

Radiation Cured Epoxy Acrylate Composites Based on Graphene, Graphite Oxide and Functionalized **Graphite Oxide with Enhanced Properties**

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Epoxy acrylate (EA) composites containing graphite oxide (GO), graphene and nitrogen-double bond functionalized graphite oxide (FGO) were fabricated using UV-radiation and electron beam radiation via in-situ polymerization. Graphene and FGO were homogenously dispersed in EA matrix and enhanced properties, including thermal stability, flame retardancy, electrical conductivity and reduced deleterious gas releasing in thermo decomposition were obtained. Microscale combustion colorimeter results illustrated improved flame retardancy; EA/FGO composites achieved a 29.7% reduction in total heat release (THR) when containing only 0.1% FGO and a 38.6% reduction in peak-heat release rate (PHRR) when containing 3% FGO. The onset decomposition temperatures were delayed and the maximum decomposition values were reduced, according to thermogravimetric analysis which indicated enhanced thermal stabilities. The electrical conductivity was increased by 6 orders of magnitude (3% graphene) and the deleterious gas released during the thermo decomposition was reduced with the addition of all the graphite samples. This study represented a new approach to functionalize GO with flame retardant elements and active curable double bond to achieve better dispersion of GO into polymer matrix to obtain nanocomposites and paved a way for achieving graphene-based materials with high-performance of graphene in enhancement of flame retardancy of polymers for practical applications.

Keywords: Graphene, Radiation Curing, Flame Retardancy, Thermal Stability, Deleterious Gas Release.

1. INTRODUCTION

As one of the most interesting materials, graphene has triggered enormous interest due to its unique properties induced by its 2D one-atom thick carbon layer structure. Individual graphene combines extraordinary high aspect ratio, enormous specific surface, high values of Young's modulus (~1100 GPa), fracture strength (~125 GPa), elastic modulus (~0.25 TPa), thermal conductivity (~5000 Wm⁻¹ K⁻¹) and mobility of charge carriers ($\sim 200000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$),¹⁻⁴ etc, which endow graphene with great potential applications such as photovoltaic devices, sensors, transparent electrodes and supercapacitors.5-10

Polymers are widely used in various fields for their flexibility, chemical resistance, endurance, waterproofing, low density and low cost. However, most polymers are flammable and the mechanical properties are far away from perfect, which limit their industrial application. To

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remedy these disadvantages, polymers are often compounded with a variety of fillers such as clay, layer double hydroxide (LDH), expandable graphite, graphite oxide and carbon nanotubes, etc.¹¹⁻²³ Recently, graphenepolymer composites have been a hot issue due to the comprehensive and efficient enhancements in various properties. The incorporation of graphene usually leads to significantly enhanced properties such as mechanical properties, electrical conductivity and gas resistance, etc.^{10, 24-26} It is well known that the dispersion and interface are two key factors to improve the property performance of polymer composites based on 2-D layered materials.²⁷⁻²⁸ Lamentedly, graphene easily re-aggregates due to its high surface area and the strong intrinsic van der Waals force between the nano-sheets, which counteracts its dispersion in polymer matrix. Thus, functionalized graphene (oxide) with functional groups on graphene (oxide) surface which may improve the dispersion and interaction has been a promising strategy to obtain high performance polymer composites.^{28–33} In addition, the layered structure

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of graphene and its derivate slows down the diffusion of pyrolysis products and oxygen in the thermo decomposition process, acting as physical barrier to increase the thermal stability of polymer composites, similar to that of montmorillonite (MMT) and layered double hydroxide (LDH), both of which have attracted considerable attention in the past two decades in polymer nanocomposites.³⁴⁻³⁸ However, due to its large value of thermal conductivity, graphene layers are not good barrier to slow down the heat transfer, thus it has not present obvious effect to improve the flame retardancy in polymer composites.

Herein, in order to efficiently improve the dispersion of graphene nano-sheets in polymeric matrix and enhance the flame retardancy of polymer composites, flame retardant elements and active double bond which can be cured with epoxy acrylate were introduced. Chemical reduction of graphite oxide (GO) has been the most convenient way to obtain graphene, which also offers chemical active points, making chemical functionalization realizable. Starting from GO, graphene and functionalized graphite oxide (FGO) were prepared and incorporated into epoxy acrylic. Epoxy acrylic (EA) with high adhesion and high strength is a UV curable polymer widely used in industry, whereas the flammable defect restricts some applications, thus flame retardant systems to reduce the fire hazards are needed to be introduced. The blending was cured with a radiation curing method, which can instantaneously convert low-viscosity oligomer into a polymerized and crosslinked polymer network with reduced solvent emission.³⁹ The obtained composites, particularly EA/graphene and EA/FGO composites, present improved electrical conductivity, enhanced flame retardancy and reduced gas releasing, which may improve the industrial application of EA and graphene.

2. EXPERIMENTAL DETAILS

2.1. Materials

Expandable graphite (EG, mesh 325, purity >99%) was supplied by Qingdao Tianhe Graphite Co., Ltd (China). Potassium permanganate ($KMnO_4$), hydrochloric acid (HCl), sodium nitrate (NaNO₃), ethanol (C₂H₅OH), hydrazine hydrate (85%), hydrogen peroxide (H_2O_2) and dibutyltin dilaurate (DBTD) were purchased from Sinopharm Chemical Reagent Co., Ltd. (China); bisphenol A epoxy acrylate, with a unsaturation concentration of 3.73 mmol g^{-1} and a molar mass of 536 g mol⁻¹, was supplied by Tianjin Tianjiao Co. (China); isophorone diisocyanate (IPDI) was purchased from the First Reagent Co. of Shanghai (China) and it was distilled before use; 2-hydroxylethyl acrylate (HEA) was supplied by Dongfang Chemical Co (China) and it was distilled before use. 2-Hydroxy-2-methyl-1-phenyl-1-propanone (Darocur 1173, photoinitiator) was kindly supplied by Ciba Specialty Chemicals (Singapore).

2.2. Preparation of Graphite Oxide, Graphene and **Functionalized Graphite Oxide**

The preparation route is shown in Scheme 1.

Graphite oxide (GO) was prepared by modified Hummers' method. Briefly, 115 mL H₂SO₄ was placed in a four-neck flask and cooled in an ice bath, followed by the addition of 5 g expandable graphite (EG) and 2.5 g NaNO₃. The mixture was stirred for 15 min below 5 °C, then 37.5 g KMnO₄ was slowly added and the temperature was controlled between 16 °C and 20 °C. After 30 min stirring below 10 °C, the mixture was heated to 35 °C to react for 60 min. Then 230 mL deionized water was added dropwise into the mixture and the temperature was controlled at 96-98 °C. After 30 min reaction, the viscous mud was diluted by 1000 mL water and suitable amount of 30% H₂O₂ was added to reduce the unreacted KMnO₄ until the slurry turned golden yellow. The suspension was centrifuged, washed with dilute hydrochloric acid and hot water until the pH value reached \sim 7, and finally wet GO was obtained.

In a typical procedure to prepare graphene, wet GO was dispersed in deionized water with ultrasonication until no visible particle was observed. Hydrazine hydrate (mass ratio of GO: hydrazine about 10:7) was added and the mixture was heated in an oil bath at 90 °C under a reflux condenser for 8 h. Graphene gradually precipitated out as black particles which was centrifuged and washed with acetone to get graphene acetone dispersion.

To prepare FGO, isophorone diisocyanate (IPDI, 0.02 mol, 4.448 g), 4-methoxyphenol (0.068 g, inhibitor) and dibutyltin dilaurate DBTD (6.8 mg, catalyst) were poured into a three-necked flask equipped with a nitrogen inlet, a mechanical stirrer, a reflux condenser and a dropping funnel; the flask was filled with nitrogen and put into an oil-bath at 40 °C, and HEA (2.23 g, 0.2 mol) was slowly dropped in. The reaction lasted 12 hours at 50 °C and was maintained for 12 h to obtain IPEA. After that, 4-methoxyphenol (0.068 g) and DBTD (6.8 mg) were added into the as-obtained blending with stirring; 0.5 g GO (in 20 mL acetone) was then added and the temperature was kept at 60 °C. After 12 hours mechanical stirring, the mixture was filtered and washed with deionzed water and chloroform to remove triethylamine hydrochloride and impurities, and FGO was finally obtained.

2.3. Preparation of Epoxy Acrylic Resin Based Nanocomposites

The EA/GO nanocomposites were prepared as follows: first, GO was dispersed in acetone with ultrasonication to obtain well dispersed suspension which was then added to the EA oligomer with stirring for 0.5 hour. The homogeneous solution was put in a vacuum oven at 50 °C overnight to remove the solvent. Second, 3% Darocur 1173 (photoinitiator) were dropped into the mixture with



Scheme 1. Preparation route of functionalized GO.

stirring to obtain homogenous blending which was then poured into a stainless steel mold, followed by pre-curing using UV irradiation equipment (80 W cm⁻¹, Lantian Co., China). Third, the molded samples were irradiated using an electron beam accelerator (RDI-Dynamitron, DPC-2000 Control System, Dasheng Co., China) under forced air cooling with irradiation doses (60 kGy). Finally, the EA/GO composites were obtained. EA/graphene and EA/FGO composites were prepared with the same process.

2.4. Characterization

X-ray diffraction (XRD) pattern was performed on the 1 mm thick films with a Japan Rigaku D/Max-Ra rotating anode X-ray diffractometer equipped with a Cu K α tube and Ni filter ($\lambda = 0.1542$ nm). The scanning rate was 4°/min and the range was 3–65°.

Fourier transform infrared (FTIR) spectra were obtained using Nicolet 6700 FTIR (Nicolet Instrument Company, by USA) between 500 and 4000 cm⁻¹. Samples were shaved to powder and mixed with KBr powders and pressed into 5.2 tablets before characterization.

X-ray photoelectron spectroscopy (XPS) was obtained using a VG ESCALB MK-II electron spectrometer. The excitation source was an Al K α line at 1486.6 eV.

Atomic force microscopy (AFM) observation was performed by DI Multimode V scanning probe microscope. The samples were dispersed in water and dip-coated onto freshly cleaved mica surfaces before the test.

Measurements of volume resistivity and surface resistivity of the samples were investigated with ZC36 high resistance meter (Cany Precision Instruments Co., LTD., China). Specimen with the size of $10 \times 10 \times 1$ mm³ was applied as the test sample.

Thermogravimetric analysis (TGA) were carried out on a TGA Q5000IR (TA Instruments, USA) thermo-analyzer instrument from 30 to 650 °C (700 °C) at a heating rate of 20 °C/min under air flow. Samples of about 5.0 mg were measured in an alumina crucible. Two parallel runs were performed in the case of each sample.

Transmission electron microscopy (TEM) images were obtained on a JEOL JEM-100SX microscope with an acceleration voltage of 100 kV. TEM specimens of GO, graphene and FGO were washed with ethanol and collected on a 200 mesh copper grids. The EA nanocomposites were performed with ultrathin sections microtomed using an Ultratome (Model MT-6000, Du Pont Company, USA) equipped with a diamond knife.

The morphologies of the surface of fracture from the composites sputtercoated with a gold layer in advance were investigated by a scanning electron microscopy (SEM) AMRAY1000B (Beijing R&D center of the Chinese academy of sciences, China).

Thermogravimetric analysis/infrared spectrometry (TG-IR) was carried out using a TGA Q5000 IR thermogravimetric analyzer interfaced to the Nicolet 6700 FTIR

J. Nanosci. Nanotechnol. 12, 1776–1791, 2012

spectrophotometer (Nicolet Instrument Company, USA). About 5.0 mg of the sample was put in an alumina crucible and heated from 30 to 650 °C at a heating rate of 20 °C/min (nitrogen atmosphere, flow rate of 45 ml/min).

Combustion testing was performed using GOVMARK MCC-2 Micro Combustion Colorimeter (MCC, USA). The incident heat flux was 45 kW/m² and about 5 mg of each sample was heated to 650 °C at a heating rate of 1 °C/s and in a stream of nitrogen flowing at 80 cm³/min; each test was repeated twice.

EA composites were scanned by differential scanning calorimetry (DSC) at 50 °C/min ramping to investigate the influence of various forms of graphite on the glass transition temperature (T_g) .

3. RESULTS AND DISCUSSION

3.1. Structural Characterization of EG, GO, y Ing Graphene and FGO South Australia 23.1.15 XRD

Figure 1 shows the XRD patterns of EG, GO, graphene and FGO. The pristine expandable graphite exhibits a strong (002) diffraction peak at $2\theta = 26.5^{\circ}$, corresponding to an interlayer distance of 0.34 nm. In the pattern of GO, the (002) peak increases to 10.31°, demonstrating the interlayer spacing expanded to 0.69 nm , which is in agreement with previous results.⁴⁰ After reduction by hydrazine, the resulting graphene sheets present no obvious peaks, indicating the exfoliation of GO sheets during the reduction process to form individual graphene nano-sheets as confirmed in the AFM section. The FGO has similar pattern as graphene, demonstrating long range disorder, and it may be caused by the introducing of IPEA which chemically bonds with graphite oxide during the modification process and extends the d-spacing to form individual sheets.



Fig. 1. XRD curves of the pristine expandable graphite, graphite oxide, graphene and functionalized graphite oxide.

3.1.2. FTIR

The FTIR spectra of samples got from the reaction vessel before and after the reaction of IPEA with GO were shown in Figure 2 to trace the functionalization process. The peak at 2267 cm⁻¹ corresponding to N=C=O vibration from IPEA gradually disappears, indicating the reaction of N=C=O with –OH and –COOH from GO.

Figure 3 shows the IR spectra of pristine EG, GO, graphene and FGO. The small peaks on EG pattern are caused by the intercalated acid and oxidant. The GO pattern shows characteristic peaks which is in good agreement with earlier work.^{41–42} After the hydrazine reduction, all the oxygen containing groups become very weak and a new peak around 1560 cm⁻¹ attributed to the stretching vibration of C=C from an aromatic group appears. In FGO, some new peaks appear: the peak at 2964 cm⁻¹ corresponds to $-CH_2$ -, the peak at 1535 cm⁻¹ is assigned to y C=C, and two peaks at 1235 cm⁻¹ and 1192 cm⁻¹ can be a scribed to -COO-. All of these peaks provide evidence for the successful grafting of IPEA onto graphene sheets, 2000 cm⁻¹ attributed to the successful grafting of IPEA onto graphene sheets, 2000 cm⁻¹ attributed to the successful grafting of IPEA onto graphene sheets, 2000 cm⁻¹ attributed to the successful grafting of IPEA onto graphene sheets, 2000 cm⁻¹ attributed to the successful grafting of IPEA onto graphene sheets, 2000 cm⁻¹ attributed sheets, 2000 cm⁻¹ attributed sheets, 2000 cm⁻¹ attributed sheets, 2000 cm⁻¹ attributed sheets, 2000 cm⁻¹ correspondence sheets, 2000 cm⁻¹ cm⁻¹ sheets cm⁻¹ cm⁻

3.1.3. XPS

The high-resolution narrow scans of the C_{1s} and N_{1s} envelope region of GO, graphene and FGO with the prominent components are marked in Figures 4 and 5. In Figures 4(a) and (b), three types of carbon can be observed: C–C, C–O and O–C=O.⁴³ The reduction process results in a remarkable decrease of O/C ratio and the peak corresponding to C–C (284.8 eV) becomes dominant in graphene, which confirms successful reduction of GO. In Figure 4(c), a new peak of C–N (284.8 eV) arises, confirming the successful bonding of IPDI and HEA onto the GO sheets, and the increment of the relative content of O–C=O (289.2 eV) is



Fig. 2. The FTIR spectra of IPEA before and after the reaction with GO.



Fig. 3. The FTIR spectra of graphite oxide, reduced graphite oxide and functionalized graphite oxide.

caused by the formation of O–C=O bond during the functionalized process of GO. N_{1s} envelope region was used to confirm the incorporation of nitrogen as shown in Figure 5. The faintness signal of nitrogen of GO is due to the NO_2 (403 eV) and NO_3 (401 eV) groups left during the oxidation of GO. Nitrogenated carbon signals in graphene can be attributed to partial reduction of carbonyl functionalities into hydrazone groups.^{44–45} As a conclusion, functionalized process of FGO results in a C–N peak (399.8 eV), indicating the successful bonding of IPEA onto the GO sheets.

3.1.4. AFM

The AFM observations of GO, graphene and FGO with the height profile taken along the lines inside were shown in Figure 6. The cross-sectional view of the typical AFM image of the exfoliated GO sheet indicated lateral dimensions of hundreds of nanometers and average height of 0.7~0.8 nm, similar to the interlayer distance of GO (0.69 nm) measured by XRD. For single graphene sheets, height profiles show steps from the mica to graphene sheet of 0.7 nm for the given cross-section (Fig. 6(b)). Compared to theoretical values for graphene, there is discrepancy of 0.3~0.4 nm in thickness demonstrating the presence of some residual oxygen groups on the sheets which is in agreement with other reports.⁴⁶ The apparent heights of FGO (Fig. 6(c)) sheets observed were around 1.3 nm, larger than that of the pristine GO, which may be caused by the modifier chemically bonding to the FGO sheets.

3.1.5. Thermal Decomposition Behavior

The thermal decomposition behavior of GO, graphene and FGO were analyzed in air and the results are shown in Figure 7. Graphite oxide is not thermally stable, and its decomposition process can be divided into two stages: the



Fig. 4. High-resolution XPS narrow scans of the C 1s region for GO (a) graphene (b) and FGO(c).

first stage, between 200–270 °C, is caused by the decomposition of oxygen containing groups such as hydroxyl, carboxyl on the graphite sheets to give birth to CO, CO_2 and steam;⁴⁷ the second stage, 440~550 °C, is due to the



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Fig. 5. High-resolution XPS narrow scans of the N 1s region for GO (a) graphene (b) and FGO (c).

combustion of the carbon framework⁴⁸ and the residual char at 650 °C is 13%. The thermal stability of graphene is greatly improved due to the decrease in defect density during the reduction process. As shown in Figure 7, graphene presents no significant mass loss detected until 500 °C, and the char residue at 650 °C is increased from 13% of GO to 24%. FGO is more stable than GO below 350 °C with a reduced char residue of 0.8%. The unstable behavior at high temperature may be caused by the functional groups with ester bonds and urethane links.

3.2. Electrical Microscopy Characterization of EA Composites

Via electrical microscopy, one can directly observe the micro-structure and dispersion of nano-fillers in polymeric matrix.^{11, 27, 49} From SEM images (Fig. 8), it is clear that the GO, graphene and FGO sheets were dispersed uniformly into the substrate and they appeared flattened without large bundles. However, the EA composites have rough



Fig. 6. AFM images of GO nanosheets dispersed in water and graphene dispersed in THF.



Fig. 7. TG and DTG curves of GO, graphene and FGO in air atmosphere.



Fig. 8. SEM micrograph showing the morphology of fracture surface of Graphite fillers in EA composites with GO (graphene or FGO) content of 1 wt%. (The scale bar is $10 \ \mu$ m).

cross-sections, indicating that nano-fillers have already been embedded in EA matrix with good dispersion.

The inner structures of EA composites with 1% addition amount of graphite fillers were examined by TEM technique as shown in Figure 9. For the EA/GO composites, the dispersion of GO is not completely uniform with some particle settlement, which is in analogy to the fact that the oxygen-containing groups such as carboxyl and hydroxyl groups form strong interactions including hydrogen bond and vander Waals force interaction between GO sheets, hindering the dispersion of GO in polymeric matrix. For EA/graphene composites, no particle settlement and aggregates were observed and isolated graphene sheets were homogeneously dispersed in the polymer matrix; one can observe single or few layer graphene nano-sheets with thickness less than several nanometers, indicating good compatibility of graphene in EA composites due to the elimination of polar groups which weakens



the interaction between graphene nano-sheets. As for the EA/FGO composites, no big bundles were observed and the dispersion was uniform throughout the EA matrix with intercalated-exfoliated structure, which can be attributed to the enhancement of interactions between FGO nano-sheets and EA matrix due to the crosslink of EA matrix and active double bond in FGO. Thus the incorporation of active double bond is effective to disperse graphene/GO sheets in polymeric matrix.

3.3. Electrical Properties

The volume resistivity (ρ_v) and surface resistivity (ρ_s) of EA composites were summarized and plotted in Figure 10. Pure EA has a volume resistivity of $6.2 \cdot 10^{15} \ \Omega \cdot cm$ and a surface resistivity of $2.3 \cdot 10^{15} \ \Omega/cm$. With the increase of graphite fillers addition amounts, the resistance decreases, respecially in EA/graphene composites. The volume resistivity is decreased approximately one order of magnitude when containing 3% GO, two orders of magnitude when containing 3% FGO and six orders of magnitude when containing 3% graphene, and the surface conductivity shows the similar trend.



Fig. 9. TEM micrograph showing the dispersion of graphite fillers in EA composites with (graphene or FGO) content of 1 wt%. (The scale bar is 0.5 μ m for EA/1 wt% GO composite and 200 nm for EA/1 wt% Graphene and EA/1 wt% FGO).

Fig. 10. The volume resistivity (ρ_v) and surface resistivity (ρ_s) of EA composites.

The high aspect ratio, large specific surface area of the graphene sheets may provide extra charge carriers linking the conductive channel of the EA matrix, thus increase the conductivity. For GO and FGO composites, there are many oxygen containing groups bonding at the edges causing defect which limits the increment in conductivity. As for graphene, the restoration of sp² C–C bonds resulted in significant improvements in electrical conductivity of EA/graphene composites. The slightly higher conductivity of EA/FGO composites compared to EA/GO composites at high content may be due to the double bonds at the FGO

edges enhancing the interaction between the FGO sheets and the EA matrix.

3.4. Thermal Stability and Flame-Retardant Properties of EA and EA/G Composites

3.4.1. TGA

The degradation process of EA and EA composites in air atmosphere are investigated by TGA as shown in Figure 11. The thermal degradation process of EA and EA



Fig. 11. TG and DTG curves of EA composites in air atmosphere.

Sample ID.	T- _{5%} (°C)	$T_{\max 1}$ (°C)	$T_{\rm max2}$ (°C)	Char residue a 700 °C
EA	310	419	569	0
EA/0.5% GO	277	426	590	1.0%
EA/1% GO	303	427	588	1.6%
EA/3% GO	289	430	585	2.0%
EA/0.5% Graphene	329	425	585	1.6%
EA/1% Graphene	309	428	587	2.0%
EA/3% Graphene	309	423	590	1.1%
EA/0.5% FGO	280	418	583	1.4%
EA/1% FGO	305	417	571	2.4%
EA/3% FGO	280	414	564	1.8%

Table I. TG data of EA composites in air.

composites have two stages in the temperature ranges of 350–450 °C and 550–650 °C, and the corresponding T_{max1} and $T_{\rm max2}$ obtained from the DTG curves as well as the onset temperature marked as $T_{5\%}$, and the char residue at 700 °C are listed in Table I. The thermal stability of EA is influenced a lot by the presence of graphite fillers. The by 1 onset degradation temperatures of EA/GO and EA/FGO Sou composites decrease due to the unstable oxygen-containing groups, while the EA/graphene composites decompose later for the elimination of oxygen containing groups on graphene sheets. The $T_{\rm max1}$ and $T_{\rm max2}$ increase by 10–20 °C and the char residue increases a little in EA/GO and EA/graphene samples, indicating improved thermal stabilities. T_{max1} of EA/FGO composites shows no obvious change, and $T_{\text{max}2}$ increases when containing 0.5% and 1% FGO but further decreases with 3% addition. Moreover, the DTG peaks are decreased compared to EA. The addition of graphite fillers can improve the thermal stability of EA composites, which can be attributed to the layer barrier effect and the absorption of free-radicals generated during polymer decomposition by the carbon surface. The layered structure of graphite fillers can act as a barrier preventing the transfer of combustion gases to the flame zone and energy feedback to increase the thermal stability.50-52

3.4.2. DSC

Figure 12 shows the DSC results. T_g of the EA composites shifts to lower temperature with the increase amount of GO (15.6 °C, 3% GO), graphene (17.3 °C, 3% graphene) and FGO (21.4 °C, 3% FGO), indicating that the graphite layers can act as a plasticizer increasing the flexibility of chain segments, thus improve the mobility of the EA chain segments.

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3.4.3. MCC

MCC is a new, direct and effective technique to investigate the combustion and heat release behaviors by directly measuring the released heat when samples are burning.⁵³ HRR (heat release rate) expressing the intensity of a fire is an important parameter to predict the combustion behavior of a material in a real fire.



Fig. 12. DSC curves of EA composites showing the $T_{\rm g}$ results in N₂ atmosphere.

The flammability properties of the EA composites are analyzed by MCC under N_2 and the results are shown in Figure 13, with the HRR, THR and T_{max} data summarized in Table II. It is found that the total heat released (THR)



Fig. 13. HRR curves of EA/G composites from MCC test in N_{2} atmosphere.

of all the EA composites decrease with increase content of graphite fillers. Compared to pure EA, the decrement of THR is 16.1%, 30.3% and 31.3% for EA/3% GO, EA/3% graphene and EA/3% FGO, respectively, indicating that graphene and FGO perform better than GO. Meanwhile, the Peak-HRR (PHRR) decreases as the additives increase,

Table II. MCC data of EA composites in N_2 .

Sample ID.	PHRR (w/g)	THR (kJ/g)	$T_{\rm max}$ (°C)
EA	331.4	21.2	440
EA/0.5% GO	243.7	21.1	438
EA/1% GO	234.1	20.0	435
EA/3% GO	205.3	17.7	427
EA/0.5% Graphene	253.2	16.4	436
EA/1% Graphene	241.0	16.2	423
EA/3% Graphene	228.6	14.7	424
EA/0.5% FGO	235.4	14.6	427
EA/1% FGO	227.4	15.0	417
EA/3% FGO	210.3	15.5	414

and the reduction is 38.6%, 32.5% and 38.6% respectively for EA/3% GO, EA/3% graphene and EA/3% FGO. In addition, the temperature at maximum pyrolysis rate (T_{max}) decreases a little because of the low initial thermal stability of the fillers. The EA/Graphene and EA/FGO composites show better flame retardant properties than EA/GO comoposites, and the mechanism can be described as follows: less effectiveness of GO is cause by the oxygen-containing groups on the GO sheet and the worse dispersion in the EA matrix; the elimination of oxygen-containing groups and the improved dispersion of graphene lead to increased flame retardancy for EA/graphene composites; the flame retardant element-nitrogen chemically bonded on the FGO sheet enhanced the flame retardant effect and improved its dispersion. THR and PHRR are apparently reduced in the presence of the graphite fillers, implying that the incorporation of GO, graphene and FGO in EA can improve the flame retardancy of EA, and the flame retardant effect of both graphene and FGO is comparatively better than that of GO.

3.4.4. TG-FTIR Analysis of EA and EA-G Composites

The TG-IR technique is used to characterize the gaseous products formed during the thermal degradation process, which is helpful to analyze the thermal degradation mechanism.54 The 3D TG-FTIR spectra of the gases formed in the thermal degradation of EA and EA composites per milligram are shown in Figure 14. EA and EA composites mainly evolve between 20 min and 30 min, generating a series of sharp peaks in the 3D spectra. The evolved gas analysis for EA, EA/1% GO, EA/1% graphene and EA/1% FGO at maximum decomposition (shown in Fig. 15) exhibited characteristic bands of H₂O and/or phenol (3738 cm⁻¹), CO₂ (2362 cm⁻¹), hydrocarbons $(-CH_3 \text{ and } -CH_2)$ groups (2970 cm⁻¹), compounds containing aromatic rings (676 cm⁻¹).⁵⁵⁻⁵⁶ Concluded from Figures 14 and 15, the absorbance intensity of gases during the degradation of EA composites decrease a lot compared to neat EA especially for the EA/FGO composites, indicating less volatile evolution.

The absorbance of pyrolysis products for EA and EA composites versus time is revealed in Figure 16. It can



Fig. 14. 3D TG-FTIR spectrum of gas phase in the thermal degradation of EA composites.



Fig. 15. FTIR spectrum of pyrolysis products for EA, EA/1% GO, EA/1% Graphene and EA1% FGO at the maximum decomposition rate.

be seen that the pyrolysis products for all the composites begin to release at about 20 min, and the EA/1%GO composite pyrolyzes a little earlier whereas EA/1%graphene and EA/1%FGO have the delayed phenomena. These differences suggest that composites containing GO degrade earlier than EA itself. In addition, the absorbance intensity of pyrolysis products for EA composites is lower than that for EA, especially the EA/1%FGO composite. The results of the pyrolysis products release is in good accordance to the MCC and TG results, and it can be interpreted that GO, graphene and FGO can reduce the release of combustible gases and the weight loss.

3.4.5. Flame Retardancy and Thermal Degradation Mechanism

Polymer nanocomposites usually present improved flame retardancy and thermal stability.^{57, 58} TGA, TG-IR and MCC studies of the composites demonstrate that the graphite samples can reduce the release of combustible gases and heat. There are three possible mechanisms responsible for the improvement in flame retardancy and thermal degradation as can be concluded as follows:

Firstly, as a layered nano-filler, the graphite materials dispersed in the matrix can act as a barrier effectively slowing down the heat released and hindering the transfer of combustion gases and energy feedback, which is similar to the performance of MMT and LDH.³⁶ Secondly, the various graphite fillers increase the melt viscosity and hinder the thermal movement of polymer chains, similar to the effect of CNT reported elsewhere.⁵⁹ In addition, the enormous specific surface of the sheets which is about $2600 \text{ m}^2\text{g}^{-1}$ reported elsewhere⁶⁰ may act as a radical scavenger to terminate the active radicals generated during the thermal degradation process, which needs further investigation.

However, differences in the thermal degradation and flame retardancy performance should be listed. GO degrades earlier than pure EA due to the oxygencontaining groups, thus the onset temperature from the TGA test and the time of maximum decomposition from the TG-IR test of EA/GO composites decrease and that is why the THR of the MCC test is relatively higher compared to EA/graphene and EA/FGO composites. PHRR is a little lower which can be ascribed to the decomposition in advance thus reduce the crest value of HRR. Compared to GO, the elimination of the oxygen containing groups on graphene sheets increases the onset degradation temperature and largely reduces the THR values. The maximum decomposition rate of EA/graphene composites is



Fig. 16. Absorbance of pyrolysis products for EP and EP3 versus time: (a) hydrocarbons; (b) CO₂; (c) carboxylic acid and (d) aromatic compounds.

delayed (TG-IR section). Attributed to the chemical bond between the FGO and EA matrix, better performance is anticipated. The lowest value of both the PHRR and THR of EA/FGO are obtained, and the maximum decomposition rate is reduced to a large extend (Fig. 15(d)), with the fewest pyrolysis products compared to other composites.

4. CONCLUSIONS

In this research, GO, graphene and FGO were prepared and used as nano-fillers incorporated into epoxy acrylic resin cured by in-situ UV-radiation and electron beam radiation to prepare series of composites containing 0.5%, 1%, 3% of additives to investigate their electrical, thermal stability and flammability properties. The high resistance meter shows that both $\rho_{\rm y}$ and $\rho_{\rm s}$ of EA/3% graphene composite are reduced for six orders of magnitude. The TGA results indicate that the graphite samples can delay the degradation process and decrease the DTG peak values of EA at high temperature. The MCC results demonstrate a considerable reduction of HRR and THR with small amount of graphite fillers, indicating flame retardant effect of graphite sample in EA composites. The TG-IR reveals that graphite sample can reduce the gas released, especially FGO, which maybe due to the radical trapping effect and layered effect hindering the transfer of combustion gases to the flame zone and energy feedback and thus enhance the flame retardancy and promote the char formation. From this study, we confirm that the graphite samples we prepared can improve the electrical conductivity, thermal stability, flame retardancy and reduce the deleterious gas releasing in thermo decomposition of the epoxy acrylic composites, especially graphene and functionalized graphite oxide. Our work provides a way to modified GO with double bond and flame retardant elements to enhance the dispersion and flame retardancy of GO in polymer matrix, and more work it needed to investigate the flame retardant performance and mechanism of graphene in other polymers.

Acknowledgments: This work was financially supported by the joint fund of NSFC and Civil Aviation Administration of China (No. 61079015) and the joint fund of National Natural Science Foundation of China (NSFC) and Guangdong Province (No. U1074001).

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Received: xx Xxxx xxxx. Accepted: xx Xxxx xxxx.



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