Covalent functionalization of graphene oxide with flame retardant and its effect on thermal stability and flame retardancy of epoxy composites

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ABSTRACT

In order to improve the dispersion and fire retardant property in epoxy resin (EP), graphene oxide (GO) was functionalized via surface modification by a flame retardant which was synthesized by the reaction of methyl dichlorophosphate and 10-(2,5-dihydroxyl-phenyl)-9,10-dihydro-9-oxa-10-phosphaphenan-threne-10-oxide (DOPO-BQ). The property of functionalized GO (FGO) was characterized by fourier transform infrared spectroscopy, H- and P- nuclear magnetic resonance, X-Ray photoelectron spectroscopy and thermogravimetric analysis (TGA). Series different ratios of GO- and FGO- epoxy nanocomposites were obtained by in situ polymerization. The incorporation of FGO enhanced the thermal stability and flame retardancy of epoxy nanocomposites effectively. The thermal properties of the nanocomposites were investigated by TGA test in nitrogen atmosphere, indicating that FGO can improve the char residues. The flame retardancy of the nanocomposites was characterized by cone calorimeter test. The results showed that the incorporation of 2 wt.% FGO into EP decreased the value of peak heat release rate, total heat release, average effective heat of combustion, peak values of the CO release rate and CO_2 release rate by 25%, 28%, 29.5%, 27% and 29%, respectively. This work confirms that the FGO is an effective solution for improving the thermal stability and flame retardancy of epoxy resins.

KEYWORDS: graphene oxide; functionalization; flame retardant; epoxy.

INTRODUCTION

Graphene, as a new emerging carbon-based material, has attracted increasing attention from industrial to academic fields owing to its thermal, mechanical, and electrical properties. [1-3] With these excellent properties, significant enhancements on the thermal, mechanical, electrical and gas barrier properties are achieved by introducing very low loadings of graphene into polymer matrix. [4-7] Like other layered materials, the unique single-atom two-dimensional sheet structure, composing of sp2 carbon atoms in a hexagonal lattice, has made graphene as a promising flame retardant additive for reducing the fire hazards of the polymer materials. To date, graphene oxide or its derivatives has been incorporated into various kinds of polymers such as Poly (vinyl alcohol) [8], epoxy resins [9-10], polystyrene [11], and ethylene-vinyl acetate [12], investigating the peak heat release rate and smoke release of nanocomposites. However, the irreversible aggregation or restacking of graphene in polymer materials limits their industrial application due to the intrinsic van der Waals force between graphene layers interferes. [13-15] Then the chemical modification could improve the dispersion of graphene in polymer matrices, but general organic compounds may not have effective efficiency to improve the flame retardancy of nanocomposites. Thus, the using of flame retardants to treat the surface of graphene with simultaneously improved dispersion and fire resistance is a feasible approach.

Over the past few years, the halogen-free products such as phosphorus, silicon, and nitrogen compounds have been developed in recent years. [16-18] Phosphorus-containing compounds, one of the promising

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halogen-free FRs, are widely applied to various polymer materials due to its high flame retardant efficiency and non-toxic.[19] Among them, 9,10-dihydro-9-oxa-10- phosphaphenanthrene 10-oxide (DOPO), a cyclic phosphate with a diphenyl structure, has attracted considerable attention due to its high thermal stability, good oxidation and water resistance. It's reported that the P-H bond of DOPO could react with epoxide group of epoxy resins or other groups, indicating DOPO or its derivatives can be used as either reactive or nonreactive FRs for epoxy resins. [20, 21] In the open literature, both the DOPO and its derivatives exhibited high flame retardancy and thermal stability effect on epoxy resins (EP). [22-24] As for the flame retardant mechanism, DOPO mainly play its role in the gas phase via flame inhibition, or in the condensed phase as char formation catalyst at the same time.

Epoxy resins，which have been widely used in surface coating, adhesives, painting and potting materials, laminates, printed circuit boards and insulating materials for electric devices, etc, owing to their excellent mechanical and chemical properties，are very important thermosetting material. [25-28] However, the easy flammability of EP limits its wide range of applications, especially in electronic fields where high flame retardancy is required. To improve the fire resistance efficiency of EP, the combination of graphene with DOPO derivative flame retardant synergistic system is developed. The DOPO-containing polymeric flame retardant is synthesized via the reaction of methyl dichlorophosphate and 10-(2,5-dihydroxyl-phenyl)-9,10-dihydro-9-oxa-10-phosphaphenan-threne- 10-oxide (DOPO-BQ), and subsequently grafted on the surface of graphene oxide. Then the FGO were incorporated into EP to fabricate FGO/EP nanocomposites with different FGO loadings. The structure and morphology of functionalized graphene oxide was characterized by fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance (NMR), X-Ray photoelectron spectroscopy (XPS) and thermogravimetric analysis (TGA). The thermal and combustion properties of FGO/EP nanocomposites were investigated by TGA and cone calorimeter tests.

EXPERIMENT

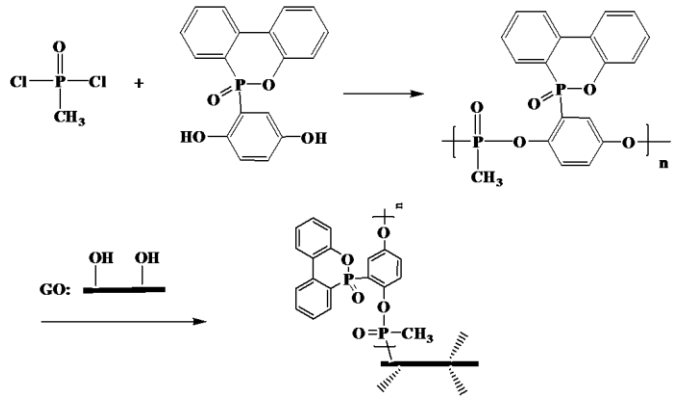
Materials

Expandable graphite (60 mesh) was supplied by Qingdao Tianhe Graphite Co., Ltd. Potassium permanganate ($KMnO_4$), ammonia (25–28% aq.), hydrazine hydrate (85% aq.), hydrogen peroxide (H_2O_2, 30% aq.), hydrochloric acid (HCl), sulphuric acid (H_2SO_4, 98%), triethylamine, dichloromethane, methanol, toluene and tetrahydrofuran (THF) were purchased from Sinopharm Chemical Reagent Co., Ltd. Hydroxyethyl acrylate (HEA), p-benzoquinone (BQ) was purchased from Aladdin Co., Ltd. 9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) was supplied by ShandongMingshan Fine Chemical Industry Co. Ltd. Methyldichlorophosphate (MDCP) was obtained from our group. Epoxy acrylates, which was supplied by Tianjin Tianjiao Co, is a bisphenol A epoxy acrylate with the unsaturation concentration of 3.73mmol/g.

Preparation of FGO with flame retardant

GO was prepared by the Hummers' method and washed with THF to remove water. [29] DOPO-BQ was synthesized by the traditional method. [30]

0.1 mol of DOPO-BQ and triethylamine as the acid-binding agent was dissolved in dried 200 ml of THF into a three-neck flask equipped with a nitrogen inlet, a mechanical stirrer, refluxed and slowly heated to 60 ℃. 0.11 g of MDCP was dispersed in 40 ml THF and then dripped into solution of flask sustained 1 h. The flame retardant oligomer PDBMP was synthesized. The reaction mixture was stirred at 60 ℃ for 12 h under a nitrogen gas atmosphere. Then, 1 g of GO was added in the three-necked flask sonicated for 30 min and the stirred of reaction mixture was continue at 60 ℃ for 12 h under a nitrogen gas atmosphere. After cooling, the suspension was filtered and washed with DMF and methanol, and then dried under vacuum at 50 ℃ for 12 h. The FGO was prepared. The schematic process of the reaction is presented in Scheme 1.



Scheme 1. Synthesis route of FGO

Preparation of EP-GO and EP-FGO nanocomposites via in situ polymerization

Typically, the required portion of GO or FGO was dispersed in THF with sonication and then added into the epoxy with 0.5 h of mechanical stirring and then put in a vacuum oven at 50 ℃ overnight to remove the solvent. The DDM (molar ratio of epoxy group: DDM¼=4: 1) was melted at 120 ℃ and then added into the blending. After that the mixture was stirred for 10 min and poured into mold, pre-cured be prepared at 120 ℃ for 2 h and post-cured at 150 ℃ for 2 h and finally the EP-GO and EP-FGO nanocomposites were prepared. Similarly, the different ratios of GO or FGO and EP (such as 1wt% (EP-GO1 or EP-FGO1) and 2wt% (EP-GO2 or EP-FGO2)) nanocomposites were obtained.

Measurement

FTIR spectroscopy (Nicolet 6700 FT-IR spectrophotometer) was employed to characterize FGO using thin KBr disc. The transition mode of the FTIR was used and the wavelength range was set from 4000 to 500 cm^{-1}. ^{1}H NMR and ^{31}P NMR measurements were conducted on AVANCE 400 Bruker spectrometer at room temperature using $CDCl_3$ as solvent. XPS was studied using a VG ESCALB MK-II electron spectrometer (V.G. Scientific. Ltd, UK). The excitation source was an Al Ka line at 1486.6 eV. TGA and TG-IR were carried out on TGA Q5000 IR thermogravimetric analyzer (TA instruments) and the heating rate is 20 °C/min. The fire safety properties of the FGO-EP nanocomposites were investigated on a Stanton Redcroft cone calorimeter according to ISO 5660-1 standard, with a heat flux of 35 kW/m^2. The dimensions of the samples were 100 × 100 ×3 mm^3.

RESULT AND DISCUSSION

Characterization of FGO

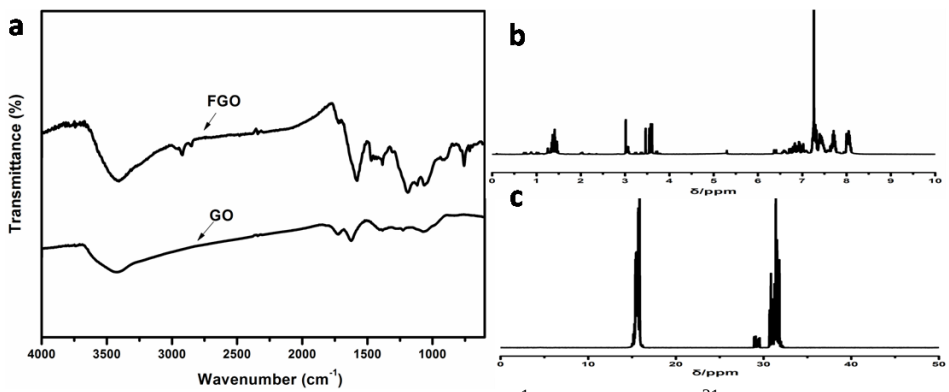


Figure 1. (a) The FTIR spectra of GO and FGO, (b) ^{1}H NMR and (c) ^{31}P NMR spectra of FGO.

The covalent linkage of flame retardant onto GO was confirmed by FTIR (Figure 1a) and ^{1}HNMR (Figure 1b) spectra. In the spectrum of GO, the peak at 1730 cm^{-1} was assigned to the C=O stretching vibration, and the other characteristic absorption bands at 1620, 1065, and 1220 cm^{-1} were assigned to the stretching

vibration of sp2 hybridized carbon, C-O stretching, and C-OH stretching, respectively, similar to the literature [31]. After being functionalized with PDBMP, the distinctive absorption bands appeared: the peak at 2930 cm^{-1} assigned to the stretching vibration of CH_2; the peak at 1460 and 1590 cm^{-1} assigned to the C=C group of phenyl group; the peak at 1190 and 1068 cm^{-1} assigned to symmetric stretching vibration and asymmetric stretching vibration of P=O and P-O; the peak at 1311 cm^{-1} assigned to P-C deformation vibration. These results clearly suggested that PDBMP had been successfully bonded to GO. As can be seen in Figure 1b, the ^{1}H NMR spectra of FGO showed that the characteristic peaks at 6.33-8.17 ppm belonged to the H atoms of phenyl group. And the peaks at 2.99-3.8 and 1.17-1.61 ppm were assigned to the $-CH_2-$ and $-CH_3$, respectively. What's more, ^{31}P NMR spectra of FGO showed that the peaks at 15.19 and 30.95 ppm belonged to the P atoms linked to methyl and phenyl group respectively, and the weak peaks at 28.98 ppm were assigned to the P atoms linked to phenyl group in terminal group of oligomer. All of these results indicated that PDBMP were successfully synthesized and covalently grafted onto the surface of GO.

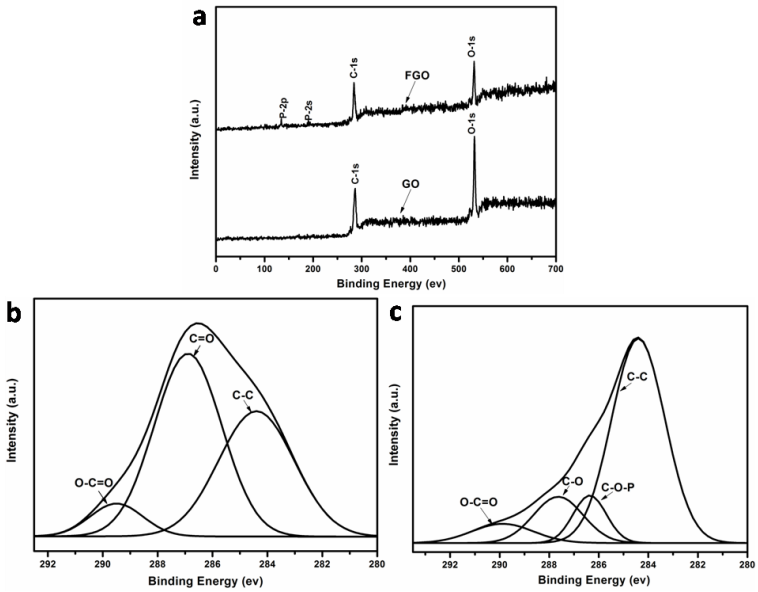


Figure 2. The XPS spectra of GO and FGO (a), C1s peak-fitting curves of GO (b) and FGO (c).

XPS was employed to demonstrate chemical components on the surface of GO and FGO. The C1s and total spectra are shown in Figure 2. It was clearly seen that the peaks at 134.7 and 190.9 eV were attributed to the P_{2P} and P_{2S} of polymer, appeared after functionalized GO in Figure 2a. The C1s XPS spectra of GO and FGO with peak-fitting curves were presented in Figure 2b and 2c. The C1s XPS spectra in Figure 2b showed that the peaks at 284, 287.1 and 289.6 eV were assigned to carbon atoms in C-C, C-O and C=O, respectively. Besides, the oxygen containing functionalities (C-O and C=O) were weakened and the additional component at 286.3 eV was observed for FGO in Figure 2c, which originated from the formation of C-O-P bond by the surface modification of GO. Obvious changes in the binding energy and the intensity was detected in the C1s XPS spectra of GO, which can be attributed to the functionalization of GO with PDBMP. From the combination of FTIR, ^{1}H NMR, ^{31}P NMR and XPS results, it could conclude that GO was successfully modified by PDBMP.

Table 1 The thermogravimetric analysis of GO and FGO in nitrogen.

Sample	Temperature at specific weight loss (°C)		Residues at 800°C (%)
	$T_{-5\%}$ (°C)	T_{max} (°C)	
GO	112	193	53
FGO	162	172	67

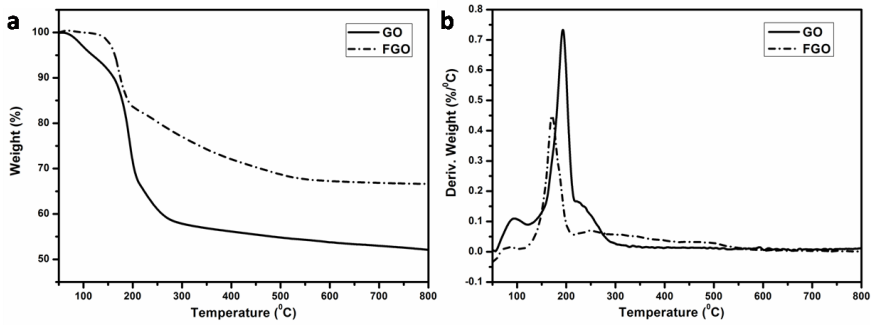


Figure 3. TGA(a) and DTG(b) curves of GO and FGO in nitrogen atmosphere.

Thermogravimetric analysis (TGA) and differential thermogravimetric (DTG) plots for the GO and FGO in nitrogen atmosphere were investigated and the results are shown in Figure 3 and Table 1. As can be seen from the curve of GO in Figure 3, the first mass loss stage below 100 ℃ was due to the evaporation of the adsorbed water, and the maximum mass loss temperature (T_{max}) around 200 ℃ is caused by the decomposition of labile oxygen functional groups[32-33]. The 52.7 % residual char at 800 ℃ was obtained after the steady loss at 300–800°C. For FGO, the 5% mass loss temperature ($T_{-5\%}$) which was defined as the initial degradation temperature increased from 112 to 165 ℃, suggesting that the labile oxygen groups in GO were partly replaced by PDBMP. The maximum weight loss of FGO around 200 ℃ was attributed to the residual oxygen functional groups, while the decomposition of the PDBMP in FGO was occurred between 200 and 300 ℃. However, the residual char of FGO was increased to 66.6% at 800 ℃, which may be due to the pyrolysis of phenyl group in PDBMP. Therefore, the TG results confirmed that the functionalization of GO not only well grafted the flame retardant onto GO but also improved the thermal stability of GO.

Thermal stability of EP-GO and EP-FGO nanocomposites

Table 2 The thermogravimetric data of EP-GO and EP-FGO nanocomposites in nitrogen.

Sample	Temperature at specific weight loss (°C)		Residues at 700°C (%)
	$T_{-5\%}$ (°C)	T_{max} (°C)	
EP	371	387	15
EP-GO1	366	384	15
EP-GO2	361	383	16
EP-FGO1	368	385	16
EP-FGO2	362	386	18

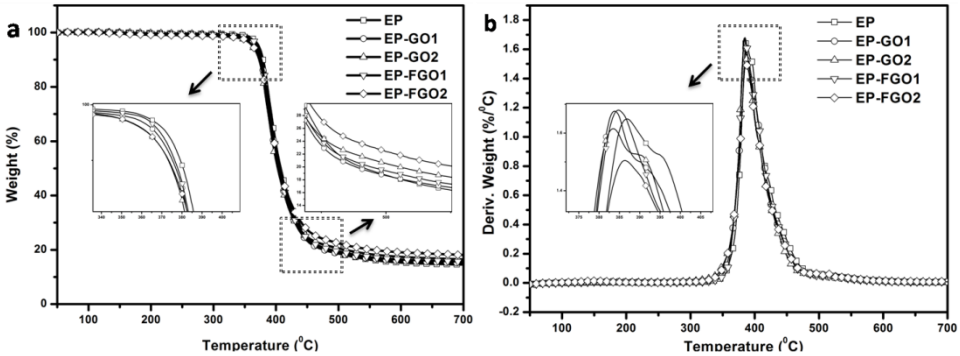


Figure 4. TGA(a) and DTG(b) curves of EP-GO and EP-FGO nanocomposites in nitrogen atmosphere.

The thermal stability and thermal degradation process of EP nanocomposites were investigated by TGA under nitrogen atmosphere. The TGA and DTG curves of EP-GO and EP-FGO nanocomposites were recorded in Figure 4 and the relative data, such as $T_{-5\%}$, T_{max} and the residues at 700 °C, were listed in Table 2. As for the thermal degradation of neat EP, the material began to lose mass at about 360 °C and degraded almost completely before 600°C. Only one DTG peak at about 370 °C was observed which corresponded to that the

macromolecular chains of EP degraded and small molecular degradation products released and then formed char residue. In comparison with EP, the $T_{-5\%}$ and T_{max} of EP-GO and EP-FGO nanocomposites were decreased due to the thermal degradation of GO and FGO, but the final char residues at 700 ^{o}C were increased. When the loading amount of GO increased from 1% to 2%, the $T_{-5\%}$ and T_{max} of EP nanocomposites decreased, which was attribute to the increase of labile oxygen functional groups on the surface of GO. However, the T_{max} value was increased after the addition of FGO, which may be due to the flame retardant grafted on GO promoted the char formation. Therefore, the increase of char residue can form a barrier to protect the nanocomposites from further oxidative degradation.

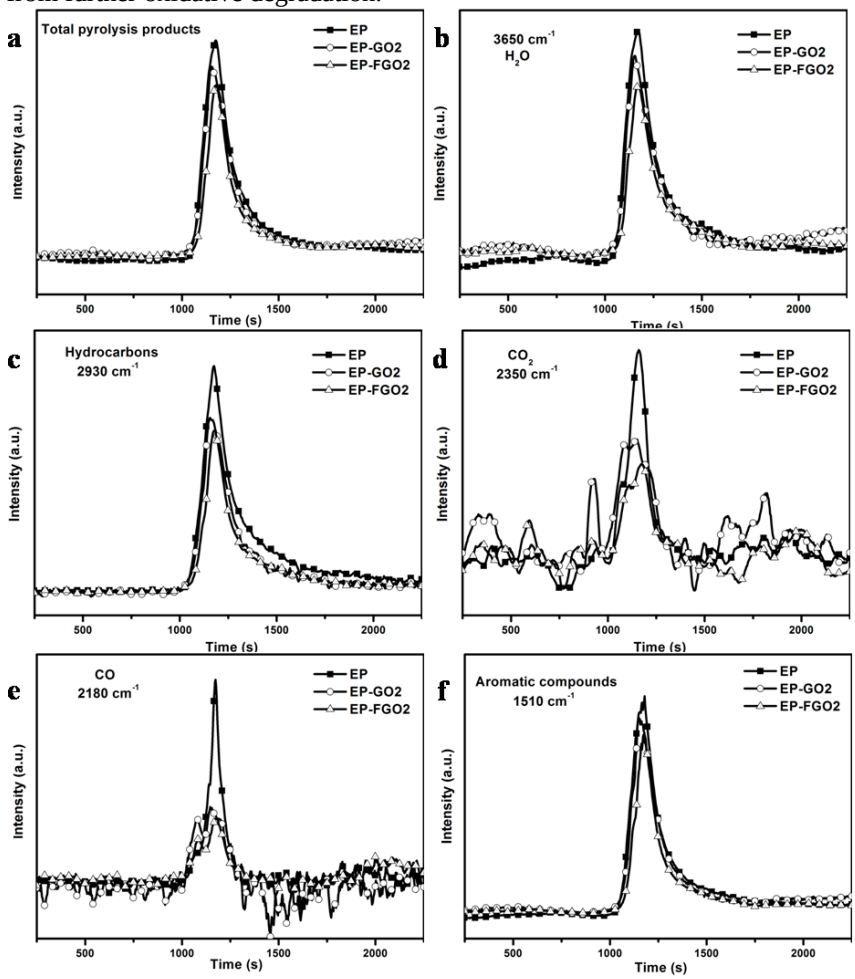


Figure 5. Absorbance of pyrolysis products for EP nanocomposites vs time: (a) total pyrolysis products; (b) H_2O; (c) hydrocarbons; (d) CO2; (e) CO and (d) aromatic compounds.

The gas products during the thermal degradation were analyzed by TG-FTIR measurement. As for FTIR, the characterized peaks at 3650, 2930, 2360, 2310 and 1510cm^{-1} were attributed to H_2O, the hydrocarbons compounds, CO_2, CO, aromatic compounds of the gaseous decomposition. It was well-known that decomposition was the main process associated with the thermal degradation of polymers. In the process of decomposition of EP nanocomposites, the main decomposition products were H_2O, the hydrocarbons compounds, CO_2, CO, aromatic compounds, and etc.

The absorbance of temporal evolution of pyrolysis products for EP, EP-GO2 and EP-FGO2 were evaluated in Figure 5. It showed that the pyrolysis products for EP began to release at about 16 min, whereas those for EP-GO2 and EP-FGO2 were decomposition early, due to the pyrolysis of functional groups on the surface of GO. However, the absorbance intensity of pyrolysis products for EP-GO2 and EP-FGO2 was lower than that for EP. It could be interpreted that the GO had the capability to prevent the pyrolysis of matrix, and the flame retardant modified GO had more effective efficiency to restrain the pyrolysis of matrix. Consequently, the GO and FGO added could reduce the release of combustible gas and the weight loss, and the results of the pyrolysis products release corresponded well to thermal analysis.

Flame retardancy of EP-GO and EP-FGO nanocomposites

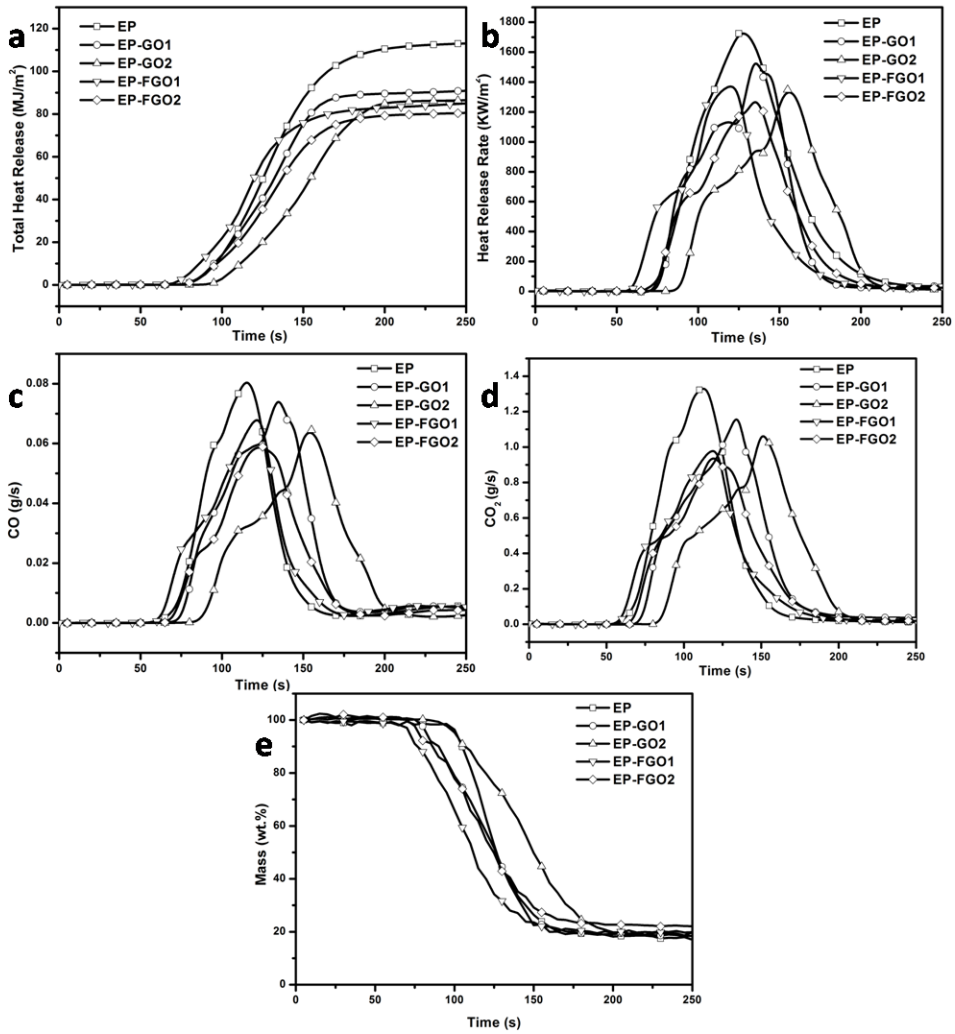


Figure 6. Cone calorimeter test results: the temporal evolution of (a) HRR curves; (b) THR curves; (c) CO_2; (d) CO yield and (e) mass of EP nanocomposites.

Table 3 The related cone calorimeter data of EP-GO and EP-FGO nanocomposites.

Sample	Time to PHRR (s)	PHRR (KW/m^2)	THR (MJ/m^2)	Average EHC (MJ/kg)	P-CO[a] ($g\ s^{-1}$)	P-CO_2[a] ($g\ s^{-1}$)	CO/CO_2 (%)
EP	130	1730	114.2	16.62	0.83	1.34	6.60
EP-GO1	135	1582	92.5	16.48	0.76	1.19	7.34
EP-GO2	155	1348	87.1	14.83	0.65	1.08	7.03
EP-FGO1	120	1406	86.1	14.12	0.69	1.03	7.03
EP-FGO2	135	1297	81.4	11.71	0.60	0.95	6.33

[a] The peak values of the CO release rate and CO_2 release rate, respectively.

Cone calorimeter is a useful bench-scale tool as a test to analyze combustion behaviors and fire safety of materials. Figure 6 showed the temporal evolution of heat release rate (HRR), total heat release (THR) curves, CO_2 yield, CO yield, mass and the related data of EP-GO and EP-FGO nanocomposites were presented in Table 3. It could be obviously seen that the THR, peak heat release rate (PHRR), average effective heat of combustion (EHC), peak values of the CO release rate and CO_2 release rate were decreased after adding GO and FGO. It was attributed to the physical barrier effect of GO or FGO and the strong interfacial interactions between GO or FGO and EP. As compared to the neat EP, the maximum reduction was occurred in EP-FGO2,

of which the PHRR, THR, average EHC, P-CO_2, and P-CO decreased by 25%, 28%, 29.5%, 27% and 29%, respectively. With the GO loading amount of 1 to 2 wt.%, the PHRR and THR decreased by about 15% and 6%, respectively, and the similar trend was observed for FGO-epoxy nanocomposites. FGO performed much better than GO to improve the fire safety properties of EP from the cone calorimeter data. In the case of 1% loading for the GO and FGO, the value of PHRR, THR, P-CO_2, and P-CO was decreased by 11%, 7%, 10% and 13%, respectively. The value of CO/CO_2 ratios showed that EP-FGO2 displayed the best extent of combustion than other samples. It may be due to that the flame retardant grafted on FGO catalyzed the more char formation of EP-FGO nanocomposites than that of GO, and then the char as the barrier restrained the release of CO and CO_2. The time to ignition (TTI) was delayed when the loading amount increased, however, the TTI value was decreased for FGO. It was attributed to the pyrolysis of the flame retardant grafted on the surface. The mass loss curve showed that the char residual of EP-FGO was more than EP and EP-GO and the time of decomposition was also delayed compared to EP and EP-GO, suggesting the results of TGA measurement. The results indicated that flame retardant modified GO lead to decrease of THR of nanocomposites because of more char residue produced to isolate the heat release. Therefore, the addition of GO enhanced the fire safety properties of the composites, and the EP-FGO displayed the better fire safety properties.

CONCLUSION

In this paper, functionalized graphene oxide with flame retardant was synthesized and then applied to prepare the epoxy nanocomposites via in situ polymerization. The results of FTIR, ^{1}H NMR, ^{31}P NMR and XPS indicated that the PDBMP was successful synthesized and covalently grafted onto the surface of GO. The TGA and TG-IR data showed that thermal stability of graphene oxide was improved after the functionalization. The incorporation of FGO into EP obviously improved the char yields and the thermal stability compared with EP-GO nanocomposites. The char formed as the physical barrier effect of GO or FGO had a great effect of flame retardancy of EP nanocomposites, of which the PHRR, THR, EHC, CO_2 yield and CO yield were decreased after adding GO and FGO. In conclusion, this work represents that functionalized GO with flame retardant is an effective additive to enhance the thermal stability and fire safety properties of polymers.

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