Synthesis and properties of iodo functionalized graphene oxide/polyimide nanocomposites

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ABSTRACT

We report an effective method to fabricate the graphene-based high performance polyimide (PI) nanocomposites via the in situ polymerization with iodo functionalized graphene oxide (I-Ph-GO). The electrical conductivity of the reduced iodo functionalized graphene oxide (R-I-Ph-GO)/PI (1/99 w/w) nanocomposites was 5.2×10^{-2} S/m, which is about 10^7 times higher than that of the reduced graphene oxide (R-GO)/PI (1/99 w/w) nanocomposites. The tensile modulus of R-I-Ph-GO/PI (0.5/99.5 w/w) nanocomposites was increased from 2.5 GPa to 6.8 GPa, and the tensile strength was increased from 75 MPa to 123 MPa, which were approximately 170% and 64% enhancement compared to those of pure PI, respectively. In addition, the water transmission rate of an I-Ph-GO/PI (0.2/99.8 w/w) nanocomposites film was lower than that of R-GO/PI nanocomposites and was reduced by about 67% compared to that of pure PI.

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1. Introduction

Graphene based polymer nanocomposites have attracted widespread industrial interest because graphene has great potential for improving the electrical conductivity, mechanical properties and gas barrier properties of the nanocomposites due to their unique properties [1–12].

Graphene is a carbon allotrope with a 2-dimensional honeycomb lattice structure which shows an excellent electron charge mobility of about 200,000 cm^2/V at room temperature [13], and electrical conductivity ($\sim 10^{-6}$ Ω cm resistivity) [14], providing a percolated pathway for electron transfer and making the graphene based nanocomposites electrically conductive [15,16].

Polyimide (PI) is a strong candidate for a variety of applications such as electronics, aerospace, vehicles, and dielectric materials, due to its good mechanical properties, flexibility, high glass transition temperature, excellent thermal stability, and radiation resistance. However, pure PI has limitations in a few applications because of its insulating nature of polymer. The exceptionally high electrical conductivity of graphene makes it an ideal candidate for the preparation of conducting PI nanocomposites. Therefore, graphene based PI nanocomposites have been developed to improve the electrical conductivity [17,18] and are widely used in

electronic device applications, such as anti-static agents (1 kΩ/ sq), EMI/RFI shielding materials (100 Ω/sq), transistors and sensors.

Improving the electrical conductivity, mechanical and thermal properties of graphene/polymer nanocomposites is an important issue for the development of high performance polymer nanocomposites. However, most of the studies of graphene oxide (GO)/PI nanocomposites merely report an improvement in either the mechanical properties or electrical conductivity of PI nanocomposites through the surface functionalization of the graphene [6,19–24]. Such a phenomenon is considered to be due to the inhomogeneous dispersion of the graphene oxide in the polymer matrix and the poor reduction efficiency of the GO. Therefore, to improve the mechanical properties, electrical conductivity and thermal properties of PI nanocomposites, it is necessary to develop surface functionalization methods for GO with good dispersibility and reduction efficiency by heat at relatively low temperatures such as 300 °C to avoid thermal degradation of polyimide.

Our previous research indicated that the iodo groups acted as a catalyst to enhance the electrical conductivity of reduced graphene oxide (R-GO) [25]. Although the electrical conductivity of reduced iodo functionalized graphene oxide (R-I-Ph-GO) was 42,000 S/m which was significantly higher than R-GO, electrical conductivity of R-I-Ph-GO/PI nanocomposites was $\sim$1 S/m at 10 wt% of R-I-Ph-GO in composites due to the defects and aggregation of R-GO. The high content of GO in polymer nanocomposites has been re-

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ported to significantly enhance the electrical conductivity of nanocomposites, but to have a trade-off effect on the mechanical properties.

Herein, we propose an effective method of fabricating graphene/PI nanocomposites to improve both electrical conductivity and mechanical properties. The highly exfoliated GO was prepared by homogenizing GO flakes and in situ polymerization method was used to disperse functionalized GO in polymer matrix. The electrical conductivity of up to 5.2×10^{-2} S/m and tensile modulus of up to 6.8 GPa were achieved for composites with less than 1 wt% of the iodo functionalized graphene oxide (I-Ph-GO).

2. Experimental methods

2.1. Materials

Natural graphite flake of conducting grade (−325 mesh) was purchased from Alfa Aesar, USA. Potassium permanganate ($KMnO_4$), 4-Iodoaniline and sodium nitrite ($NaNO_2$) were purchased from Sigma–Aldrich, USA. Sulfuric acid (H_2SO_4) and hydrogen peroxide (H_2O_2) were purchased from PFP Matunoen Chemicals Ltd., Japan. Poly(amic acid) (PAA) was prepared via in situ polymerization. Pyromellitic dianhydride (PMDA) and 4, 4′-oxidianiline (ODA) were used as precursors of poly(amic acid). PMDA, ODA, and 1-methyl-2-pyrolidinone (NMP) were purchased from Sigma–Aldrich, USA.

2.2. Preparation of graphite oxide

The oxidation of graphite was carried out following a modified hummer's method. In a typical procedure, graphite (1 g) was added into 50 mL sulfuric acid (H_2SO_4) under stirring. After 10 min, 3 g of $KMnO_4$ was added slowly. The mixture was then heated up to 35 °C and stirred for 6 h. Subsequently, 80 mL of water was added under vigorous stirring, resulting in a quick rise in the temperature to ~80 °C. The slurry was further stirred at the same temperature for another 30 min.

Afterwards, 200 mL of DI-water and 6 mL of H_2O_2 solution were added in sequence to dissolve the insoluble manganese species. The resulting graphite oxide suspension was washed repeatedly by a large amount of DI-water until the solution pH reached a constant value at ~5, and finally the suspension was diluted with 1000 mL of DI-water. Finally, the graphite oxide suspension was centrifuged (1000 rpm for 1 h), and a setting product was dialyzed for 1 week. The product was dried for 24 h in a freezing drier.

2.3. Preparation of iodo phenyl and phenyl functionalized graphite oxide (I-Ph-GO and Ph-GO)

0.05 g of GO was immersed in 100 mL of H_2SO_4 solution at room temperature and sonicated for 30 min. The mixture was then poured into a flask. After that, 1.8 g of 4-iodoaniline (or aniline) and 0.69 g of sodium nitrite ($NaNO_2$) were quickly added via a syringe. The mixture was vigorously magnetically stirred at 60 °C for 1 h. After cooling to room temperature, the suspension was diluted and washed with DMF until colorless to remove any unreacted diazonium salt from the mixture. Finally, the product was washed with ethanol and dried at 60 °C for 24 h in a vacuum oven.

2.4. Preparation of functionalized graphene oxide (GO and I-Ph-GO) reinforced polyimide (PI) nanocomposites

Surface functionalized graphite oxide (GO or I-Ph-GO) was immersed in a NMP solution and homogenized for 1 h at room temperature. After that, ODA was added to the mixture. The surface functionalized GO and diamine mixture continued to be stirred for 1 h before adding the PMDA to completely dissolve the ODA. Once the ODA was dissolved in NMP followed by the addition of PMDA, the mixture was stirred overnight at room temperature. The prepared surface functionalized GO incorporated poly(amic acid) (PAA) was casted on the polyimide film using a doctor blade. The cast films were dried at 80 °C for 4 h in a vacuum oven to remove the residual solvent. R-GO/PI and R-I-Ph-GO composites films were prepared with the thermal curing of PAA. The GO/PAA and I-Ph-GO/PAA composites were thermally imidized via the following procedure: (1) heating them up to 100 °C at a rate of 10 °C/min and then annealing them for 2 h, (2) heating them up to 200 °C at a rate of 10 °C/min and annealing them for 15 min, (3) heating them up to 300 °C at a rate of 5 °C/min and annealing them for 6 h, and (4) heating them up to 430 °C at a heating rate of 2 °C/min and then annealing them for 30 min.

2.5. Characterization

The dispersibility of functionalized graphene oxide (GO, Ph-GO and I-Ph-GO) in DI-water was measured by UV–vis spectroscopy (V-670, JASCO, USA). The spectra were measured in a 300–900 nm wavelength range. By measuring the absorbance of functionalized graphene dispersion at 660 nm, the concentration functionalized graphene solution was calculated based on Lambert–Beer law.

The thickness of the I-Ph-GO was measured by atomic force microscopy (AFM) (NanoscopeIIIa-Multimode AFM, Veeco-Digital instrument, USA). The electrical conductivities of the R-GO/PI and R-I-Ph-GO/PI nanocomposite films were measured using a 4-point probe (FPP-RS8, Dasol Eng, Korea).

The tensile strength and modulus of the R-GO/PI and R-I-Ph-GO/PI nanocomposite films were measured by a universal testing machine (UTM, 5567A, Instron. USA). Twenty specimens with length of 25 mm and width of 5 mm were prepared for each sample. The speed of the crosshead was 1 mm/min. The resulting cross-section formed after the rupture of the tensile specimen was analyzed by field emission scanning electron microscopy (FE-SEM: S-4700, Hitachi, Japan).

The water vapor permeability of the R-GO/PI and R-I-Ph-GO/PI composite films was measured using a water vapor transmission analyzer (AQUATRAN Model 1, Mocon, USA).

Thermogravimetric analysis (TGA, Q5000, TA Instruments, USA) was performed to determine the thermal stability of the R-GO/PI and R-I-Ph-GO/PI nanocomposite films. The TGA was performed in the temperature range from room temperature to 750 °C at a heating rate of 5 °C/min in an air atmosphere.

3. Results and discussion

3.1. Characterization of functionalized graphene oxide (GO and I-Ph-GO)

These dispersions were then characterized by UV/vis spectroscopy, with the absorption coefficient plotted versus wavelength. The absorption coefficient, α, which is related to the absorbance (α) per unit path length (l), A/l, through the Lambert–Beer law A/$l = \alpha C$, is an important parameter in characterizing any dispersion. In order to accurately ascertain the graphene concentration, the absorption coefficient, α, must be determined experimentally. So we prepared a large volume of graphene dispersion in DI-water. Each of the five dispersions was diluted a number of times and the absorption spectra were recorded. The absorbance (660 nm) divided by cell length was plotted versus concentration (Fig. 1). The maximum solubility for I-Ph-GO in DI-water was determined to be