

Simultaneous Functionalization and Reduction of Graphene Oxide with Polyetheramine and Its Electrically Conductive Epoxy Nanocomposites^{*}

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Abstract Simultaneous functionalization and reduction of graphene oxide (GO) is realized by refluxing of GO suspension with polyetheramine (D2000) followed by thermal treatment at 120 °C. Compared to GO, the D2000-treated GO (GO-D2000) becomes hydrophobic, thermally stable and highly conductive with an electrical conductivity of 11 S/m, which is almost 8 orders of magnitude higher than that of GO. Due to the high conductivity and improved dispersion of GO-D2000, its epoxy nanocomposites exhibit a sharp transition from electrically insulating to conducting with a low percolation threshold of 0.71 vol%. With 3.6 wt% GO-D2000, the glass transition temperature of the epoxy nanocomposite is 27 K higher than that of neat epoxy.

Keywords: Graphene oxide; Epoxy; Chemical reduction; Electrical conductivity; Glass transition temperature.

INTRODUCTION

Graphene has received considerable attention since 2004^[1] because of its extraordinary electronic, mechanical and thermal properties^[2–6], which make it a great promise for potential applications in nanotechnology including flexible thin-film transistors, capacitors, sensors and nanocomposites^[7–16]. Among the methods of graphene preparation^[17, 18], chemical reduction of graphene oxide (GO) has been demonstrated to be an efficient approach for large-scale production of graphene^[19]. Various reducing agents such as hydrazine^[20], hydrogen sulfide^[21], sodium borohydride^[22], hydroquinone^[23] and dimethylhydrazine^[5] were used to reduce GO. Unfortunately, these agents are harmful to environment and their usage should be minimized. Additionally, the surface of GO sheets had to be pre-modified by surfactants or polymers before the chemical reductions to avoid the re-stacking of the reduced GO sheets (RGO) and improve the compatibility between RGO sheets and polymer matrices. To address the aforementioned issues, simultaneous reduction and surface functionalization of GO with non-toxic chemicals has been developed. Wang *et al.*^[24] used green tea to simultaneously reduce and functionalize GO based on the interaction between GO and the aromatic tea polyphenol. Khanra *et al.*^[25] explored the surface functionalization and reduction of GO with baker's yeast that contains nicotinamide adenine dinucleotide phosphate. GO was also reduced with dopamine and simultaneously functionalized by polydopamine that resulted from self-

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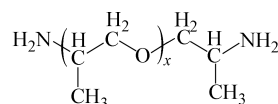
polymerization of dopamine^[26]. Simultaneous surface functionalization and reduction of GO was realized by refluxing of GO with octadecylamine (ODA) and *p*-phenylene diamine without the use of any reducing agents^[27, 28]. The resultant RGO became electrically conductive and showed greatly improved dispersion in polystyrene matrix, and thus its polystyrene nanocomposites exhibited high electrical properties.

Polyetheramine JEFFAMINE[®] D2000 (D2000) is a difunctional, primary amine with an average molecular weight of about 2000^[29]. Ma *et al.*^[30] utilized D2000 to modify graphene nanoplatelets (GNPs) obtained from graphene intercalation compound at 150 °C for 48 h. The as-prepared epoxy nanocomposites exhibited improved electrical and mechanical properties. Zeng *et al.*^[31] reported a process to prepare liquefied GO through grafting of GO with JEFFAMINE[®] D2070 (a monoamine with the molecular weight of approximately 2070). Compared to D2070, D2000 possesses two-terminal amine groups and is expected to be more efficient in reacting with the epoxide groups of GO. Herein, we demonstrate an efficient approach to simultaneously reduce and functionalize GO with D2000 followed by thermal treatment at 120 °C. The resultant D2000-reduced and functionalized GO (GO-D2000) is then used to improve thermal and electrical properties of epoxy resin. The epoxy nanocomposites exhibit a sharp transition from electrically insulating to conducting with a low percolation threshold.

EXPERIMENTAL

Materials

Natural graphite flakes were supplied by Huadong Graphite Factory (Pingdu, China) with an average diameter of 48 µm. Fuming nitric acid (65%–68%), concentrated sulphuric acid (95%–98%), hydrochloric acid (36%–38%), potassium chlorate (98%), and dichloromethane (99.5%) were purchased from Beijing Chemical Factory (China). Diglycidyl ether of bisphenol A epoxy resin with the trade name of Epon-828 was bought from Shell Co. Curing agent, diethyltoluene diamine (E-100) was supplied by Albemarle (USA). Polyetheramine JEFFAMINE[®] D2000 was kindly supplied by Huntsman (USA) and its molecular formula is shown below:



where $x \approx 33$ and its average molecular weight is about 2000.

Reduction and Functionalization of GO with D2000

GO was synthesized from natural graphite by a modified Staudenmaier method^[32]. In a typical procedure for the reduction and surface functionalization of GO with D2000, GO (0.3 g) was dissolved and exfoliated in deionized water (150 mL) by ultrasonication with a JY99-2 DN ultrasonicator (Ningbo, China). After D2000 (300 g) was added, the mixture was refluxed with mechanical stirring at 95 °C for 10 h, and subsequently heated at 120 °C for 10 h in an air-circulating oven. The resultant mixture was diluted with dichloromethane (600 mL) and filtrated with a PP membrane with a pore size of ~0.45 µm. The filter cake was rinsed in dichloromethane by ultrasonication for 5 min and then filtrated. The rinsing-filtration process was repeated for 5 times to remove the physically adsorbed D2000 and the resulting filter cake was dried at 80 °C for 24 h and denoted as GO-D2000. To explore the contribution of the thermal treatment at 120 °C, GO-D2000-5h and GO-D2000-20h were prepared by simple refluxing of GO suspension with D2000 at 95 °C for 5 h and 20 h, respectively. Note that both GO-D2000-5h and GO-D2000-20h did not undergo the thermal treatment. Table 1 gives the information on the preparations of GO-D2000, GO-D2000-5h, and GO-D2000-20h.

Table 1. Information on the preparations of GO-D2000-5h, GO-D2000-20h, and GO-D2000

Sample	Temperature and time of refluxing
GO-D2000-5h	95 °C, 5 h
GO-D2000-20h	95 °C, 20 h
GO-D2000	95 °C, 10 h followed by 120 °C, 10 h

Preparation of Epoxy/GO-D2000 Nanocomposites

GO-D2000 was dispersed and exfoliated in dichloromethane by the ultrasonicator for 1 h. The resulting suspension was then mixed with epoxy monomer and the curing agent. After homogenizing for 2 h with an IKA T18 homogenizer (Germany) at ambient temperature, the mixture was heated at 60 °C for 10 h under vacuum to thoroughly remove the residual solvent and then poured into a stainless steel mold (4 mm × 8 mm × 80 mm), pre-cured in an oven at 90 °C for 2 h and post-cured at 120 °C for 6 h. For comparison purpose, both epoxy/GO-D2000 nanocomposites and epoxy/GO composites were prepared.

Characterization

The surface compositions of GO and GO-D2000 were characterized with a ThermoVG RSCAKAB 250X high-resolution X-ray photoelectron spectroscope (XPS). X-ray diffraction (XRD) measurements were carried out by using a BRUKER AXS D8 ADVANCE diffractometer with $\text{CuK}\alpha$ radiation ($\lambda = 0.154$ nm) at a generator voltage of 40 kV and a generator current of 40 mA with a scanning speed of 10 °/min. GO and GO-D2000 were analyzed with a Nicolet Nexus 670 Fourier-transform infrared spectroscope (FTIR). Raman spectra were obtained with a Renishaw inVia Raman spectroscope (Britain) using an excitation wavelength of 514.5 nm. GO and GO-D2000 films were prepared by vacuum filtrating with PP membranes (pore size ~ 0.45 μm), dried at 80 °C for 24 h, peeled off from the membranes, and their volume conductivities were then measured with a 4-Probes-Tech RTS-8 four-probe resistivity meter (China). A JEOL FE-JSM-6701F field-emission scanning electron microscopy (SEM) was used to observe the dispersion of GO-D2000 in epoxy matrix at an accelerating voltage of 5 kV. The exfoliation quality of GO-D2000 sheets in the epoxy matrix was observed with a JEOL JEM-3010 transmission electron microscopy (TEM) at an accelerating voltage of 300 kV. Ultrathin sections of thinner than 100 nm were cryogenically cut with a diamond knife using a Leica Ultracut S ultramicrotome and collected on 200-mesh copper grids. The surface morphologies of GO and GO-D2000 were observed with a Bruker multimode 8 atomic force microscopy (AFM) in the tapping mode. The AFM samples were prepared by ultrasonication of GO/water and GO-D2000/dichloromethane suspensions followed by depositing on freshly cleaved mica surfaces. Nitrogen contents of GO and GO-D2000 were obtained by a Elementar Analysensysteme GmbH Vario EL cube elemental analyzer (CHNS). The thermal stabilities of GO, D2000 and GO-D2000 were measured with a TA Q50 thermal analyzer under nitrogen atmosphere at a heating speed of 5 K/min. Dynamic mechanical properties were measured with a Rheometric Scientific DMTA V dynamic mechanical analyzer (DMA) using a single cantilever clamp with a frequency of 10 Hz and a heating rate of 5 K/min from 25 °C to 250 °C. The volume conductivities of the epoxy nanocomposites were measured with the RTS-8 four-probe resistivity meter if their conductivity is higher than 1×10^{-4} S/m, while a 6517B resistivity meter from Keithley Instruments (USA) was used if the conductivity is lower than 1×10^{-4} S/m.

RESULTS AND DISCUSSION

Reduction and Functionalization of GO with D2000

The functionalization of GO with D2000 is confirmed by the FTIR spectra of GO, D2000 and GO-D2000 (Fig. 1). The typical peaks of GO are 1704 cm^{-1} (C=O stretching vibration), 1620 cm^{-1} (C=C in aromatic ring), 1390 cm^{-1} (C—OH deformation vibration), 1056 cm^{-1} (C—O—C in epoxide group) and a wide peak around 3403 cm^{-1} (hydroxyl groups). As for GO-D2000, the peak intensities assigned to C=O stretching vibration (1704 cm^{-1}) and O—H deformation vibration (1390 cm^{-1} and 3403 cm^{-1}) decrease. The presence of D2000 component in GO-D2000 is supported by the appearance of new peaks at 2863 cm^{-1} and 2967 cm^{-1} that correlate with the presence of —CH₂ and —CH stretching vibrations, along with the characteristic absorption peak of aliphatic ether (1101 cm^{-1}). Furthermore, the disappearance of the characteristic peaks of primary amine groups (3309 cm^{-1} and 3376 cm^{-1}) and the appearance of new peaks at 3426 cm^{-1} and 1567 cm^{-1} for N—H stretching vibration indicate the formation of —C—NH—C— bands. It is thus believed that D2000 chains are grafted to GO sheets by the nucleophilic substitution reaction between the epoxide groups of GO and the amine groups of D2000.

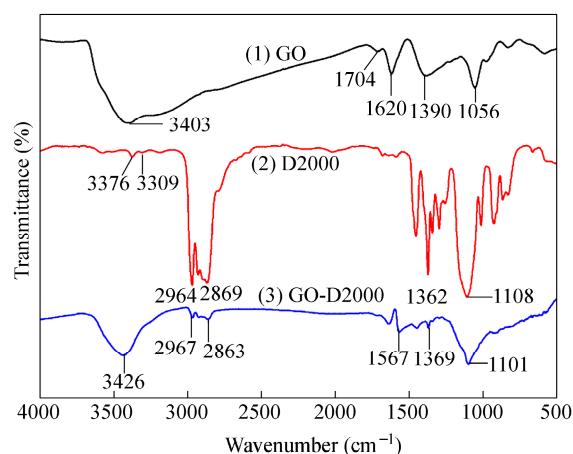


Fig. 1 FTIR spectra of (1) GO, (2) D2000 and (3) GO-D2000

XPS is applied to compare the chemical compositions of GO and GO-D2000 (Fig. 2). The C1s XPS spectrum of GO presents four types of carbon: C—C (284.8 eV), C—OH (286.7 eV), C—O—C (287.2 eV) and O—C=O (289.4 eV)^[27, 33]. In contrast, most of the peak intensities corresponding to the oxygen-containing

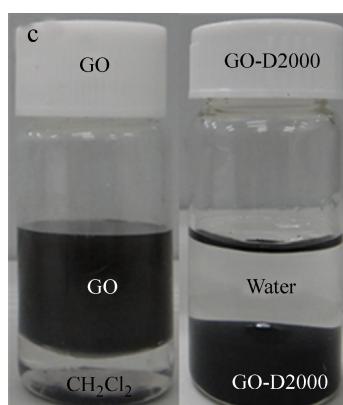
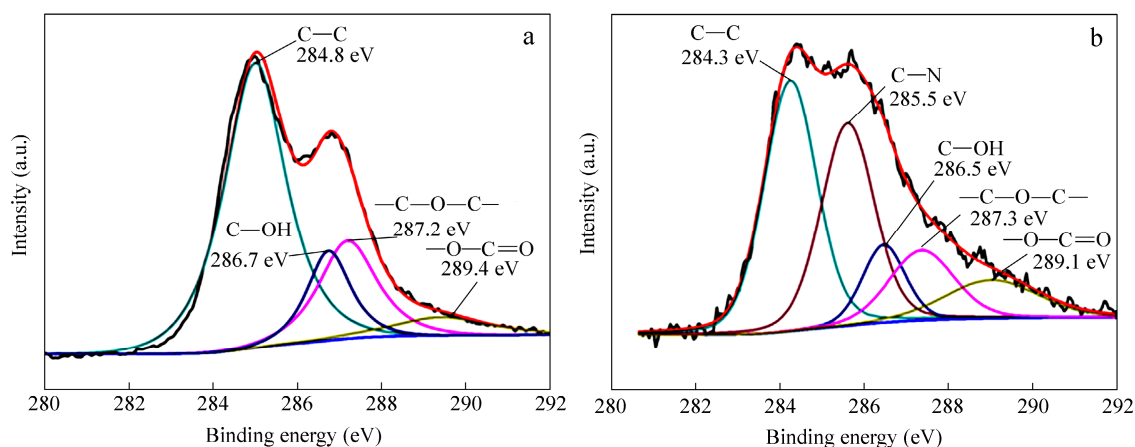


Fig. 2 C 1s XPS spectra of (a) GO and (b) GO-D2000; (c) Solubility of GO and GO-D2000 in the dichloromethane/water solvents (1 mg/mL, 1 h standing)

groups of GO are dramatically decreased after the functionalization of D2000 (Fig. 2b). The new characteristic peak assigned to C—N bond (285.5 eV) further suggests the covalent bonding between GO and D2000, which is consistent with the abovementioned FTIR results. It should be noted that the peak of C—O—C is retained due to the abundant C—O—C groups of D2000 that chemically bonded to GO sheets^[24, 33]. The presence of D2000 chains makes hydrophilic GO hydrophobic as evidenced by the solubility tests of GO and GO-D2000 in CH₂Cl₂/H₂O (1/1, *V/V*) solvents. As CH₂Cl₂ and water are immiscible, a phase separation is observed in their mixture. Polar GO sheets like to be dispersed in water phase while GO-D2000 sheets are selectively dispersed in CH₂Cl₂ phase. The change of hydrophilic GO to hydrophobic GO-D2000 confirms the functionalization of GO with D2000 (Fig. 2c). In addition, the color change from brown for GO powders to black for GO-D2000 powders is also an indication of the reduction of GO.

XRD patterns reveal the microstructure evolution of GO upon chemical functionalization with D2000 (Fig. 3). Compared to natural graphite, GO sheets exhibit an enlarged intra-gallery of 0.69 nm (12.8°) because of the introduction of the oxygen-containing groups on the sheets. After refluxing with D2000, the intra-gallery of GO-D2000-5h is further increased to 2.59 nm (3.4°) and 1.23 nm (7.2°) due to the chemical grafting of D2000 on GO sheets. By extending the refluxing time to 20 h, only a shoulder peak is observed in the XRD pattern of GO-D2000-20h. At the same time, a broad peak centered at 18.6° emerges, which is an implication of the restacking of exfoliated and functionalized GO-D2000 sheets^[34]. Interestingly, after the mixture of GO and D2000 was refluxed at 95 °C for 10 h and then heated at 120 °C for 10 h, the diffraction peaks at both 3.4° and 7.2° for the resultant GO-D2000 almost disappear, implying a higher extent of intercalation of GO-D2000 than GO-D2000-5h and GO-D2000-20h.

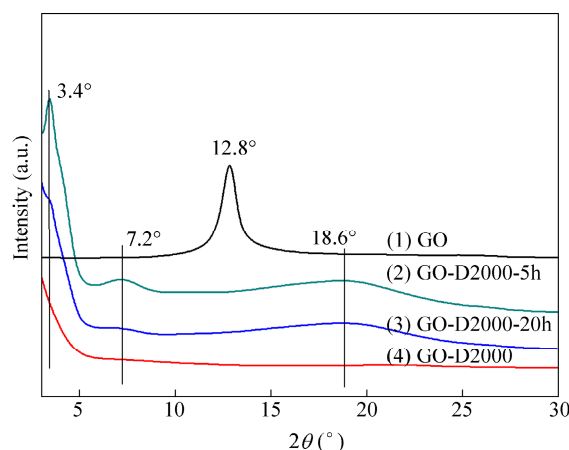


Fig. 3 XRD patterns of (1) GO, (2) GO-D2000-5h, (3) GO-D2000-20h and (4) GO-D2000

Figure 4 shows SEM images of GO and GO-D2000 films prepared by compression of GO and GO-D2000 powders at 10 MPa. The surface of GO film is smoother compared to that of GO-D2000 film. As reported^[3, 35], the distinct surface roughness is explained by the rigid groups that act as covalently linked nanoscale spacers impeding the face-to-face stacking of the GO sheets. Considering the flexible and long chains of D2000, the rough surface may be due to the D2000 grafted onto the surface of GO, which hinders the re-stacking of the modified GO sheets. Figure 5 shows AFM images of GO and GO-D2000. It is seen that the average thickness for the exfoliated GO-D2000 is 1.90 nm, much higher than that of GO (0.82 nm) as a result of the functionalization.

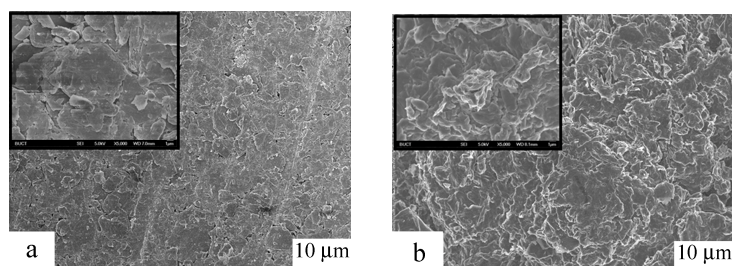


Fig. 4 SEM microphotographs of (a) GO and (b) GO-D2000 films prepared by compression of GO and GO-D2000 powders (The insets are high magnification SEM images of the corresponding films.)

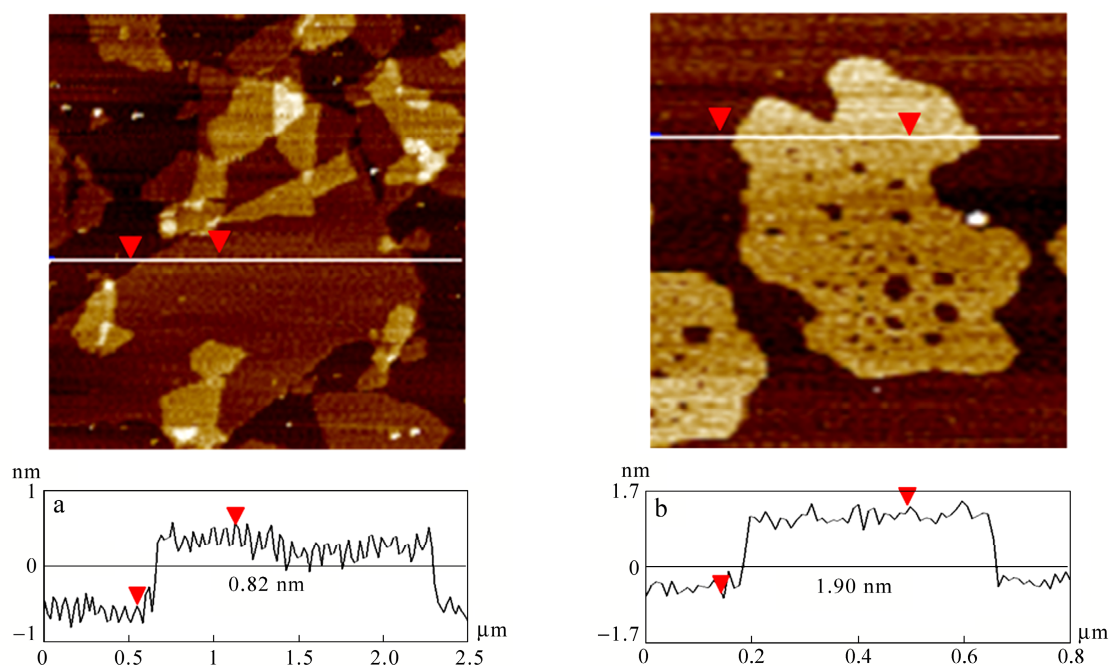


Fig. 5 AFM images of (a) GO and (b) GO-D2000

To explore the structure variations during the reduction and functionalization of GO, Fig. 6 shows the Raman spectra of graphite, GO, GO-D2000-5h, GO-D2000-20h, and GO-D2000. Generally, there are two main characteristic peaks for graphene materials, where the G mode arises from first order scattering of the E_{2g} phonon of sp^2 C atoms ($\sim 1575\text{ cm}^{-1}$) and the D mode from a breathing mode of κ -point phonons of A_{1g} symmetry ($\sim 1350\text{ cm}^{-1}$)^[18]. Natural graphite only shows a G band at 1581 cm^{-1} and there is no obvious D band observed due to its structure perfection. However, the G band of GO becomes broad and shifts to 1596 cm^{-1} with the presence of isolated double bonds that resonate at higher frequencies^[36]. The prominent D band of GO at 1344 cm^{-1} may be related with the decrease in the size of the in-plane sp^2 domains and the defects introduced during the oxidation of graphite. After refluxing with D2000, the G band of GO shifts back near the corresponding localization of natural graphite, which also indicates the reduction of GO and is in agreement with abovementioned FTIR and XPS results. The D and G bands of GO-D2000-5h localize at 1342 cm^{-1} and 1575 cm^{-1} , respectively. Interestingly, much higher D/G intensity ratios are observed for D2000-treated samples compared to that of GO (0.94). The D/G ratio is increased to 1.14 for GO-D2000-5h, 1.20 for GO-D2000-20h, and 1.29 for GO-D2000. The increased D/G ratio suggests a decreased average size of the sp^2 domains upon the reduction of exfoliated GO sheets^[18, 20, 27, 33], and it can be further explained if new graphitic domains were formed after reduction that are smaller in size to the ones in GO, but more in number^[20].

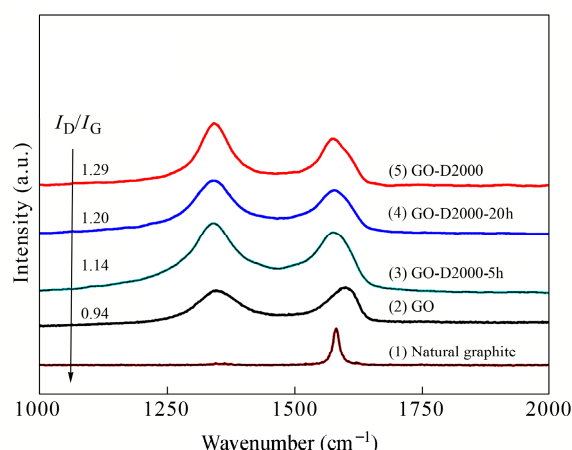


Fig. 6 Raman spectra of (1) natural graphite, (2) GO, (3) GO-D2000-5h, (4) GO-D2000-20h and (5) GO-D2000

Electrical Conductivity and Thermal Stability of GO-D2000

The direct evidence of the reduction of GO during refluxing with D2000 is to measure its electrical conductivity (Fig. 7). In the absence of D2000, the heating of GO at 120 °C for 20 h (GO-120) does not result in an apparent reduction of GO because the conductivity of GO-120 (3×10^{-7} S/m) is only slightly higher than that of GO. However, the presence of D2000 results in an increased conductivity of 5×10^{-5} S/m even at low temperature of 95 °C, indicating the vital role of D2000 in the reduction of GO. The conductivity of GO-D2000 is increased to 11 S/m, approximately 8 orders of magnitude higher than that of GO, which can be attributed to the efficient reduction of GO at higher temperature of 120 °C in comparison with GO-D2000-20h.

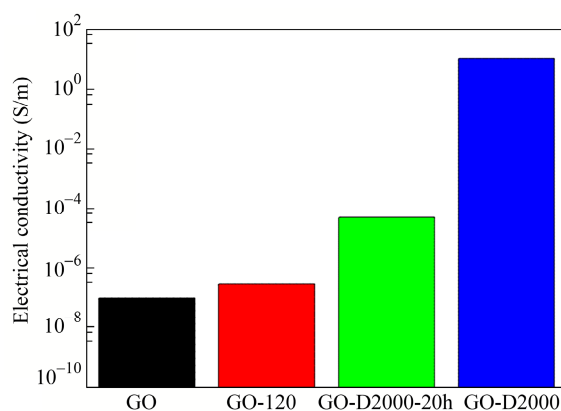


Fig. 7 The electrical conductivities of GO, GO-120, GO-D2000-20h and GO-D2000

The thermal stability of GO is also greatly improved by its refluxing with D2000 (Fig. 8). It is clear that GO is not thermally stable and exhibits a main mass loss of 36.2 wt% at ~300 °C due to the decomposition of its oxygen-containing groups and the release of yielding CO₂, CO and steam. The final mass loss of 42.3 wt% at 650 °C may result from the removal of more oxygen functionalities. Just heating of GO at 120 °C for 20 h does not change the thermal stability of GO, which is in consistent with the low electrical conductivity of GO-120. The refluxed GO with D2000 exhibits greatly enhanced thermal stability. The mass loss at 300 °C is 22.7% for GO-D2000-5h, 17.0% for GO-D2000-20h and 4.5% for GO-D2000, which are much less than that of GO at the same temperature (36.2%). The less mass loss should result from the reduction of GO in the presence of D2000 by removing most of its oxygen-containing groups. At higher temperature of 650 °C, the mass loss of refluxed GO at different conditions is much higher than that of GO due to the degradation of its grafted D2000

component, which can be confirmed by almost the same decomposition temperatures between GO-D2000 and D2000. This interesting phenomenon in turn indicates the efficient functionalization of GO with D2000. Therefore, the mass loss from 300 °C to 400 °C is considered as the content of D2000 grafted on GO, which is 42.1 wt% for GO-D2000-20h and 43.6 wt% for GO-D2000. Such resemble contents reveal that the heating of the refluxed GO/D2000 mixture at 120 °C does not affect the functionalization of GO with D2000 but promotes the reduction extent of GO. In addition, based on the nitrogen content of GO-D2000 obtained from the elemental analysis, the D2000 content of GO-D2000 is 39.2%, quite close to the value (43.6%) obtained from the TGA curve.

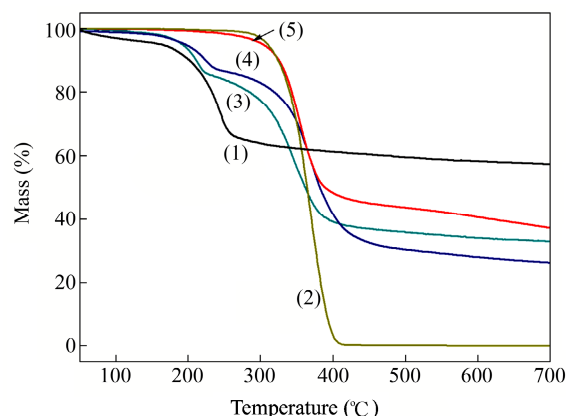


Fig. 8 TGA curves of (1) GO, (2) D2000, (3) GO-D2000-5h, (4) GO-D2000-20h and (5) GO-D2000

Glass Transition Temperature and Electrical Conductivity of Epoxy Nanocomposites

Figure 9 shows plots of damping spectra ($\tan\delta$) of neat epoxy and epoxy/GO-D2000 nanocomposites. Compared to the glass transition temperature of neat epoxy (154 °C), those of its nanocomposites are increased to 158 °C and 163 °C with the addition of 0.2 wt% and 1.2 wt% of GO-D2000, respectively. A significant increase in glass transition temperature of over 27 K is observed by increasing the GO-D2000 content to 3.6 wt%. The striking increase of glass transition temperature is one of the highest values for graphene-filled polymer nanocomposites^[37, 38] and confirms the strong interactions between epoxy and GO-D2000 due to the successful functionalization of GO with D2000. The enhanced interfacial adhesion may hinder the mobility of epoxy chains near the filler surface and is similar to the restricted relaxation behavior in polymer nanocomposites containing covalently bonded interfacial interaction or sheet-like nanoclay^[9, 39–42]. Moreover, the hindered motion of epoxy

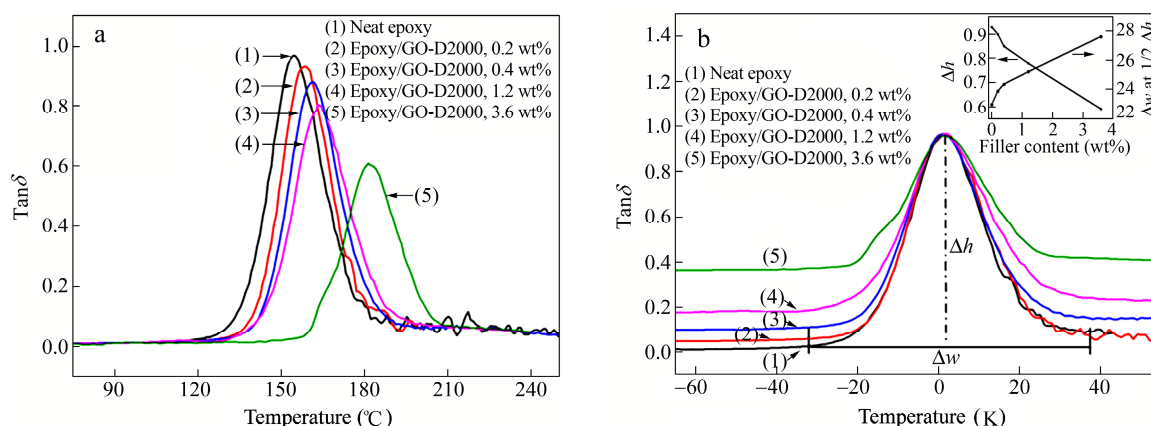


Fig. 9 (a) Damping spectra of neat epoxy and epoxy/GO-D2000 nanocomposites and (b) damping spectra of neat epoxy and epoxy/GO-D2000 nanocomposites with curves horizontally and vertically shifted for clarity (The inset shows changes of the height of loss peaks (Δh) and the full temperature width at half Δh (Δw at $1/2 \Delta h$) of the loss peaks.)

chains is also verified by the low $\tan\delta$ amplitude (Δh) and the wide temperature range (Fig. 9b). Epoxy segments near GO-D2000 surface only relax at higher temperatures so that the relaxation of the nanocomposites occurs in a wider temperature range. The higher the content of GO-D2000, the wider the temperature range where the relaxation occurs^[9]. The amplitude of loss peak (Δh) decreases with the increased content of the restricted segments, suggesting a high efficiency for load transfer at interfaces. The dependence of Δh and the full temperature width at half Δh (Δw at $1/2 \Delta h$) of the loss peaks on the GO-D2000 content are shown in the inset of Fig. 9(b). Δh decreases from 0.93 to 0.59 with increasing the content of GO-D2000 while Δw at $1/2 \Delta h$ increases from 22.9 to 27.6 K. These results further confirm the important role of D2000 in improving the compatibility and interfacial interaction between GO and epoxy matrix.

To characterize electrical properties of the epoxy nanocomposites, the content of D2000 grafted on GO is determined to be 43.6 wt% and should be deducted from the GO-D2000 content. Figure 10 shows plots of electrical conductivity versus filler content (GO and GO-D2000) for epoxy nanocomposites. Different from GO, GO-D2000 is efficient in improving the electrical conductivity of epoxy resin. After the D2000 component is excluded from the filler content, the redrawn conductivity curve shifts to lower filler contents with a percolation threshold of 0.71 vol% (Curve 3). With 2.4 vol% of GO-D2000, the epoxy nanocomposite exhibits an electrical conductivity of 6.1×10^{-5} S/m, which satisfies the antistatic criterion of 10^{-6} S/m^[43]. The conductivity is increased to 0.16 S/m with 4.8 vol% GO-D2000. Such a good conductivity results from the simple refluxing GO in the presence of D2000 and no additional reducing agent is required. In contrast, epoxy/GO composite exhibits a lower conductivity than 10^{-8} S/m even with 16 vol% of GO. In addition to the efficient reduction of GO during the refluxing with D2000, the high electrical conductivity of epoxy/GO-D2000 nanocomposites should also be attributed to the good dispersion of GO-D2000 in the epoxy matrix (Fig. 11). The simultaneous reduction and functionalization of GO by the refluxing and subsequent thermal treatment provides an efficient approach to prepare electrically conductive epoxy nanocomposites with well dispersed graphene sheets.

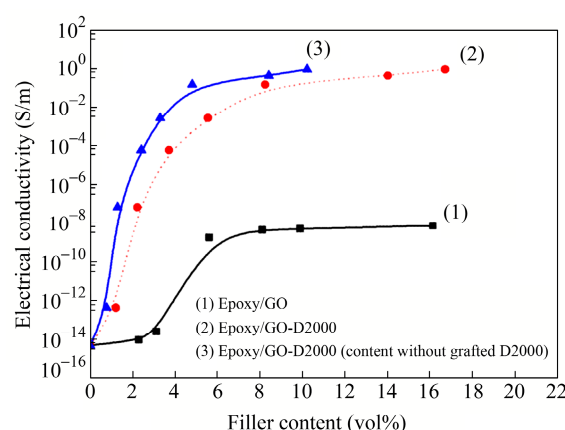


Fig. 10 Plots of electrical conductivity versus filler content for epoxy nanocomposites

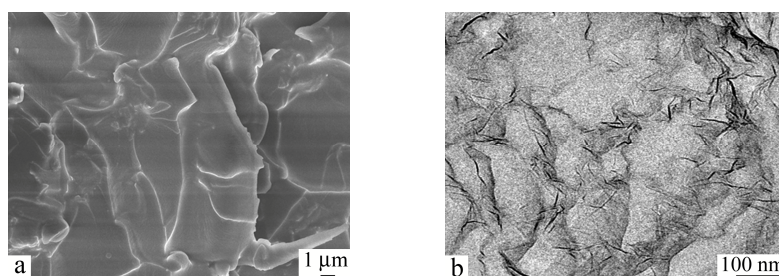


Fig. 11 (a) SEM and (b) TEM microphotographs of the epoxy/3.6 wt% GO-D2000 nanocomposite

CONCLUSIONS

GO is reduced and functionalized simultaneously by refluxing with D2000 followed by thermal treatment at 120 °C for 10 h. The resultant GO-D2000 is highly conductive with an electrical conductivity of 11 S/m, nearly 8 orders of magnitude higher than that of GO. Different from the thermally unstable and hydrophilic GO, GO-D2000 is thermally stable and hydrophobic. The presence of D2000 improves the dispersion of GO-D2000 in the epoxy matrix and the interfacial interaction between GO-D2000 and epoxy. GO-D2000 is confirmed to be efficient in improving the electrical conductivity of epoxy resin. The epoxy/GO-D2000 nanocomposites exhibit a sharp transition from electrically insulating to conducting with a low percolation threshold at 0.71 vol%, which is attributed to the high conductivity of GO-D2000 sheets and their good dispersion in epoxy matrix.

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