



Electrically conductive rubbery epoxy/diamine-functionalized graphene nanocomposites with improved mechanical properties



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ABSTRACT

Simultaneous reduction and surface functionalization of graphene oxide (GO) was achieved by refluxing GO with a diamine, polyetheramine (D230) at 95 °C followed by thermal treatment at 120 °C. The D230-treated GO (GO-D230) exhibits a high electrical conductivity of 1.0 S/m, much higher than that of GO, due to the chemical and thermal reduction. The incorporation of GO-D230 significantly improves the electrical conductivity of epoxy, exhibiting a sharp transition from electrically insulating to conducting with a low percolation threshold of 0.78 vol%. With 2.7 vol% of GO-D230, the electrical conductivity of its epoxy nanocomposite is 1.0×10^{-4} S/m, nearly 11 orders of magnitude higher than that of neat epoxy; meanwhile, compared to the low Young's modulus and tensile strength of the rubbery epoxy, those of the nanocomposite are increased by 536% and 269%, respectively.

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1. Introduction

As a layered carbon nanomaterial with high aspect ratio and excellent electronic, mechanical and thermal properties [1,2], graphene is widely used in improving electrical, mechanical, and thermal properties of polymers [3–11]. Many studies have shown improved electrical conductivities and mechanical performances for rigid epoxy/graphene nanocomposites [12–14]. Till now, there are few studies on rubbery epoxy/graphene nanocomposites although they would be useful as flexible electronic devices and electronic packaging for antistatic and vibration damping [15]. It has been reported that the rubbery matrix could be reinforced more efficiently than the glassy matrix by layered silicates and carbon nanotubes [16,17]. As graphene possesses a layered structure similar to layered silicate and high thermal and electrical conductivities like carbon nanotubes, it would be an ideal nanofiller to endow rubbery epoxy with improved electrical and mechanical properties.

Among the approaches for the preparation of graphene [18], chemical reduction of graphene oxide (GO) sheets has been confirmed to be efficient and cost-effective. However, conventional reducing agents such as hydrazine [19], hydrogen sulfide [20] and hydroquinone [21] are toxic and usually result in the restacking

of graphene sheets. To overcome the above problem, eco-friendly reducing agents [22–25], such as baker's yeast [24], tea [25] and dopamine derivatives [22], have been reported to simultaneously reduce and functionalize GO. For example, Wang et al. [25] reported a green method for the reduction of GO with green tea based on the reducing capability and the aromatic rings of tea polyphenol (TP) that contains in tea solution. Due to the strong interactions between the reduced GO (RGO) and the aromatic TP, the highly conductive RGO exhibited a good dispersion in both aqueous and organic solvents. Our previous studies showed that the refluxing of GO with octadecylamine (ODA) or *p*-phenylene diamine (PPD) resulted in simultaneously reduced and functionalized GO sheets, which exhibited homogeneous dispersion in polystyrene matrix and were efficient in improving the electrical conductivity of polystyrene [26,27].

In the present study, polyetheramine D230, a flexible-chain diamine, is used to simultaneously reduce and functionalize GO. It is expected that the reduced and functionalized GO (GO-D230) would be readily dispersed in epoxy matrix, leading to significant improvements in both electrical and mechanical properties of epoxy.

2. Experimental

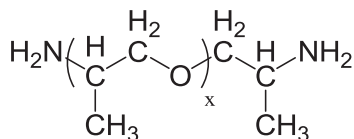
2.1. Materials

Natural graphite flakes were supplied by Huadong Graphite Factory (Pingdu, China) with an average diameter of 48 μm.

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Concentrated sulphuric acid (95–98%), fuming nitric acid (65–68%), hydrochloric acid (36–38%), potassium chlorate (98%), and dichloromethane (99.5%) were purchased from Beijing Chemical Factory (China). Diglycidyl ether of bisphenol A epoxy monomer with a trade name of Epon-828 was bought from Shell Co. JEFFAMINE® D230 and D2000 were kindly supplied by Huntsman (USA) and their structural formula was shown below:



D230 has an average molecular weight of 230 with $x = 2.5$ while D2000 has the same molecular structure as D230 and its average molecular weight is 2000 with $x = 33.1$.

2.2. Functionalization and reduction of GO

GO was prepared from natural graphite by a modified Staudenmaier method [28]. For preparation of GO-D230, GO (0.1 g) was dispersed and exfoliated in deionized water (100 ml) by ultrasonication with a JY99-II DN ultrasonicator (Ningbo, China). After desired amount of D230 (8 g, 4 g or 0.5 g) was added, the GO/D230 mixture was refluxed with mechanical stirring at 95 °C for 10 h followed by heating at 120 °C for 10 h in an oven. The obtained mixture was diluted with dichloromethane (600 ml) and filtrated with a PP porous membrane (pore size $\sim 0.45 \mu\text{m}$). 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 D230 and the filter cake was dried in an oven at 80 °C for 24 h. The resultant GO-D230 was designated as GO-D230- x , where x indicates the weight ratio of D230/GO used for the preparation. For comparison, hydrazine-reduced GO (GO-hydrazine) was prepared using the method described in the literature [19]. In a typical procedure, GO (150 mg) was exfoliated and dispersed in deionized water (150 ml) by ultrasonication. After hydrazine hydrate (1.5 ml, 49.6 mmol) was added, the suspension was refluxed under mechanical stirring at 100 °C for 10 h, diluted with water (600 ml) and finally filtrated with a PP membrane with a pore size of $\sim 0.45 \mu\text{m}$. The filter cake was rinsed in dichloromethane by ultrasonication for 5 min and then filtrated. The rinsing-filtration process was repeated for 5 times and the resultant filter cake was dried at 80 °C for 24 h. Ammonia-reduced GO (GO-ammonia) was also prepared with ammonia as the reducing agent by the same approach.

2.3. Preparation of epoxy/GO-D230 and epoxy/GO nanocomposites

GO-D230 was first dispersed in dichloromethane by ultrasonication for 1 h. The resultant suspension was then mixed with epoxy monomer and the mixture was homogenized for 2 h with an IKA T18 homogenizer (Germany) at ambient temperature, followed by heating for 10 h at 60 °C in a vacuum oven to remove the solvent. After the slurry cooled to room temperature, D2000 was added as the curing agent and mixed with an IKA EUROSTAR high-speed mixer (Germany). The resultant mixture was put into a vacuum chamber to degas for about 1 h and then poured into a stainless steel mold, pre-cured in an oven at 90 °C for 2 h and post-cured at 120 °C for another 6 h. Finally, rubbery epoxy/GO-D230 nanocomposites were prepared. The schematic illustrating the fabrication process of epoxy/GO-D230 nanocomposites is shown in Fig. 1a. Epoxy/GO nanocomposites were also prepared using the same procedure.

2.4. Characterization

The compositions of GO and GO-D230 were recorded with a ThermoVG RSCAKAB 250X high-resolution X-ray photoelectron spectroscopy (XPS). X-ray diffraction (XRD) spectra were measured using a Bruker AXS D8 ADVANCE diffractometer with $\text{CuK}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$) at a generator voltage of 40 kV and a generator current of 40 mA with a scanning speed of $10^\circ/\text{min}$. Fourier-transform infrared (FT-IR) spectra were recorded with a Nicolet Nexus 670 FT-IR spectrometer. Raman spectra were obtained with a Renishaw inVia Raman microscope (Britain) using an excitation wavelength of 514.5 nm. The dispersion of GO-D230 sheets in the epoxy matrix was observed with a JEOL JEM-3010 transmission electron microscope (TEM) at an accelerating voltage of 300 kV. Ultrathin sections with thicknesses less than 100 nm were cryogenically cut with a diamond knife using a Leica Ultracut S ultramicrotome and collected on 200-mesh copper grids. The N contents in GO and GO-D230-80 were characterized with an Elementar Analysensysteme GmbH Vario EL cube elemental analyzer. The thermal stabilities of GO, D230, GO-D230-80, GO-hydrazine and GO-ammonia were measured using a TA Q50 thermogravimetric analyzer (TGA) under nitrogen atmosphere at a heating speed of 10 °C/min. Dynamic damping ($\text{Tan } \delta$) was determined using a Rheometric Scientific DMTA V dynamic mechanical analyzer in a single-cantilever mode from $-100 \text{ }^\circ\text{C}$ to 80 °C with a heating rate of 5 °C/min and a frequency of 10 Hz. The volume conductivities were measured with a 4-Probes-Tech RTS-8 resistivity meter (China) when the conductivity is higher than $1 \times 10^{-4} \text{ S/m}$, whereas a Keithley Instruments 6517B resistivity meter (USA) was used when the conductivity is lower than $1 \times 10^{-4} \text{ S/m}$. The tensile properties of the nanocomposites were measured with an Instron 1185 testing machine (UK) according to the National Standard Test Methods of China, GB2567-2008. The dimensions of the tensile specimens are $4 \times 8 \times 80 \text{ mm}^3$ and five specimens were tested for each composition.

3. Results and discussion

3.1. Reduction and functionalization of GO with polyetheramine D230

It is expected that the simultaneous reduction and surface functionalization of GO with D230 is realized during the refluxing process by the reaction between amine groups of D230 and epoxide groups of GO. To confirm the reaction, Fig. 2 shows the FT-IR spectra of GO, D230 and GO-D230. GO exhibits typical peaks at 1704 cm^{-1} (C=O stretching vibration), 1620 cm^{-1} (C=C in aromatic ring), 1390 cm^{-1} (—OH deformation vibration), 1056 cm^{-1} (C—O—C in epoxide), and a wide peak around 3405 cm^{-1} due to its hydroxyl groups. After refluxing of GO with D230, the resulting GO-D230 presents two new peaks at 2854 and 2958 cm^{-1} due to the presence of —CH₂ and —CH stretching vibrations, and a new peak at 1099 cm^{-1} that is the characteristic absorption peak of aliphatic ether, implying the presence of D230 in GO-D230. Furthermore, the new peak at 1172 cm^{-1} (C—N stretching vibration) indicates the covalent bonding between D230 and GO, which is ascribed to the nucleophilic substitution reaction between the epoxide groups of GO and the amine groups of D230. The visual evidence for the grafting of D230 on GO-D230 is the selective dispersion of the hydrophobic GO-D230 in dichloromethane solvent while the hydrophilic GO likes to disperse in water phase (Fig. 1b).

The grafting of D230 on the sheets would enlarge the intragallery of GO. Fig. 3 shows the XRD patterns of GO, GO-D230-5, GO-D230-40, and GO-D230-80. The typical diffraction peak of GO at 12.8° corresponds to an interlayer distance of 0.69 nm, which is larger than that of graphite (0.34 nm) as a result of the

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