Convenient preparation of tunably loaded chemically converted graphene oxide/epoxy resin nanocomposites from graphene oxide sheets through two-phase extraction†

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Received 27th July 2009, Accepted 18th September 2009
First published as an Advance Article on the web 15th October 2009
DOI: 10.1039/b915228h

We report a facile method to create the chemically converted graphene oxide/epoxy resin nanocomposites from graphene oxide sheets through two-phase extraction. Great improvements in mechanical properties such as compressive failure strength and toughness have been achieved for the chemically converted graphene oxide/epoxy resin for a 0.0375 wt% loading of chemically converted graphene oxide sheets in epoxy resin by 48.3% and 1185.2%, respectively. In addition, the loading of graphene is also conveniently tunable even to 0.15 wt% just by increasing the volume of the graphene oxide dispersion.

1. Introduction

Nanocomposites have been heralded¹ as a ‘radical alternative to conventional filled polymers or polymer blends’, especially in the fields of transportation and electronics. Ideally, polymer-based nanocomposites will provide materials that possess the ease of processing inherent to plastics but with dramatically improved and even multifunctional properties, opening the way to completely new applications of polymers.

Of the carbon-based nanofillers, CNTs have attracted considerable attention due to their intrinsic mechanical and electrical properties. Improvements in modulus and strength of 30% and 15% have been reported for 1 wt% loading of functionalized single-walled carbon nanotubes (SWNTs) in epoxy,⁴ and electrical percolation was observed at loadings as low as 0.1 wt%.³ However, the use of CNTs in nanocomposites to date has been limited by challenges in processing and dispersion, and their prohibitively high cost.

In recent years, graphene has attracted numerous investigations due to its unique physical, chemical, and mechanical properties,⁴⁻⁸ opening up a new research area for materials science. The remarkable properties of graphene reported so far include high values of its fracture strength (125 GPa),¹¹ thermal conductivity (~5000 W m⁻¹ k⁻¹),¹² mobility of charge carriers (200 000 cm² g⁻¹ s⁻¹),¹³ and specific surface area (calculated value, 2630 m² g⁻¹).¹⁴ Derived from these remarkable properties, the graphene sheets may hold considerable potential as a new carbon-based nanofiller. It has recently been demonstrated that incorporation of well-dispersed graphene-based sheets into polymers at extraordinarily low filler content resulted in remarkable impact on the mechanical properties of the polymer.¹⁵ In order to efficiently affect the properties of the host matrix, two important processing issues had to be addressed: the homogeneous dispersion of graphene into the matrix, and the strong interfacial interactions required between the graphene and the matrix.¹⁶ However, challenges remaining to achieve good dispersion of graphene pose significant obstacles to these goals.

Graphene oxides (GO) containing many oxygen groups result in an enhanced mechanical interlocking with the polymer chains and, consequently, in better adhesion.¹⁷ Thus, the graphene-based composite can be created from GO as precursor. Recent studies have shown that graphene can be dispersed throughout a polymeric or inorganic matrix¹⁷ to make graphene-based composites and paper-like materials with excellent mechanical properties.⁹,¹⁵,¹⁸⁻¹⁹ The traditional procedure to create the graphene-based materials includes three steps as follows: firstly, hydrophilic GO sheets were prepared; secondly, a functionalization process was carried out to change the surface properties of GO, leading to good dispersibility of these resulting graphene sheets in organic solvent⁹,¹¹⁻¹⁴ or a thermal exfoliation was performed at high temperature giving rise to dispersible graphene sheets;²⁵ finally, the resulting graphene sheets homogeneously dispersed together with organic materials in the same solvent, especially with conjugated polymers.²⁶ Such a typical process of creation of the graphene-based materials is relatively inconvenient, since the second step is necessary for the traditional procedure. Whether a new and facile method can be developed to prepare the graphene-based nanocomposites remains an important question.

The GO sheets which have been suggested to contain many epoxy groups²³ should be able to make an ideal filler of epoxy resin which also contains epoxy groups, based on the principle of dissolution in a similar material structure. Here, we develop a facile and feasible method to obtain economically viable graphene oxide/epoxy resin nanocomposite materials directly from GO dispersion through a two-phase extraction. Skillfully, the chemically converted graphene oxide/epoxy resin nanocomposites are obtained during the solidification procedure of...
the GO/epoxy resin nanocomposite with the amine curing agent. In addition, the mechanical properties of the resulting chemically converted graphene oxide/epoxy resin nanocomposites were also investigated.

2. Experimental

2.1. Materials

Graphite powders (spectral pure) were obtained from Shanghai Chemicals, China; epoxy resin (NPEL-128, a liquid resin) which is manufactured from bisphenol-A and epichlorohydrin was obtained from Huili Chemicals, China; amine hardener (H-1618) was obtained from Huili Chemicals, China; all other reagents and solvents were purchased from commercial suppliers and used as received. Dialysis membrane (Mw 8000–14 000) was purchased from Beijing Tingguo Biology Chemicals Company. All aqueous solutions were prepared with ultra-pure water (>18 MΩ) from a Milli-Q Plus system (Millipore).

2.2. Preparation of homogenous dispersion of GO in epoxy resin

10 g of epoxy resin was mixed with 1.5, 3.75, and 7.5 mL of as-prepared GO dispersion (0.5 mg mL⁻¹) in three 50 mL glass vials, respectively and the weight ratios were 0.0075 wt%, 0.01875 wt%, and 0.0375 wt%, respectively. The mixtures were vigorously shaken or stirred for 4 h in an oil bath (50 °C), and then allowed to stand for several hours to separate into two layers. From Fig. 1A, the upper layer of water is colorless and transparent, indicating that the GO sheets in water have been completely extracted into the epoxy resin phase as expected. To obtain homogenous GO/epoxy resin composites, the mixtures were subjected to being shaken and stirred for several additional hours in an oil bath, completely removing water. Finally, homogenous composites were obtained.

2.3. Preparation of bulk monoliths

10 g of the resulting homogenous dispersion of GO in epoxy resin at different GO weights (0.0075 wt%, 0.01875 wt% and 0.0375 wt%) was mixed with 5 g of amine hardener. In control experiments, 10 g of neat epoxy resin monolith was prepared with 5 g of amine hardener by a similar way. Then the final mixtures were added into cylindrical molds (H = 8.34 mm and D = 11.18 mm) and cured at 150 °C for 2 h. Photos of the resulting monoliths are shown in Fig. S5 (ESI†).

2.4. Measurements and characterizations

X-Ray photoelectron spectroscopy (XPS) analysis was carried on an ESCALAB MK II X-ray photoelectron spectrometer. Fourier transform infrared spectroscopy (FTIR) was recorded on a CaF₂ substrate containing the target materials in the solid state with a Bruker Tensor 27 Spectrometer (4 cm⁻¹). Thermogravimetric analysis (TGA) was measured under a nitrogen atmosphere with a Perkin Elmer Thermal Analyzer at a heating rate of 5 °C min⁻¹. Scanning electron microscopy (SEM) measurements were conducted with an XL30 ESEM FEG field emission scanning electron microscope. Transmission electron microscopy (TEM) pictures were imaged by JEOL 2000 transmission electron microscope operating at 200 kV. Atomic force microscope (AFM) images were obtained by a Digital Instruments Nanoscope IIIa (Santa Barbara, CA). The sample was prepared through drop-casting on freshly cleaved mica surface. Compressive tests were performed using an Instron 1121 with a crosshead speed of 0.1 mm min⁻¹.

3. Results and discussion

Scheme 1 illustrates the synthesis process of chemically converted graphene oxide/epoxy resin nanocomposite monoliths. The studied GO sheets were prepared by oxidizing natural graphite powder based on the literature (see ESI†). Finally, as-purified GO powders were distributed in water to create a homogenous yellow-brown dispersion (0.05 wt%) ready for use. The resulting GO sheets have been characterized by combined methods (see ESI†). It is clear that the C–O epoxy/ether group be in the majority, which was proved by XPS (see ESI†, Fig. S1) and FTIR (see ESI†, Fig. S2) measurements. Moreover, the well-exfoliated samples of GO sheets were imaged using AFM (see ESI†, Fig. S3). On average, the interlay space of the GO sheets is ca. 0.96 nm, indicating that exfoliation of graphite down...
to individual GO nanosheets was indeed achieved. Finally, TEM and SEM measurements (see ESI†, Fig. S4) have also been performed. Distortions caused by the oxygen groups and the extremely small thickness of the resulting GO sheets lead to a wrinkled topology as shown in the SEM and TEM images. The surface roughness will also result in an enhanced mechanical interlocking with the epoxy resin and, consequently, in better adhesion.

All the results demonstrate that the well peeled-off GO nanosheets with many epoxy groups have been obtained successfully in this work. Subsequently, we skilfully transferred the resulting GO sheets into an epoxy resin matrix from a water phase through extraction and obtained a mixture (see Fig. 1A, lower layer). After completely removing the water in the mixture, the homogenous dispersion of GO in epoxy resin was achieved as expected (Fig. 2C). In a control experiment, the water-soluble chemically converted graphene sheets were extracted with epoxy resin in a similar way. After vigorously being shaken or stirred for 4 h, the layer of water is still black and the layer of epoxy resin is gray owing to the presence of water (Fig. 1B), indicating that the graphene sheets without any surface treatment can not be directly transferred into the epoxy resin from water phase. In order to conveniently observe the dispersibility of the GO sheets in epoxy resin matrix, a colorless and transparent liquid epoxy resin (NPEL-128) was used in this work.

In a typical solidification procedure of an epoxy resin, a curing agent is required. As GO sheets have been suggested to contain many reactive epoxy groups, its reaction with amine materials should easily occur. In our previous work, chemically-converted graphene oxides with silanes and ionic liquids, based on the reaction of the amino groups and epoxy groups, have been reported. So a colorless and transparent amine hardener (H-1618) was used in this procedure of solidification. The curing agent not only solidified the GO/epoxy resin nanocomposites but also chemically converted GO sheets encapsulated in epoxy resin matrix into chemically converted graphene oxide through the reaction between epoxy groups of GO and amine units of the curing agent. In short, the chemically converted graphene oxide sheets were simultaneously obtained during the process of the solidification of the GO/epoxy resin composites. The chemically converted graphene oxide/epoxy resin nanocomposite monoliths were obtained successfully from as-prepared homogenous dispersion of GO in epoxy resin as the precursor. The resulting composite monoliths are black not yellow-brown owing to the restoration of electronic conjugation of graphene sheets brought about during the interaction between GO sheets and amine curing agent.

Compressive tests were carried out to investigate how the chemically converted graphene oxides impact on mechanical properties of the epoxy matrix. The neat epoxy resin monolith and chemically converted graphene oxide/epoxy resin monolith for 0.0375 wt% loading were chosen for compressive tests. Fig. 3 shows stress–strain curves. The control sample exhibited typical compressive behavior of epoxy resin. However, the chemically converted graphene oxide/epoxy resin nanocomposite monolith at 0.0375 wt% (dotted) showed a clear change in their compressive behavior with a remarkable increase in compressive failure strength and toughness (the area under the stress–strain curve) by 48.3 and 1185.2%, respectively. The complete results of mechanical properties were summarized and illustrated in Fig. 3 (inset a, b and c). The remarkable influence on the properties of epoxy resin at extraordinarily low filler content can be attributed to two main reasons. First, distortions caused by the oxygen functionalization and the resultant defects during thermal treatment of the precursor graphene oxide/epoxy resin, as well as the extremely small thickness of the chemically converted graphene oxide sheets, lead to a wrinkled topology at the nanoscale.

This nanoscale surface roughness can result in an enhanced mechanical interlocking with the polymer chains and, consequently, better adhesion. Second, graphene oxide contains pendant oxygen-containing groups across the surfaces which may form covalent bonds with epoxy component. Together with the high surface area and nanoscale surface roughness of

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**Fig. 2** Photos of (A) epoxy resin, (B) dispersion of GO sheets in water (0.5 mg mL⁻¹), and (C) homogenous dispersion of GO in epoxy resin matrix at 0.0375 wt% GO sheets.

**Fig. 3** Stress–strain curves of neat epoxy resin monolith (solid) and chemically converted graphene oxide/epoxy resin nanocomposite monolith (dotted), and summarized mechanical properties of monoliths (a) compressive failure stress (b) strain, and (c) toughness. Inset: photographs of monolith columns for the compressive tests. From left to right: neat epoxy resin monolith and chemically converted graphene oxide/epoxy resin nanocomposite monolith.
chemically converted graphene oxides which were encapsulated into the epoxy matrix, this surface chemistry reaction leads to stronger interfacial interactions with epoxy resin and thus substantially larger influence on the properties of the host polymer.

To get more information concerning the interfacial interaction between the matrix and chemically converted graphene oxide sheets, fractured sections of the monoliths after compressive tests were further investigated by SEM. As shown in Fig. 4, most graphene sheets were well dispersed and embedded into the epoxy resin monolith matrix (Fig. 4B), and no obvious chemically converted graphene oxide sheets can be observed to be pulled out, indicating that chemically converted graphene oxide sheets had stronger covalent interfacial bonding with the matrix in virtue of the covalent interaction between graphene oxide sheets and resin matrix. Moreover, a flake-like morphology of the chemically converted graphene oxide sheets dispersed in epoxy resin matrix was also observed (inset in Fig. 4B). This indicated that these chemically converted graphene oxide sheets in epoxy resin matrix remained well as flakes. Finally, the thermal analysis data (TGA) to further examine the interaction of graphene oxide and polymer matrix could be obtained in Fig. S6 (ESI†). The TGA was performed on GO (solid), epoxy resin (dashed), and chemically converted graphene oxide sheets/epoxy resin (dotted) and heated to 1000 °C at a heating rate of 5 °C min⁻¹ under N₂. As shown in Fig. S6 (ESI†), the thermal stability of chemically converted graphene oxide/epoxy resin nanocomposite monolith at 0.0375 wt% graphene (dotted) have slightly improved, compared with the neat epoxy resin.

4. Conclusion

In summary, we have successfully developed a simple and feasible method to obtain economically viable chemically converted graphene oxide/epoxy resin nanocomposites directly from the dispersion of GO sheets in water through a two-phase extraction. Owing to the homogeneous dispersion and stronger interfacial interactions with the epoxy resin matrix, as well as the high surface area, great improvements in mechanical properties have been achieved for chemically converted graphene oxide/epoxy resin at 0.0375 wt% chemically converted graphene oxide sheets (based on GO weight). The compressive failure strength and the toughness have been improved by 48.3% and 1185.2%, respectively. In general, high strength and high toughness are difficult to achieve at same time for common materials but the chemically converted graphene oxide/epoxy resin nanocomposites with strong interfacial linkages do exhibit this unique property well. In addition, the loading of graphene in an epoxy resin is also conveniently tunable even to 0.15 wt% just by increasing the volume of the graphene oxide dispersion.

This new method to create the chemically converted graphene oxide/epoxy resin nanocomposite is facile, feasible, and economical, compared with recently reported procedures. This method can bypass the second step which is necessary for the traditional process. Additionally, the new method allows graphene oxide sheets to be intimately mixed with various organic polymers similar to epoxy resin, facilitating the synthesis of graphene-based polymer composites.

In short, this method may make broad applications of graphene in the realms of physics and chemistry, and mechanical improvement come true. Moreover, graphene-based polymers similar to epoxy resin will provide materials which possess ease of processing inherent to polymers, but with dramatically improved and even multifunctional properties, opening a way to completely new applications of graphene and polymer composites.

Acknowledgements

The authors are most grateful to the NSFC, China (No.20673109 and 20827004) for the financial support.

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