Simultaneous reduction and surface functionalization of graphene oxide with POSS for reducing fire hazards in epoxy composites

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Abstract

Simultaneous reduction and surface functionalization of graphene oxide (GO) was realized by simple refluxing of GO with octa-aminophenyl polyhedral oligomeric silsesquioxanes (OapPOSS) without the use of any reducing agents. The presence of OapPOSS made the hydrophilic GO hydrophobic, evidenced by the good dispersion of the OapPOSS-reduced GO (OapPOSS-rGO) in tetrahydrofuran solvent. The structure of OapPOSS-rGO was confirmed by XPS, FTIR and TEM. Morphologic study showed that, due to the good interfacial interaction between the functionalized graphene and epoxy, OapPOSS-rGO was dispersed well in the matrix. With the incorporation of 2.0 wt% of OapPOSS-rGO, the onset thermal degradation temperature of epoxy composite was significantly increased by 43 °C. Moreover, the peak heat release rate, total heat release and CO production rate values of OapPOSS-rGO/EP were significantly reduced by 49%, 37% and 58%, respectively.
compared to that of neat epoxy. This dramatically reduced the fire hazards were mainly attributed to the synergistic effect of OapPOSS-rGO: the adsorption and barrier effect of reduced graphene oxide inhibited the heat and gas release and promoted the formation of graphitized carbons, while OapPOSS improved the thermal oxidative resistance of the char layer.

**Introduction**

As a new member of the family of carbon-based materials, graphene, an atomically thick, two-dimensional (2-D) sheet composed of sp2 carbon atoms in a hexagonal lattice,[1] has aroused extensive interests in both scientific and industrial fields. Graphene exhibits fascinating electronic,[2, 3] thermal,[4, 5] and mechanical properties[6, 7] due to its unique structure. These extraordinary properties and ability to be dispersed in various polymer matrices make graphene suitable to be a new reinforced filler for developing next-generation polymer nanocomposites.

Graphene sheets have been obtained by micromechanical cleavage, epitaxial growth, chemical vapour deposition (CVD) and reduction of graphene oxide (GO). Among these methods, the reduction of GO is the most promising method for large scale production of graphene, also known as reduced graphene oxide (rGO).[1] As the precursor of graphene, GO has been demonstrated as a promising flame retardant nano-additive in polymers.[8] However, GO is thermally instable, and thereby it is essential to convert GO into a more stable form, reduced-GO. Huang *et al.* has demonstrated that the reduction of GO is highly exothermic and rGO is actually very
stable even after exposing clean rGO to a flame, clearly indicating the high intrinsic flame resistance of rGO. [9] Very recently, Huang’s group [10] and our group [11] have reported the application of graphene as flame retardant additive in polymer composites; however, the flame retardant used in the previous reports is bare graphene so that high loading is needed to achieve good fire resistance, and the polymer matrices investigated are all thermoplastic resins. Herein, to improve the fire retardant efficiency of graphene, we demonstrated a facile approach to functionalize and in situ reduce GO with octa-aminophenyl polyhedral oligomeric silsesquioxanes (OapPOSS) without the addition of conventional chemical reducing agents. For electrical applications, the OapPOSS-rGO composite was applied into flame retarding epoxy resins, which provides a path to obtain a new class of graphene-based flame retardant additives.

**Experimental**

**Raw materials**

Graphite powder (Spectrum Pure) was purchased from Sinopharm Chemical Reagent Co. LtdS (Shanghai, China). Octa-aminophenyl polyhedral oligomeric silsesquioxanes (OapPOSS) was provided by Hybrid Plastics Incorporation (USA). Biphenol A-type epoxy resin (EP) was supplied by Hefei Jiangfeng Chemical Industry Co. Ltd. (Anhui, China). Concentrated sulfuric acid (98%), sodium nitrate, potassium permanganate, 30% H$_2$O$_2$ solution, hydrochloric acid, ethylene glycol (EG), 4,4’-diamino diphenyl methane (DDM) and tetrahydrofuran (THF) were all reagent grade and provided by Sinopharm Chemical Reagent Co. LtdS (Shanghai, China).
Synthesis of functionalized and reduced graphene oxide (OapPOSS-rGO)

Graphene oxide (GO) was prepared from graphite using Hummers’ method.[12] The as-prepared GO (200 mg) was first suspended in THF (200 ml) with the assistance of sonication for 60 min. Subsequently, the suspension was introduced into a 500 ml three-neck flask, and another THF solution (50 ml) containing OapPOSS (400 mg) was added with stirring. The mixture was heated to 70 °C and refluxed for 12 h under nitrogen atmosphere. Afterwards, the mixture was separated by filtration through a 0.2-μm PTFE membrane and thoroughly washed with anhydrous THF to remove the residual OapPOSS. The filter cake was then dried in a vacuum oven at 80 °C overnight to remove the solvent. Scheme 1 illustrates the synthesis of functionalized and reduced graphene oxide (OapPOSS-rGO).

Preparation of OapPOSS-rGO/epoxy composites

Briefly, the preparation of epoxy composite with 2 wt% OapPOSS-rGO was as follows: OapPOSS-rGO (200 mg) was dispersed into acetone and sonicated until OapPOSS-rGO completely dissolved to form a black suspension. Then, epoxy resins (7.6 g) and DDM (2.2 g) were added to the suspension above and stirred until homogeneous mixtures were obtained. The mixtures were heated in a vacuum oven at about 60 °C to remove excess solvent. Then, the samples were cured at 100 °C for 2 h and post cured at 150 °C for 2 h. After curing, all samples were cooled to room temperature. For comparison, pristine GO/epoxy and OapPOSS/epoxy composites with equivalent filler content were also prepared under similar processing conditions.

Characterization
High resolution transmission electron microscopy (HRTEM) analysis was conducted using a JEOL JEM-2100 instrument with an acceleration voltage of 100 kV. The GNS/PU composites were dropped on copper grid for TEM imaging directly. X-ray photoelectron spectroscopy (XPS) was carried out with a VG Escalab Mark II spectrometer (Thermo-VG Scientific Ltd, UK), using Al Ka excitation radiation ($h\nu = 1253.6$ eV). Fourier transform infrared (FTIR) spectra were recorded using a Nicolet 6700 spectrophotometer in KBr pellets. Thermogravimetric analyse (TGA) of samples were carried out with Q5000 thermal analyzer (TA Co., USA) from 30 °C to 700 °C at a heating rate of 10 °C/min in air atmosphere (flow rate of 100 ml/min). The combustion properties were evaluated using a microscale combustion calorimeter (MCC, GOVMARK). Approximately $4 \pm 1$ mg of each sample was raised into the heated tube of a pyrolysis-combustion flow calorimeter (PCFC) that was purged with nitrogen. The sample was gradually heated to 900 °C at a heating rate of 1 °C/s. The gaseous pyrolysis products mix in the gas stream with oxygen prior to entering the combustion zone of the PCFC, where they are completely oxidized. Oxygen and nitrogen flow rates were set at 20 and 80 cm$^3$/min, respectively. Flammability of the samples was also characterized by cone calorimeter (Fire Testing Technology, UK) according to ISO 5660. Samples were irradiated horizontally at a heat flux of 35 kW/m$^2$. All the measurements were repeated three times and the results averaged. Raman spectra were recorded from 500 to 2000 cm$^{-1}$ on a LabRAM-HR Confocal Raman Microprobe (Jobin Yvon Instruments, France) using a 514.5 nm argon ion laser.
Results and discussion

Characterization of GO and OapPOSS-rGO

The presence of the OapPOSS has a significant influence on the solubility of OapPOSS-rGO. Fig. 1 shows the digital photos of (a) GO and (b) OapPOSS-rGO at a concentration of 1 mg/ml. As is well known, GO is easily exfoliated in aqueous media due to the carboxylic, epoxy, carbonyl, and hydroxide groups on its surface and edge.

[13, 14] After a suitable ultrasonic treatment, GO can produce stable dispersions of very thin graphene oxide sheets in water,[15, 16] exhibiting a color of light yellow (Fig. 1a). In the one-step functionalization and reduction process, the presence of the OapPOSS makes the hydrophilic GO hydrophobic. Therefore, OapPOSS-rGO can readily form stable colloidal suspensions in THF (Fig. 1b) due to the strong interaction between OapPOSS and THF.

Interestingly, there is a color change from yellow GO in water to black OapPOSS-rGO in THF (Fig. 1), which is usually considered to be a sign of GO reduction.[17] XPS was employed to evaluate the chemical bonds formed on the surface of GO before and after its functionalization with OapPOSS. The survey XPS spectra of (a) GO and OapPOSS-rGO, and higher resolution C1s spectra of (b) GO, (c) OapPOSS-rGO and (d) N1s spectra of OapPOSS-rGO are shown in Fig. 2. As can be observed, the XPS spectrum of OapPOSS-rGO displays a significant increase in the Si peak and N peak compared to that of GO. This increased intensity of Si and N elements is originated from OapPOSS. Fig. 2b clearly demonstrates that GO has a considerable degree of oxidation with four peaks appearing at 284.8, 285.6, 286.8 and
288.4 eV, which could be ascribed to the non-oxygenated ring C atoms, the C atoms bonded to C atoms in defective structures, the C atoms in hydroxyl and epoxy/ether groups, and the carbonyl C structure, respectively.[16, 18] The C1s XPS spectrum of GNS (Fig. 2c) also exhibits these same oxygen functionalities, however, the peak intensities of oxygenated C in epoxy/ether groups are much lower than those in GO, indicating the occurrence of the reduction of GO. In the N1s spectra of OapPOSS-rGO (Fig. 2d), there are two peaks at 406.0 eV and 399.6 eV. The former is ascribed to the amino group, while the latter is due to C-N-Ph, suggesting the successful covalent functionalization of GO by OapPOSS.

FTIR spectra of GO, and OapPOSS-rGO are presented in Fig. 3. The absorption bands of GO at 1730 cm⁻¹, 1622 cm⁻¹ and 1045 cm⁻¹ are ascribed to carboxyl groups, C=C and epoxy ring, respectively. After the functionalization of GO by OapPOSS, there are some new absorption bands in the spectra of OapPOSS-rGO. The strong absorption band at around 1105 cm⁻¹ is attributed to Si-O-Si group in POSS, and the peak at 1536 cm⁻¹ is corresponding to the stretching vibrations of the -NH₂ groups. The characteristic band of the -C-N- appears at 1352 cm⁻¹, which together with the significantly reduced intensity of epoxy ring at 1045 cm⁻¹ are indicative of the occurrence of covalent functionalization of GO by OapPOSS.

In order to obtain the morphological information of GO, OapPOSS-rGO and epoxy composite, TEM observations were conducted, as shown in Fig. 4. TEM analysis displays that GO sheets exhibit a typically flat yet wrinkled nano-platelet shape with several hundred nanometers large (Fig. 4a). After surface functionalization, many
small dark dots, which are corresponding to OapPOSS particles, are observed to be uniformly distributed on the graphene plane (Fig. 4b). In the OapPOSS-rGO/EP composite, thin graphene sheets with high aspect ratio are randomly oriented over the entire imaging area (Fig. 4c). The good dispersion of OapPOSS-rGO could be attributed to the good interfacial interaction between the functionalized graphene and polymer matrix.

**Thermal properties**

TG/DTG profiles for epoxy and its composites as a function of temperature at the heating rate of 10 °C min⁻¹ are shown in Fig. 5. The onset degradation temperature (T_onset) is defined as the temperature at which the weight loss is 5%. As can be observed, the thermal degradation process of pure epoxy has three stages based on the DTG profile, which are mainly corresponding to the vaporization of small molecules, the decomposition of the macromolecular chains, and the oxidation of char residue, respectively. In the case of the GO/EP composite, its T_onset is lower than pure EP, since GO is thermally unstable and its major mass loss occurs below 250 °C due to the decomposition of the oxygen-contained functional moieties.[19] The addition of OapPOSS exhibits a reverse trend in the T_onset compared to GO, and the T_onset of OapPOSS/EP is increased by 24 °C compared to that of pure EP. Owing to the multifunctional groups of OapPOSS, the cross-linking density of OapPOSS/EP is increased, resulting in the improvement of thermal stability. When GO is reduced by OapPOSS to convert into OapPOSS-rGO, OapPOSS-rGO/EP shows the best thermal stability, a 43 °C increment compared to that of pure EP. This significant improvement
in thermal stability could be attributed to the so-called “tortuous path” effect of graphene, which retards the permeation of heat and the escape of volatile degradation products.[18]

**Fire hazards evaluated by MCC and cone calorimeter**

As is well known, expand graphite or carbon nanotubes have been used to impart the flame retardant properties to polymers. Similarly, as carbon-based materials, graphene is expected to reduce fire hazards of polymers due to its unique two-dimensional (2D) atomic carbon sheet structure. To confirm this idea, the micro combustion calorimeter (MCC) was used to characterize the epoxy composites with respect to their potential flammability performance. Fig. 6 presents the heat release rate (HRR) curves of pure EP, GO/EP, OapPOSS/EP and OapPOSS-rGO/EP. The addition of GO and OapPOSS gives rise to a 36% and 31% reduction in peak HRR, respectively, compared to that of pure EP. Furthermore, incorporating OapPOSS-rGO into EP exhibits the lowest peak HRR value (nearly 58% reduction). The mechanism of OapPOSS-rGO in reducing the flammability of polymers is probably attributed to create a barrier effect on the surface of the polymers which could slow down the heat and mass transfer between gas and condensed phases, and prevent the underlying material from further combustion.

Cone calorimeter is an useful bench-scale tool for measuring the flammability of materials in real-world fire conditions.[20] Fig. 7 gives the HRR, total heat release (THR) and CO production rate (COPR) versus time curves of all the samples. From Fig. 7a, it can be observed that pure epoxy resin burns very rapidly after ignition and
the peak heat release rate value is 1730 kW/m². As expected, incorporating GO into epoxy resins makes the peak heat release rate decrease to 1345 kW/m². For the sample of OapPOSS/EP, the PHRR also decreases by 38% compared to that of pure EP. Moreover, the PHRR of OapPOSS-rGO/EP exhibits further reduction compared to both GO/EP and OapPOSS/EP. The best fire retardant properties of OapPOSS-rGO/EP could be attributed to two aspects: firstly, the reduction of GO by OapPOSS occurs to convert GO into a more stable form, reduced-GO (rGO); secondly, POSS can create a stable silica layer on the char surface of EP, which reinforces the barrier effect of graphene.[21] The THR curves (Fig. 7b) show similar trend as HRR, and THR value of GO/EP, OapPOSS/EP and OapPOSS-rGO/EP is significantly reduced by 17%, 23% and 37%, respectively, compared to that of pure EP. In Fig. 7c, it can be seen that the COPR of pure EP remains the highest among the four samples. Addition of GO and OapPOSS suppresses the release of CO. In addition, CO production for OapPOSS-rGO/EP is much lower than that of pure epoxy resins, which is probably due to the adsorption and barrier effect of graphene. The reduction of toxic CO in the smoke and gases will be beneficial to fire rescue when an accident happens.

The fire growth rate index (FIGRA), which indicates the burning propensity of a material, has been calculated from the ratio of PHRR and time to PHRR for all samples. The FIGRA value of pure EP is 13.3 kW/(m² s), while that of GO/EP, OapPOSS/EP and OapPOSS-rGO/EP is 10.5, 8.3 and 6.7 kW/(m² s), respectively. The lowest FIGRA value of OapPOSS-rGO/EP means the lowest fire hazard of the
material.

Flame retardant mechanism

Flame retardant additives in polymers may have an action either in the condensed phase or in the gas phase or also in both phases at the same time. According to the previous reports, numerous different nanoparticles, including organo-modified clays,[22] layered silicate,[23] carbon nanotubes,[24] layered double hydroxides (LDH),[25] or polyhedral silsesquioxanes (POSS),[26] act as “char reinforcer” or “char expander” in the condensed phase. When a condensed phase action is the main mechanism of the flame retardant additives, the efficiency depends strongly on the structure and composition of the char during burning. Therefore, investigating the properties and the structure of the resultant carbonaceous layers will provide the insight into understanding how the flame retardant additives act in the condensed phase.

Raman spectroscopy offers a powerful tool for characterizing carbonaceous materials. Fig. 8 shows the Raman spectra of the residual char of EP, GO/EP, OapPOSS/EP and OapPOSS-rGO/EP after cone calorimeter. As can be observed, the Raman spectra of all the four samples exhibit similar shape, with two peaks at 1593 cm\(^{-1}\) and 1358 cm\(^{-1}\). The characteristic peak at 1593 cm\(^{-1}\) is called G band, corresponding to the first-order scattering of the E\(_{2g}\) mode,[16] while the other is called D band, arising from the activation in the first order scattering process of sp\(^3\) carbons.[27] However, the intensity of the Raman spectra of GO/EP is much higher than that of EP, indicating the improvement of the graphitized carbons in the residual char.[28] Furthermore,
incorporating OapPOSS-rGO into EP slightly increases the intensity compared to that of GO/EP, suggesting GO is the main contributor for the formation of graphitized carbons. The high content of graphitized carbons in the residual char is known to be compact and efficient in terms of thermal insulation, which provides a protective shield that leads to a decrease in heat and mass transfers between the flame and the material.

The exterior and interior residual char of EP and OapPOSS-rGO/EP obtained from cone calorimeter are further investigated by XPS analysis, and the results are summarized in Table 1. As aforementioned, the characteristic C1s bands at 284.6, 286.8 and 288.4 eV are ascribed to C-H and C-C in aliphatic and aromatic species, C-O (ether and/or hydroxyl group) and C = O, respectively. To study the thermal oxidative resistance, \( \frac{C_{ox}}{C_a} \) (\( C_{ox} \): oxidized carbons and \( C_a \): aliphatic and aromatic carbons) values are calculated.[29] The \( \frac{C_{ox}}{C_a} \) values of the exterior and interior residual char of OapPOSS-rGO/EP are 0.55 and 0.39, respectively, which are much lower than those of EP. Moreover, the silicon concentration in the exterior residual char of OapPOSS-rGO/EP is higher than that in the interior char, implying that silica can be migrated and accumulated on the surface of burned char. As a result, the presence of the silica layer improves the thermal oxidative resistance of the protective char layer, which could effectively inhibits the heat and mass transmission, and the release of combustible gases from the matrix.

**Conclusion**

In this article, an efficient and facile method was demonstrated to simultaneously
functionalize and reduce GO without the use of any reducing agents. The functionalization of GO with OapPOSS makes the hydrophilic GO hydrophobic and provides the active sites linked between GO and epoxy matrix, which ensures the good dispersion of OapPOSS-rGO in epoxy matrix. With the incorporation of OapPOSS-rGO, a significant enhancement in thermal stability is achieved, a $43 \degree C$ increment in $T_{\text{onset}}$ compared to neat epoxy. Moreover, the flammability of the OapPOSS-rGO/EP composite has also been dramatically reduced, especially the PHRR, THR and COPR values, indicating that OapPOSS-rGO is highly effective in reducing the fire hazards of EP. The improvement of fire retardant properties is mainly attributed to that addition of OapPOSS-rGO leads to the formation of the compact and insulating char layer to protect the inner polymer matrix from further burning. The approach described herein could provide a promising solution in the development of a novel and efficient POSS-based/rGO flame retardant for polymer nanocomposite applications.

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References

Captions

Scheme 1. Schematic illustration of the synthetic route of functionalized and reduced graphene oxide (OapPOSS-rGO).

Figure 1. Photographs of (a) GO dispersions in water and (b) OapPOSS-rGO dispersions in tetrahydrofuran.

Figure 2. XPS spectra of (a) GO and OapPOSS-rGO, and higher resolution C1s spectra of (b) GO, (c) OapPOSS-rGO and (d) N1s spectra of OapPOSS-rGO.

Figure 3. FTIR spectra of GO, and OapPOSS-rGO.

Figure 4. TEM images of (a) GO, (b) OapPOSS-rGO and (c) OapPOSS-rGO/EP composite.

Figure 5. TG/DTG profiles for epoxy and its composites as a function of temperature under air atmosphere.

Figure 6. Heat release rate (HRR) curves of pure EP, GO/EP, OapPOSS/EP and OapPOSS-rGO/EP.

Figure 7. Heat release rate (HRR), total heat release (THR) and CO production rate (COPR) versus time curves of epoxy and its composites.

Figure 8. Raman spectra of the residual char of epoxy and its composites.
Table 1  XPS data of the residual char of EP and OapPOSS-rGO/EP.

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