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Synergistic Flame-retardant Effect of Epoxy Resin Combined with Phenethyl-bridged DOPO Derivative and Graphene Nanosheets

Wei Yan^{a,b,c*}, Ming-Qiu Zhang^{a*}, Jie Yu^c, Sheng-Qiang Nie^b, Dai-Qin Zhang^b, and Shu-Hao Qin^c

^a School of Chemistry, Sun Yat-sen University, Guangzhou 510275, China

^b School of Chemistry and Materials Engineering, Guiyang University, Guiyang 550005, China

^c National Engineering Research Center for Compounding and Modification of Polymer Materials, Guiyang 550014, China

Abstract Phenethyl-bridged DOPO derivative (DiDOPO) was combined with graphene nanosheets (GNSs) in epoxy resin (EP) to improve its flame retardancy. The results indicated that the introduction of only 1.5 wt% DiDOPO/1.5 wt% GNS in EP increased the limited oxygen index (LOI) from 21.8% to 32.2%, hence meeting UL 94 V-0 rating. The thermogravimetric analyses revealed that char yield rose in presence of GNSs to form thermally stable carbonaceous char. The decomposition and pyrolysis products in gas phase were characterized by thermogravimetry-Fourier transform infrared spectroscopy (TG-FTIR), and the release of large amounts of phosphorus was detected in the gas phase. The evaluation of flame-retardant effect by cone calorimetry demonstrated that GNSs improved the protective-barrier effect of fire residue of EP/DiDOPO/GNS. The latter was further confirmed by digital photography and scanning electron microscopy (SEM). Also, Raman spectroscopy showed that GNSs enhanced graphitization degree of the resin during combustion. Overall, the combination of DiDOPO with GNSs provides an effective way for developing high-performance resins with improved flame retardancy.

Keywords Epoxy resin; DOPO derivative; GNS; Flame retardancy

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INTRODUCTION

Epoxy resins (EPs) have widely been applied in adhesives, surface coating and laminated composites due to their desirable properties in terms of low shrinkage during curing, excellent mechanical strength, superior insulation, dielectric properties, and satisfactory resistance to moisture and organic solvents.^[1–5] However, pure EPs are highly flammable, hence limiting their applications. Therefore, developing high-efficiency flame retardants to improve flame retardancy of EPs is imperative, and numerous investigations have been performed to improve flame retardancy of epoxy resins by adding various flame retardants.^[6,7]

Derivatives based on 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) are phosphorus-containing flame retardants. Numerous studies have suggested that many DOPO derivatives including triazine,^[8] phenethyl,^[9,10] diphosphonate,^[11] silsesquioxane^[12] and bismaleimide^[13] are active species thanks to PO· radicals produced by gaseous-phase mechanism, as well as interaction with decomposing polymer to induce charring in condensed phase.

Inorganic flame retardants have frequently been applied in flame-retardant epoxy resins due to their low cost, moderate toxicity, and elevated thermal stability.^[14,15] Graphene-based flame retardants can improve flame retardancy of polymers by inhibiting the two key terms—heat and fuel. First, graphene possesses unique two-dimensional layered structure and can promote the formation of dense and continuous char layers during decomposition. The char can act as a physical barrier to prevent heat transfer from the heat source and delay escape of pyrolysis products from the substrates. Second, graphene has a large specific surface area and can effectively adsorb flammable organic volatiles or hinder their release and diffusion during combustion.^[16,17] Recently, graphene and its derivatives have been demonstrated useful as flame retardant nano-additives to reduce fire hazards of various polymers, such as epoxy resins.^[18,19] For instance, Liu *et al.*^[20] reported that char barrier effect in EP matrix could be promoted from 400 °C to 430 °C by graphene nanosheets (GNSs) with large surface areas. Also, GNS could change the path of thermal degradation of EP thereat. Moreover, synergistic flame-retardant effect of GNS combined with conventional and inorganic-nanomaterials was reported.^[21,22] Consequently, with the assistance of synergist, graphene may perform a good effect on flame retardancy for polymers even at low loading.

In this study, phenethyl-bridged DOPO derivative

* Corresponding authors: E-mail lrasyw@163.com (W.Y.)

E-mail ceszmq@mail.sysu.edu.cn (M.Q.Z.)

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(DiDOPO) was used as flame-retardant additive, and GNSs were introduced into EPs. In our previous work, DiDOPO showed good flame-retardant effect in gas phase^[23] and synergistic flame-retardant effect with the addition of Mg-Al layered double hydroxides (LDHs).^[24] To improve the flame-retardant efficiency of EP composites, DiDOPO and GNS were incorporated in an epoxy resin based on diglycidyl ether of bisphenol-A (DGEBA) and 2-ethyl-4-methylimidazole (EMI-2,4). GNSs were found effective in inducing protective barrier effects on EP/DiDOPO. The flame retardancy of the obtained EP/DiDOPO/GNS composite was found promising, and hence flame-retardant mechanism was proposed.

EXPERIMENTAL

Materials

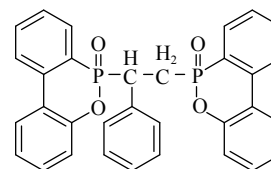
Diglycidyl ether of bisphenol-A (DGEBA, epoxide value of 0.48–0.52 mol/100g, commercial name: E-51) was purchased from Laizhou Baichen Insulation Materials, China. 2-Ethyl-4-methylimidazole (EMI-2,4) was used as curing agent and was obtained from Tianjin Weiyi Chemical Technology, China. The flame retardant phenethyl-bridged DOPO derivative (DiDOPO) was synthesized in our laboratory.^[10,25] GNSs (average outer diameter of 5–10 μm , thickness of 3–10 nm) were provided by Nanjing Xianfeng Nano-material, China. Other reagents were obtained from Chongqing Chuandong Chemical Group, China.

Preparation of Flame-retardant EP Composites

First, DiDOPO was evenly dispersed in EP under mechanical stirring at room temperature. The mixture was then slowly heated to 130 $^{\circ}\text{C}$ and stirred until DiDOPO was fully dissolved in EP. For EMI-2,4 curing system, the EP/DiDOPO mixture was cooled down to 50 $^{\circ}\text{C}$. Next, EMI-2,4 was added to the mixture and blended adequately to form a uniform hybrid. After degassing for 20 min in a vacuum oven at 40 $^{\circ}\text{C}$, the hybrid was poured into preheated molds and cured at 80 $^{\circ}\text{C}$ for 1 h then at 140 $^{\circ}\text{C}$ for 2 h. All samples were prepared following the same procedure.

Appropriate content of GNS was ultrasonically dispersed and mechanically stirred in acetone (1 g/100mL acetone) for 1 h at room temperature. Next, EP was added to the slurry and stirred for 2 h. The slurry was then transferred into an oil bath and stirred at 130 $^{\circ}\text{C}$ for 0.5 h to distill off any remaining acetone. A certain amount of DiDOPO was added to EP and stirred for 0.5 h, and the mixture was cooled down to

50 $^{\circ}\text{C}$. The curing agent was then introduced to the system through mixing. The curing conditions were set the same as those of EP/DiDOPO composite. The chemical structure of DiDOPO is shown in Scheme 1, and formulations of EP thermosets are listed in Table 1. The same procedure was also followed for the preparation of EP/GNS composites.



Scheme 1 The chemical structure of DiDOPO

Characterization

The UL-94 measurements (CZF-2, Jiangning, China; dimension of 130 mm $\times$ 13 mm $\times$ 3.2 mm) were performed according to ASTM D3801. LOI (according to ASTM D2863-77) was measured on a JF-3 oxygen index meter (Jiangning, China) using samples with 100 mm $\times$ 6.5 mm $\times$ 3.2 mm in size. The cone calorimeter tests (CCT; FTT, United Kingdom) were conducted on a ASTM E1354/ISO 5660. Specimens with dimensions of 100 mm $\times$ 100 mm $\times$ 6 mm at external heat flux of 50 $\text{kW}\cdot\text{m}^{-2}$ were used, and typical cone calorimetry data were replicable within $\pm 5\%$.

The thermal stabilities of all tested materials were characterized by thermogravimetry (TG, Netzsch Model TG 219 F3 thermal analyser, Netzsch Instruments, Germany) at constant scanning rate of 10 $^{\circ}\text{C}\cdot\text{min}^{-1}$ under nitrogen atmosphere and temperatures ranging from 40 $^{\circ}\text{C}$ to 800 $^{\circ}\text{C}$.

The microstructure of carbon residues deposited on EP thermosets issued from CCT test was observed by FEI Quanta 250 FEG field-emission scanning electron microscopy (SEM, FEI, U.S.A.) under high vacuum conditions and voltage of 20 kV. The SEM instrument was coupled with energy dispersive X-ray (EDX) for elemental analysis.

The thermogravimetric-Fourier transform infrared spectroscopy (TG-FTIR) instrument consisted of a thermogravimeter (TG219 F3, Netzsch Instruments, Germany), a Fourier transform infrared spectrometer (Nicolet IS50, Thermo Fisher Scientific, U.S.A.), and a transfer tube with the inner diameter of 1 mm connecting the thermogravimeter with a infrared cell. The investigation was carried out at temperatures ranging from 40 $^{\circ}\text{C}$ to 700 $^{\circ}\text{C}$ at linear heating rate of

Table 1 Formulations and flame-retardant results of EP composites

Sample	Formulation (wt%)			Flame retardancy	
	EP	DiDOPO	GNS	LOI (%)	UL-94
EP	100	0	0	21.8	NR
EP/DiDOPO0.5	100	0.5	0	23.7	V2
EP/DiDOPO1	100	1	0	24.1	V2
EP/DiDOPO3	100	3	0	32.7	V0
EP/GNS0.5	100	0	0.5	23.1	NR
EP/GNS1	100	0	1	24.9	NR
EP/GNS3	100	0	3	26.7	NR
EP/DiDOPO0.25/GNS0.25	100	0.25	0.25	23.2	NR
EP/DiDOPO0.5/GNS0.5	100	0.5	0.5	27.1	V0
EP/DiDOPO1.5/GNS1.5	100	1.5	1.5	32.2	V0

20 °C·min⁻¹ under nitrogen flow of 30 mL·min⁻¹.

The laser Raman spectroscopy (LRS) measurements were performed at room temperature using Renishaw RM2000 Raman apparatus excited by 514 nm laser line with wavelength range of 200–4000 cm⁻¹.

RESULTS AND DISCUSSION

Flame Retardant Properties of EP Composites

In general, higher LOI values above 26% can imply superior flame retardancy of polymers. The flammability data obtained by LOI and UL-94 tests for all EP composites are listed in Table 1. During UL-94 testing, neat EP showed easy-burning behavior with a low LOI value of 21.8% and no rating (NR) in vertical UL-94 testing. The addition of 3 wt% DiDOPO increased LOI value of EP composites to 32.7% and UL-94 rating reached V-0. The UL-94 rating of EP composites deteriorated to V-2 for less addition of DiDOPO. Compared to epoxy resin containing only one flame retardant, the co-addition of 1.5 wt% DiDOPO and 1.5 wt% GNS raised LOI value of EP composite to 32.2% with the UL-94 rating remaining at V-0. This resulted from the synergistic effect between DiDOPO and GNS on flame retardancy of epoxy resins. The DiDOPO component acted as aromatic phosphates, imparting the flame retardancy through flame inhibition in gas phase and char formation in condensed phase.^[26] In gas phase, phosphorus-containing flame-retarding pyrolysis products, such as PO· and HPO· radicals, probably reacted with H· and OH· radicals. In condensed phase, the radicals promoted formation of char to act as barriers. On the other hand, the layered GNS hindered the transfer of heat and gas in EP/GNS composite, retarding the combustion. These decreased the rate of polymer degradation.^[27]

To further investigate the flame retardancy of EP composites, the samples were subjected to flame using cone calorimeter test (CCT). The heat release rate (HRR) and total heat release (THR) curves are shown in Figs. 1(a) and 1(b). The main characteristic parameters, such as time to ignition (TTI), total heat release (THR), peak of heat release rate (pHRR), total mass loss (TML), average value of effective heat of combustion (av-EHC), total smoke release (TSR), average CO yield (av-COY) and average CO₂ yield (av-CO₂Y) are compiled in Table 2. Fig. 1 and Table 2 revealed that neat EP burned very quickly after ignition, with sharp and huge increase in HRR. A pHRR of 827 kW·m⁻² was recorded, where the sample burned out within 550 s. The pHRR value of EP/DiDOPO1.5/GNS1.5 flame-retardant thermoset was estimated to be 374 kW·m⁻². This suggested that in the presence of both components in the epoxy thermosets, the inhibition effect in the EP/DiDOPO/GNS composite not only

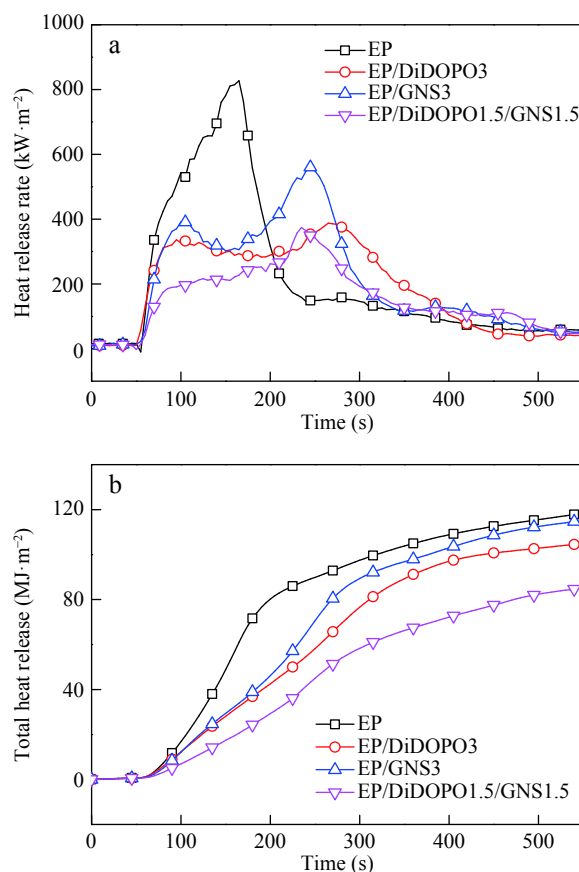


Fig. 1 (a) Heat release rate and (b) total heat release curves of the flame-retardant epoxy composite

increased the combustion intensity but also improved the total combustion reaction quantity of thermosets. Fig. 1(b) depicts the THR curves of the composites. After burning, THR value of neat EP reached 116 MJ·m⁻². Compared to neat EP, EP/DiDOPO3 composites exhibited lower THR values, indicating that DiDOPO could effectively promote the formation of protective char layer during combustion. The THR values of EP/GNS3 and EP/DiDOPO1.5/GNS1.5 also exhibited decreasing trends. The THR of EP/DiDOPO1.5/GNS1.5 was lower than those of other EP composites. During combustion, DiDOPO component might decompose early to promote decomposition of the matrix, which then interacted with GNS. By contrast, DiDOPO and GNS showed additional flame-retardant effects in EP/DiDOPO/GNS due to the barrier of incombustible GNS. The char layers produced in EP/DiDOPO/GNS composites effectively prevented heat and oxygen from transferring into the EP matrix interior, thus decreasing the HRR value.

To gain a better understanding, the TSR analyses were

Table 2 Data obtained from cone calorimetry testing of different samples

Sample	TTI (s)	pHRR (kW·m ⁻²)	THR (MJ·m ⁻²)	av-EHC (MJ·kg ⁻¹)	TSR (m ² ·m ⁻²)	TML (wt%)	av-COY (kg·kg ⁻¹)	av-CO ₂ Y (kg·kg ⁻¹)
EP	32	827	116	19.5	3867	90.4	0.12	1.32
EP/DiDOPO3	41	387	104	16.9	6290	87.6	0.15	1.06
EP/GNS3	35	560	113	17.9	5196	90.8	0.15	1.24
EP/DiDOPO1.5/GNS1.5	51	374	99	13.3	7072	85.1	0.21	1.04

combined with effective heat of combustion (av-EHC) results. Note that higher TSR accompanied by lower av-EHC always indicates the formation of noncombustible in the gaseous phase. The other parameters, such as TSR, av-COY and av-CO₂Y in cone tests, provide both the combustion state and secondary fire hazard effect. High TSR and low av-EHC value implied the absence of such hazard effect during combustion. These phenomena should be caused by the presence of both flame retardants. The TSR of neat EP was recorded as 3867 m²·m⁻², whereas those of EP/DiDOPO3, EP/GNS3 and EP/DiDOPO1.5/GNS1.5 were estimated to be 6290, 5196 and 7072 m²·m⁻², respectively. The obvious decrease in av-EHC and increase in TSR may be related to the formation of PO· and phenoxy free radicals. The obvious reduction in av-EHC of EP/DiDOPO/GNS could explain the changes in both COY and CO₂Y.

Table 2 reveals av-COY and av-CO₂Y of each EP composite. Among the samples, EP/DiDOPO1.5/GNS1.5 generated the highest amount of CO and the lowest CO₂. Furthermore, flame inhibition occurs with incomplete combustion, thus increasing the smoke and CO release in the gas phase. These results confirmed that incomplete combustion was induced by flame inhibition effect from combination of DiDOPO and GNS. The above results suggested that DiDOPO and GNS might yield better flame-retardant effect to epoxy resin than the other two flame retardants in condensed and gaseous phases. Therefore, the composites could produce more noncombustible gases than EP, and gaseous-phase flame-retardant effect may play an important role in EP composites.^[28–30]

In condensed phase, TML determined by cone calorimeter testing confirmed the effect of DiDOPO/GNS. In contrast to neat EP, the flame-retardant thermosets containing DiDOPO3 and GNS3 alone reduced TML values to 87.6% and 90.8%, respectively. However, the addition of DiDOPO/GNS into thermosets further declined the TML value of EP/DiDOPO1.5/GNS1.5 to 85.1%. In sum, less decomposed matrix should preserve more char in EP/DiDOPO/GNS compared to EP/DiDOPO and EP/GNS thermosets. The latter highlighted the effect of DiDOPO and GNS in promoting the formation of more additional carbonaceous char. Overall, the DiDOPO/GNS system can impose better flame-retardant effect in condensed phase to thermosets because less decomposed matrix should reduce fuel while presence of more char would inhibit heat spreading to the matrix. The appropriate mass fraction of DiDOPO and GNS can endow the thermosets with better performances in LOI testing, UL-94, and cone calorimetry.

Quantitative Assessment of Flame-retardancy Mechanisms

To gain a better understanding of the flame-retardant effect, quantitative analyses of the cone calorimeter data were

carried out.^[31–33] According to literature,^[31] the flame-retardant effects during combustion can be divided into three parts: (1) flame inhibition effect, (2) barrier and protective effect from char layer, and (3) charring effect (decrease fuel). The first effect occurs in gaseous phase and the other two in condensed phase. All the three effects can be calculated quantitatively. Firstly, EHC can be regarded as heat release by unit mass fuel and considered as ratio of HRR to mass loss rate measured at certain point. Hence, EHC quantitatively showed flame inhibition effect according to Eq. (1). The additional reduction was caused by the barrier and protective effect of intumescent char.

The calculation method of barrier and protective effect is shown in Eq. (2). The charring effect can also be quantitatively obtained from the residue weight in Eq. (3). The decreased ratio of pHRR_{FR-EP} in each sample appeared much smaller than that of THR_{FR-EP}. According to Eqs. (1)–(3), the three different flame retardant effects can be quantitatively assessed, and the resulting data are listed in Table 3. The flame inhibition effect of EP/DiDOPO1.5/GNS1.5 system increased to 31.8%, which was higher than values observed for EP/DiDOPO3 (13.3%) and EP/GNS3 (8.2%). This confirmed the increased synergistic effect of DiDOPO/GNS in gaseous phase. The barrier and protective effects of EP/DiDOPO1.5/GNS1.5 (47.1%) were also better than that of EP/GNS3 (29.9%) but slightly worse than that of EP/DiDOPO3 (47.8%).

The barrier and protective effects of EP/DiDOPO1.5/GNS1.5 were located between the other two flame retardants, with additional synergistic effect. Also, the charring effect of EP/DiDOPO1.5/GNS1.5 was enhanced to 5.9%, which was higher than those obtained for EP/GNS3 (−0.4%) and EP/DiDOPO3 (3.1%). This confirmed the strong charring ability issued from the synergistic effect of DiDOPO/GNS in condensed phase. Therefore, DiDOPO/GNS could produce excellent flame retardants in both gaseous and condensed phases thanks to the synergistic effect.

$$\text{Flame inhibition effect} = 1 - \text{EHC}_{\text{FR-EP}} / \text{EHC}_{\text{EP}} \quad (1)$$

$$\text{Barrier and protective effect} = 1 - (\text{pHRR}_{\text{FR-EP}} / \text{pHRR}_{\text{EP}}) / (\text{THR}_{\text{FR-EP}} / \text{THR}_{\text{EP}}) \quad (2)$$

$$\text{Charring effect} = 1 - \text{TML}_{\text{FR-EP}} / \text{TML}_{\text{EP}} \quad (3)$$

Macroscopic and Microscopic Morphologies of Fire Residues

The digital photographs of charring residue issued from cone calorimetry tests are shown in Fig. 2. Neat EP was depleted after combustion (Figs. 2a1 and 2a2). The residual char of EP was very thin and broken, implying the poor charring ability of EP. In Figs. 2(b1) and 2(b2), GNSs were incorporated in EP to yield continuous and uniform char layer. This phenomenon could be attributable to increased viscosities of

Table 3 Quantitative assessment of the three flame-retardant effects

Sample	Flame inhibition effect (%)	Barrier and protective effect (%)	Charring effect (%)
EP/DiDOPO3	13.3	47.8	3.1
EP/GNS3	8.2	29.9	−0.4
EP/DiDOPO1.5/GNS1.5	31.8	47.1	5.9

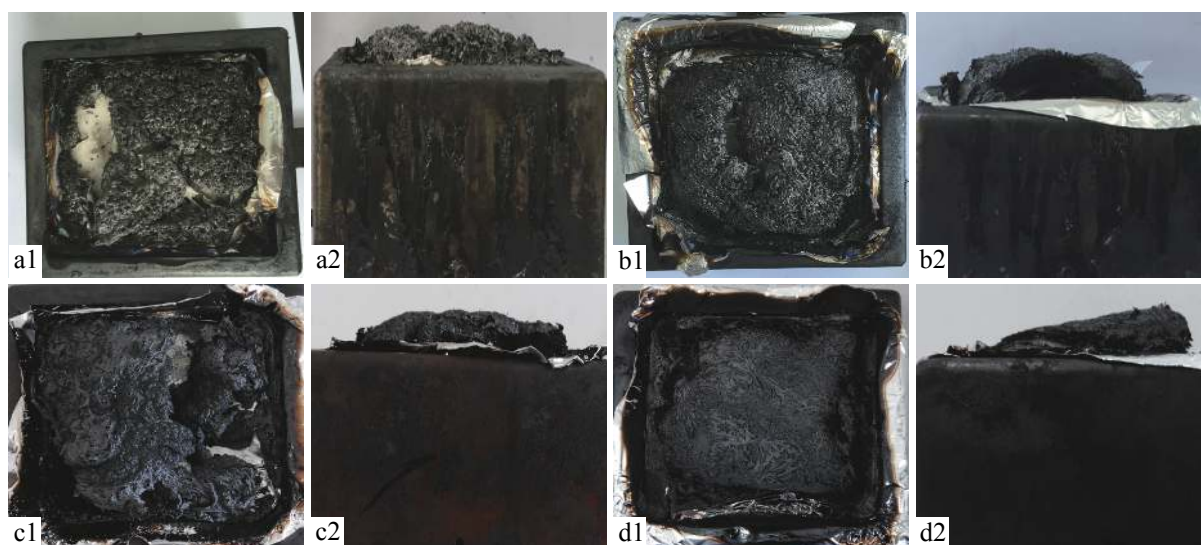


Fig. 2 (a1–d1) Top view and (a2–d2) side view of char residues after cone calorimetry testing: (a1, a2) EP, (b1, b2) EP/DiDOPO3, (c1, c2) EP/GNS3, and (d1, d2) EP/DiDOPO1.5/GNS1.5 composites

thermal degradation products, which could swell during gas release.

The structure of char layers became dense and distinctly intumescent charred in EP/DiDOPO3 (Figs. 2c1 and 2c2). Compared to EP/GNS3, the residual char of EP/DiDOPO1.5/GNS1.5 exhibited more compact and tight morphology (Figs. 2d1 and 2d2). The compact char layer protected the matrix from burning and obstructed heat release, yielding better flame retardancy of EP/DiDOPO/GNS. These findings were consistent with those of LOI and UL-94 tests.

To clarify the reason behind this phenomenon, the microstructures of carbon layers were investigated. Fig. 3 shows SEM morphologies of the residues after cone calorimetry testing. The residue of EP displayed badly broken carbon layer structures forming stable char layers (Fig. 3a). Most of char layer's surface exhibited smooth and flat morphology. After combustion, the residue of EP/DiDOPO3 became denser, forming thick and compact char layer. Also, the surface was covered with decomposition products issued from phosphorus-containing groups (Fig. 3b).^[34] As shown in the enlarged section of Fig. 3(c), numerous small particles were deposited on the char layer surface, suggesting the embedding of GNS. The incorporation of GNS in the residue generated by EP/DiDOPO probably improved the protective-barrier effect of carbonaceous char layer during flame combustion. Compared to EP/DiDOPO and EP/GNS, the charred layers of EP/DiDOPO/GNS showed more solid and compact morphology, indicating that GNS promoted the char strength.

Elemental Analysis of Residues

The morphologies and elemental analysis of EP composites of chars obtained from cone calorimetry testing were observed and conducted by SEM-EDX and the results are illustrated in Fig. 4. The char of neat EP presented a cracked surface, associated with fierce combustion. Such broken char layer would not resist flames. By contrast, the char of EP/DiDOPO3 showed compact and continuous surface,

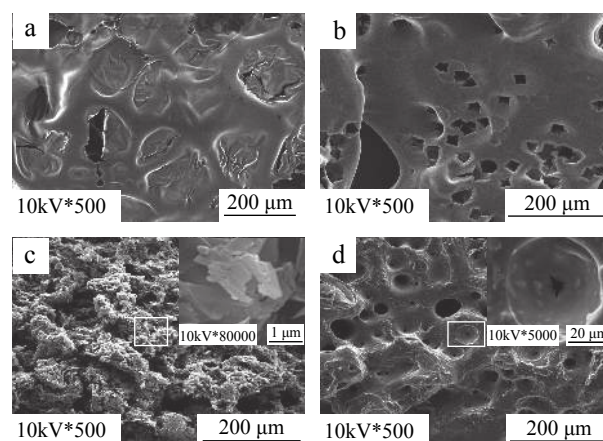


Fig. 3 SEM images of char residues after cone calorimetry testing: (a) EP, (b) EP/DiDOPO3, (c) EP/GNS3, and (d) EP/DiDOPO1.5/GNS1.5. The inside represents the enlarged views of (c) and (d).

implying thermally stable char capable of inhibiting flame spread. The C/O ratio of residual chars of neat EP was estimated to be 8.25, and those of EP/DiDOPO3 and EP/GNS3 were 7.03 and 39.2, respectively. The C/O ratio of residual chars of EP/DiDOPO1.5/GNS1.5 was 31.2, implying that the incorporation of GNS reduced both heat and oxygen exchange efficiencies when compared to EP/DiDOPO1.5/GNS1.5. In addition, both phosphorus and oxygen contents significantly increased as more DiDOPO/GNS was incorporated. All measured phosphorus contents were very low, suggesting the release of most phosphorus into the flame to form $\text{PO}\cdot$ radicals and exert quenching effect in gas phase. This meant that DiDOPO was decomposed to form phosphorus-containing fragments. The GNS incorporated in the residue generated from EP/DiDOPO was believed to further improve the protective-barrier effect. The morphology study disclosed that EP composites containing DiDOPO/GNS exhibited better flame retardancy than neat EP.

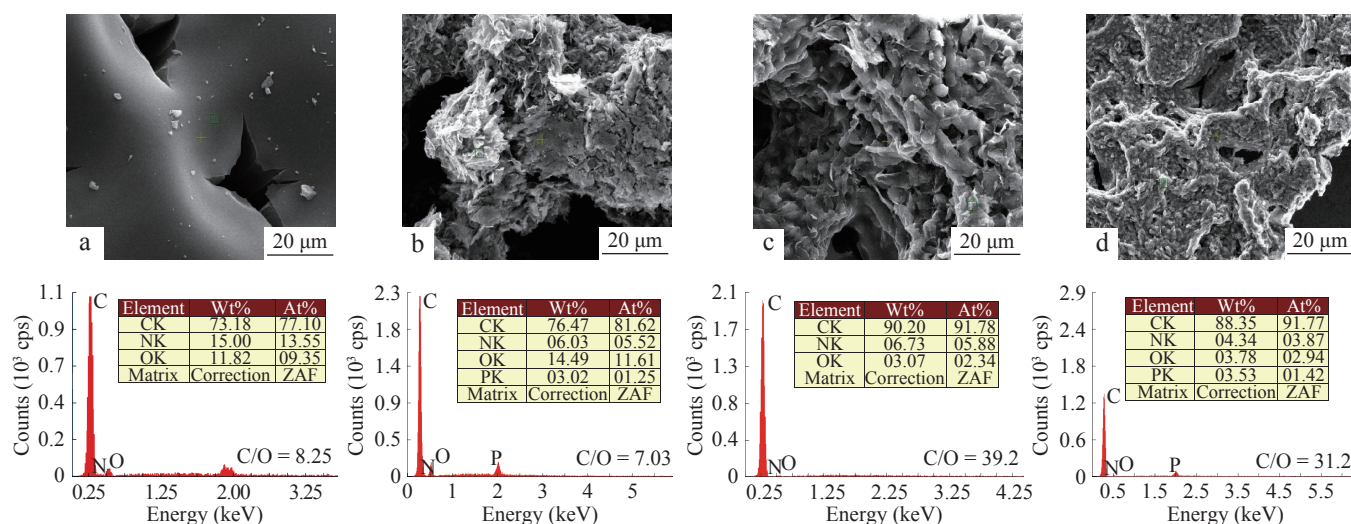


Fig. 4 SEM images and elemental analysis of residual chars: (a) EP, (b) EP/DiDOPO3, (c) EP/GNS3, and (d) EP/DiDOPO1.5/GNS1.5

Thermal Analysis of EP Composites

The thermogravimetry (TG) and differential thermogravimetry (DTG) curves of epoxy and its flame-retardant composites under nitrogen are shown in Figs. 5(a) and 5(b), respectively. The onset degradation temperatures ($T_{5\%}$) of the samples were evaluated by the temperature at 5 wt% weight loss. Solid residues at 700 and 800 °C were obtained after TG measurements. The temperature at the maximum weight loss rate ($T_{\max}$) of the samples was obtained from DTG curves, and typical TGA results are gathered in Table 4.

As shown in Fig. 5(a), the decomposition processes of all samples occurred mainly from 350 °C to 500 °C, with one distinguishable weight loss maximum. The $T_{5\%}$ of neat EP was estimated to be 396 °C. The mass loss rate at $T_{\max}$ showed the highest value at 437 °C (22.6 wt%·min⁻¹) and char yield at 800 °C (9.7 wt%) under N₂ atmosphere. The decrease in $T_{5\%}$ of EP/DiDOPO3 was partially due to the formed phosphorus-based compounds, which catalyzed the decomposition of EP matrix. DiDOPO exerted only a limited effect in condensed phase. Thus, relevant reduction in fire risk due to enhanced charring of fuel was ruled out. Moreover, a limited action in condensed phase of DGEBA-based EP was reported in the literature for similar flame retardants based on DOPO-isocyanurate.^[35–37] The decomposition of EP/GNS3 composites occurred earlier than that of the neat EP. This is because the oxygen-containing groups on the surface of GNS were decomposed earlier than EP. The solid residue of EP/GNS3 decreased to 11.3 wt% at 800 °C. In addition, the solid residue of EP/DiDOPO1.5/GNS1.5 composites increased to 16.6 wt% at 800 °C. The char residues of EP/DiDOPO1.5/GNS1.5 were higher than those

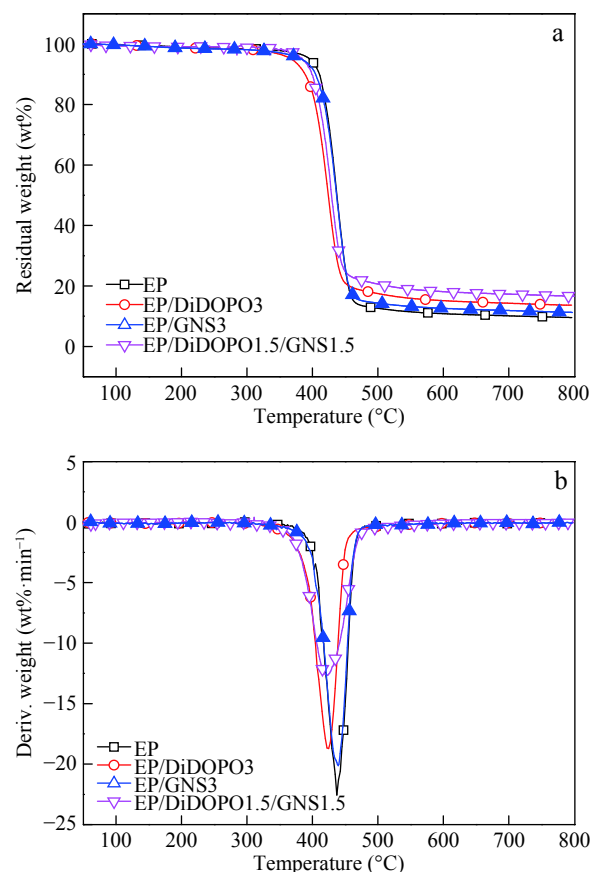


Fig. 5 (a) Thermogravimetry (TG) and (b) differential thermogravimetry (DTG) curves for flame-retardant epoxy composites under N₂ atmosphere at heating rate of 10 °C·min⁻¹

Table 4 TG and DTG data of flame-retardant epoxy composites under N₂ atmosphere

Sample	$T_{5\%}$ (°C)	$T_{\max}$ (°C)	Rate of $T_{\max}$ (wt%·min ⁻¹)	Char residue (wt%)	
				700 °C	800 °C
EP	396	437	22.6	10.1	9.7
EP/DiDOPO3	367	425	18.7	14.3	13.6
EP/GNS3	383	439	20.1	11.9	11.3
EP/DiDOPO1.5/GNS1.5	385	422	12.6	17.2	16.6

of EP/DiDOPO3 and EP/GNS3. Therefore, incorporation of DiDOPO promoted the formation of char on EP composites.

TG-IR Characterization of EP Composites

To investigate the flame-retardant mechanism taking place in gas phase, the gas products generated by the resins during thermal degradation under nitrogen atmosphere were analyzed by TG-IR. The 3D TG-FTIR spectra of the gas phase induced by thermal degradation of EP composites are shown in Fig. 6. The FTIR gas spectra of EP, EP/DiDOPO3, EP/GNS3 and EP/DiDOPO1.5/GNS1.5 at different reaction time are gathered in Fig. 7. It can be seen that the main products of the thermal decomposition were dominated by EP, showing the release of H₂O (4000–3400 cm⁻¹ and 2200–1700 cm⁻¹), CO₂ (2359 cm⁻¹), OH (3649 cm⁻¹), CO (2182 cm⁻¹), C–O and C–H of bisphenol A (1256 cm⁻¹), C_{aromatic}–H (3034 cm⁻¹, 828 cm⁻¹, 748 cm⁻¹), C_{aromatic}–C_{aromatic} stretch (1606 cm⁻¹, 1510 cm⁻¹), C_{aliphatic}–H (2972 cm⁻¹, 2936 cm⁻¹, 2884 cm⁻¹), C–H of bisphenol A (1332 cm⁻¹, 1176 cm⁻¹), and RC=CH₂ (887 cm⁻¹).^[38–41] Most peaks were associated with bisphenol-A, part of DGEBA resin component.^[42,43]

In addition, DiDOPO or GNS did not generate any new peaks or shoulders with noticeable heights. However, differences in peak ratio existed. Hence, the spectra were considered qualitatively identical with respect to the same main decomposition products, confirming the existence of quantitative differences related to variations in concentration of released decomposition products. Furthermore, any increase in peak height may be due to additional peak overlapping with the peaks originating from EP. The absorption band at 1261

cm⁻¹ (P=O) was similar to the characteristic peak of EP matrix, suggesting the formation of polyphosphate structures issued from decomposition of DiDOPO. These polyphosphate structures may react with other pyrolysis products such as phenol or bisphenol to form P–O–Ph bonds.^[10,21] The presence of the peak around 750 cm⁻¹ suggested the specific contribution from the phosphorous-containing DOPO component of DiDOPO. The released amount of CO₂ from EP/GNS3 was higher than those of EP/DiDOPO3 and EP/DiDOPO1.5/GNS1.5. The overall analysis of the evolved gases indicated the release of phosphorus into the gaseous phase with some minor additional changes in amounts of the products. Both EP/DiDOPO and EP/DiDOPO/GNS did not affect the evolved gases, consistent with the negligible changes seen in decomposition temperatures and char yields. The release of phosphorus during the main decomposition step resulted in flame inhibition of EP/DiDOPO and EP/DiDOPO/GNS.

Analysis of Graphitization Degree of Chars

Raman spectroscopy is often used to characterize graphitic structures of materials and evaluate the order degrees of carbon materials. These include the identification of the two characteristic bands: D-band at ~1360 cm⁻¹ and G band at ~1580 cm⁻¹. The D-band is associated with vibration of carbon atoms with dangling bonds in plane terminations of disordered graphite or glass carbons (unorganized carbon structure). On the other hand, the G-band corresponds to an E_{2g} mode of hexagonal graphite and relates to the vibration of sp² bonded carbon atoms in graphite layers (graphitic structure). Fig. 8 shows the Raman spectra of the char

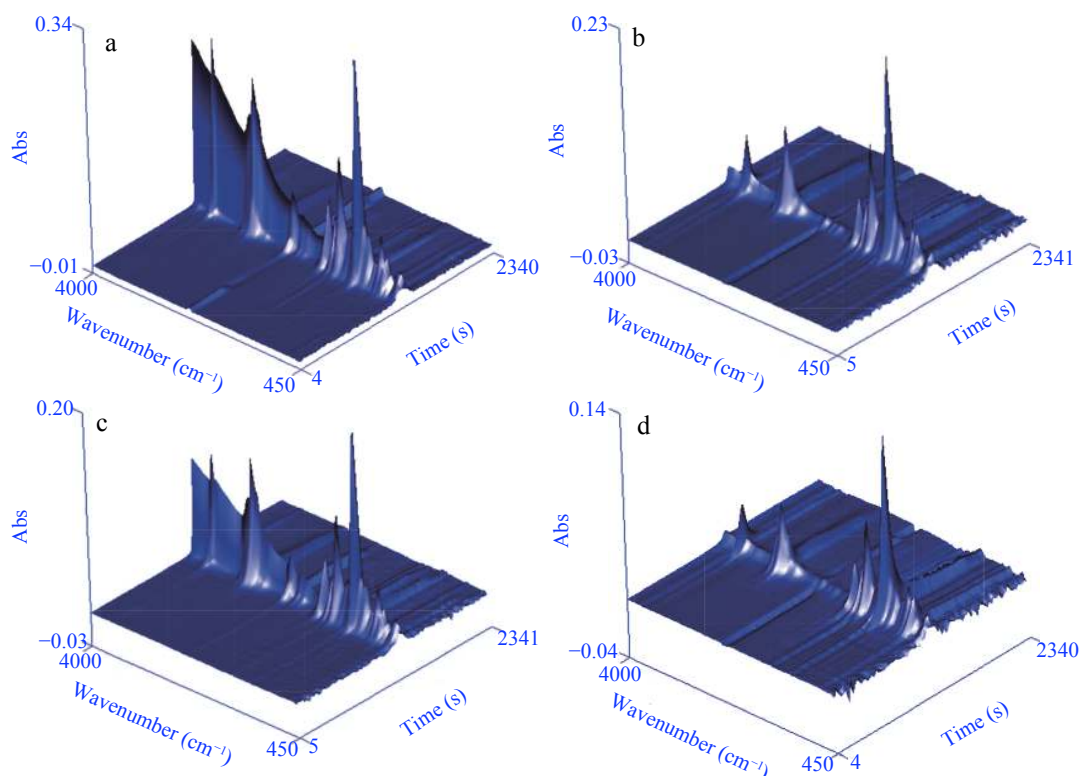


Fig. 6 3D TG-FTIR spectra of pyrolysis products for (a) EP, (b) EP/DiDOPO3, (c) EP/GNS3, and (d) EP/DiDOPO1.5/GNS1.5 composites

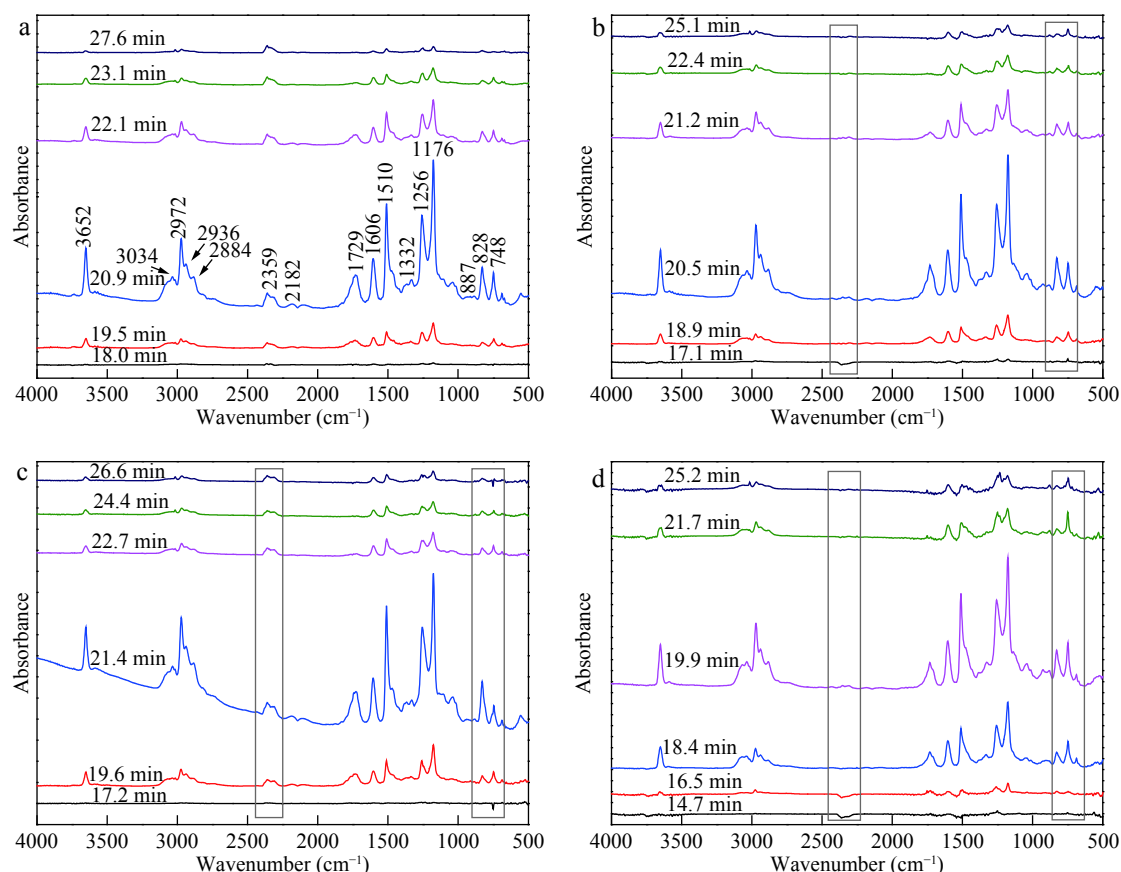


Fig. 7 FTIR spectra of pyrolysis products of EP composites at different time: (a) EP, (b) EP/DiDOPO3, (c) EP/GNS3, and (d) EP/DiDOPO1.5/GNS1.5 composites

residue of different flame-retardant samples after CCT. Two features appeared in Raman profiles of graphitic materials assigned to G-band at 1590 cm^{-1} (graphite) and D-band at 1355 cm^{-1} (disordered char). The relative intensity ratio of D peak to G peak ($R = I_D/I_G$) reflects the proportion of amorphous carbon, as well as the microcrystalline carbon obtained from Raman spectroscopy. Therefore, R -value is a good indicator of the degree of graphitization of carbon materials. Higher R -values mean lower degrees of graphitization of char residue, and consequently worse flame-retardant performances.^[44,45] As shown in Fig. 8, the incorporation of DiDOPO in the epoxy resin increased R when compared to neat epoxy resin, suggesting an increase in graphitization degree of residual char. Furthermore, EP/GNS3 showed the lowest value of R among all three investigated resins, indicating that the incorporation of GNS led to improvement in graphitization degree. This confirmed the highest graphitization degree of EP/DiDOPO1.5/GNS1.5 char, where GNS played an important role in enhancing the graphitization degree. More specifically, the connection between GNS and the matrix could yield intact graphic structure when faced strong compression during burning. Also, it should be noted that the char with higher graphitization degree is compact and efficient in thermal insulation, which may reduce the heat and mass transfer between the flame and matrix. Thus, it can be concluded that the introduction of GNS enhanced the thermal stability and

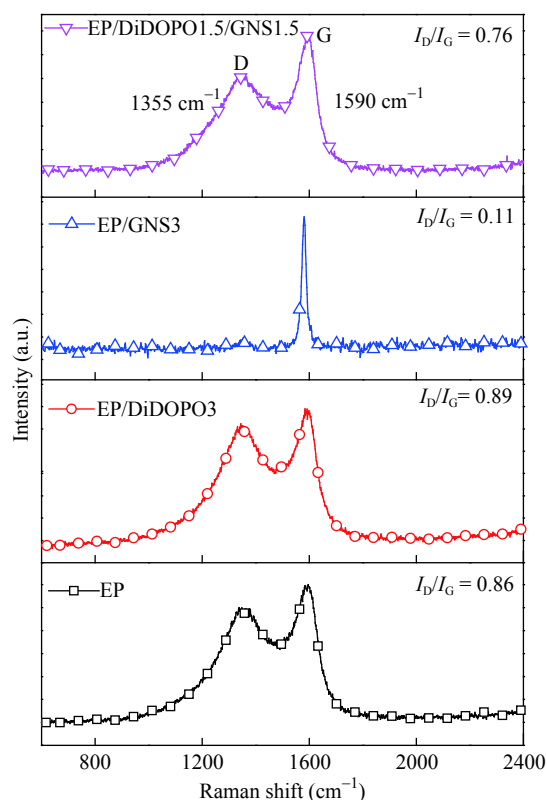


Fig. 8 Raman spectra of EP composites after CCT

fire retardancy of the resin. In turn, this increased the char yield when GNSs were added to the matrix, as shown by TG tests.

CONCLUSIONS

GNSs and phenethyl-bridged DOPO derivatives (DiDOPOs) were used as flame retardants in EP resin. UL-94 tests indicated that the EP/DiDOPO/GNS composites met V-0 classification. The cone calorimetry data revealed lower pHRR values of EP/DiDOPO1.5/GNS1.5 when compared to EP/DiDOPO3 and EP/GNS3. The DiDOPO/GNS showed primary flame-inhibitor behavior in flammability tests, such as CCT and SEM. TG suggested that increased amounts of DiDOPO/GNS positively affected char yield of EP resins. The Raman spectra depicted that GNSs enhanced the graphitization degree of EP resin during combustion. The morphology analyses of the residues confirmed that compact char could effectively prevent exchange of heat and mass between the underlying polymer material and flame zone. Overall, the introduction of DiDOPO and GNS in the epoxy resin led to improved performances. GNS exerted a protective-barrier effect in condensed phase and DiDOPO showed flame-inhibition effect in gas phase. Both effects resulted in EP/DiDOPO/GNS composites with outstanding flame-retardant performances.

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