't strengthen the intensity of residue due to the absence of the group-synergistic effect. Similarly, it can be observed that the residue of Trif-DOPO/DGEBA/DDS-1.0 also shows slight deformation and has a 6.7 cm height. It indicates sufficient quantity of Trif-DOPO is still essential to form the rigid char layer.

Moreover, the height of residue also discloses their viscosity and toughness because residue with higher expansion rate need thicker and tougher melting char layer to support the gases and keep it from releasing. Therefore, according to the results observed from Figure 4, Trif-DOPO can promote the formation of thicker and tougher melting char layer. To testify the opinion, the surface morphologies of residue were detected by SEM and

the results were illustrated in Figure 5. As shown in Figure 5, the residue of Trif-DOPO/DGEBA/DDS-1.2 has been stretched and thinned. Remarkably, the thin film hasn't obvious break from the residue of Trif-DOPO/DGEBA/DDS-1.2, which is different from that of DOPO-DGEBA/DDS with more holes. Herein, it can be sure that Trif-DOPO promotes the formation of thicker and tougher char layer. It should be resulted from the decomposition of hydroxyl-methylene fragments which boost the phosphaphenanthrene and aromatic fragments to combine with the matrix and produce the thick, tough, and rigid residue.

Group-Synergistic-Effect Flame Retardant Mechanism of Trif-DOPO

According to all of the above discussions, the group-synergistic-effect flame retardant mechanism of Trif-DOPO in Trif-DOPO/DGEBA/DDS can be preliminarily concluded. The group-synergistic-effect flame retardant mechanism is illustrated in Figure 6. Trif-DOPO has three main constituents, namely, phosphaphenanthrene, hydroxyl-methylene, and tri-phenoxyl-triazine. The hydroxyl-methylene group is an unstable structure and it will become trigger point when Trif-DOPO is heated. The group starts the decomposition, and then phosphaphenanthrene, water vapor and phenoxyl fragments begin to be released. All the fragments can break or hinder the chain reaction of combustion, and thus the Trif-DOPO/DGEBA/DDS owns high LOI value and flammability rating. In condensed phase, the hydroxyl-methylene group reacts with chains of matrix, which produce the flexible and thick polyether compounds. The tri-phenoxyl-triazine groups are also introduced into the residue and increase its rigidity. The phosphaphenanthrene groups gradually decompose with the increase of temperature to form phosphate and polyphosphate, which react with the residue to produce thick, tough and rigid char layer. All these boost the appearance of more excellent flame retardant behaviors of Trif-DOPO/DGEBA/DDS. In a word, the three fragments jointly work to achieve higher
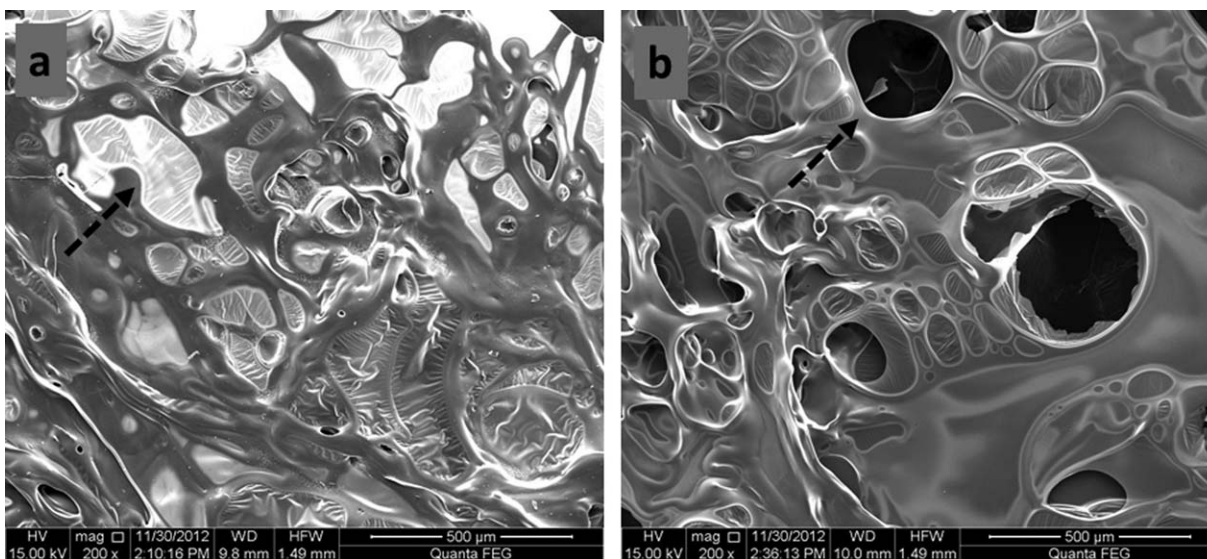
Figure 5. The SEM photos of residue (a) Trif–DOPO/DGEBA/DDS-1.2 and (b) DOPO–DGEBA/DDS.

flame retardancy of Trif-DOPO. Namely, Trif-DOPO has an obvious flame retardant group-synergic-effect.

CONCLUSIONS

A flame retardant tri-(phosphaphenanthrene-hydroxyl-methyl-phenoxyl)-1, 3, 5-triazine (Trif-DOPO) was applied in flame retardant epoxy resin. The Trif-DOPO/DGEBA/DDS thermoset with only 1.2 wt % phosphorus has the LOI value of 36.0% and UL94V-0 flammability rating, and has more excellent flame retardancy than DOPO-DGEBA/DDS containing the same phosphorus content do. In addition, Trif-DOPO can also decrease the pk-HRR and reduce the THR. All these testify that Trif-DOPO has an excellent flame retardant performance.

It can be confirmed that Trif-DOPO has a flame retardant group-synergic-effect during combustion. The hydroxyl-methylene fragments of Trif-DOPO trigger the early decomposition and boost the release of phosphaphenanthrene and phenoxyl flame retardant free radical and it also promotes the combination of Trif-DOPO and matrix; some phosphaphenanthrene is released to gas phase as flame retardant free radical and the others remain in condensed phase to form thick residue; some of phenoxyl fragments is also released to gas phase as flame retardant free radical and the others strengthen the rigidity of the residue. In sum, the three fragments in Trif-DOPO jointly work both to release PO_2 fragments, phosphaphenanthrene and phenoxyl free radical in gas phase and to form thick,
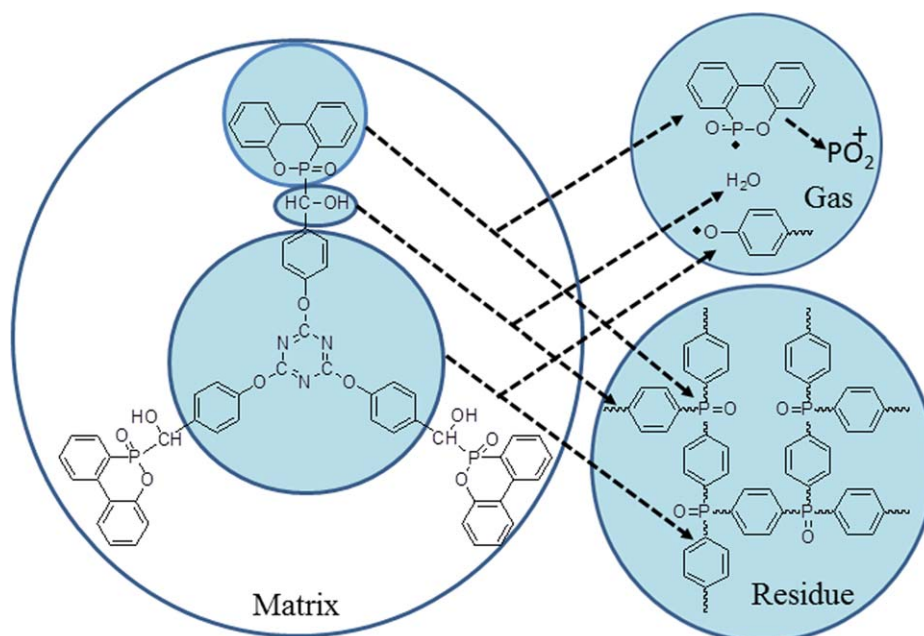

Figure 6. The group-synergic-effect flame retardant mechanism of Trif–DOPO in matrix. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

tough and rigid char layer in condensed phase. All the perform-ances confirm that the three fragments of Trif-DOPO show a group-synergistic-effect, which is the main reason of excellent flame retardant behaviors of Trif-DOPO.

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