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Preparation and properties of reduced graphene oxide/polyacrylonitrile nanocomposites using polyvinyl phenol

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ABSTRACT

Nanocomposites of polyacrylonitrile (PAN) with reduced graphene oxide (rGO) were prepared using a solution mixing technique employing polyvinyl phenol (PVP) as a compatibilizer. The PVP can facilitate composite formation by interacting with both rGO and PAN via π-π and H-bonding respectively. Various amounts of rGO were used to prepare PAN nanocomposites. The cross-sectional morphology of the composite films shows a uniform dispersion of rGO sheets in the PAN matrix. The Fourier transform infrared (FT-IR) studies revealed that good interaction of the rGO/PVP hybrid with PAN. The wide angle x-ray diffraction (WAXS) study confirms that the rGO sheets were uniformely dispersed as individual sheets in the PAN matrix. Thermogravimetric analysis shows enhanced thermal stability of the composite compared to pure PAN. The tensile strength and elastic modulus of the nanocomposites increased with increasing rGO content. A 102% enhancement in tensile strength and a 62.9% enhancement in elastic modulus were observed in the nanocomposite with 5% rGO.

1. Introduction

During the last decades, polymer nanocomposites have gained significant interest as light weight nanocomposite materials for a wide variety of applications, such as automobiles, aerospace, packaging materials, coatings, pigments and construction materials. For this purpose, various types of fillers including cellulose nanocrystal, silicate, clay, carbon black, expanded graphite, carbon nanofibers, carbon nanotubes, and graphene have been used to fabricate polymer nanocomposites [1–6]. Among these materials, graphene is the most promising material due to its high aspect ratio and intriguing thermal, mechanical and electrical properties [7]. To develop graphene-based technologies, graphene sheets must be able to be uniformly integrated into the polymer matrix [8]. However, the use of pristine graphene as a filler for composite application is very difficult due to the existence of strong van der Waals forces among the graphene sheets, resulting in a strong aggregation potential of the graphene sheets within the polymer matrix [9]. Usually, the aggregation among graphene sheets and weak interfacial interaction between graphene sheets and polymer matrix result in weak properties of such polymer nanocomposites [10]. To overcome this drawback and make rGO sheets compatible with the polymer matrix, surface modification of graphene sheets with a suitable compatibilizer is important as a prospective method to improve the dispersibility of graphene into the polymer matrix [11–13]. Generally, two techniques, (i) covalent [14] and (ii) non-covalent [15], are widely used to enhance dispersion and make graphene compatible with the polymer matrix in order to fabricate high-performance graphene/polymer nanocomposites. Polystyrene-functionalized graphene nanocomposites with polystyrene matrix have been fabricated using the compatiblizing property of graphene functionalized polystyrene with matrix polystyrene [16]. Thermally reduced graphene oxide (rGO) was functionalized using the Bingel reaction to produce carboxylic acid groups on its surface; using the compatiblizing property of this modified graphene, a nanocomposite with epoxy resin was fabricated [17]. Non-covalently-functionalized graphene with pyrene-end poly(glycidyl methacrylate) (Py-PGMA)/epoxy

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nanocomposites were prepared as a thermally conductive nanocomposite using the compatibilizing property of Py-PGMA with epoxy resin [18]. A long alkyl chain-modified graphene/polymethyl methacrylate composite was prepared using the compatiblizing property of alkyl chains with PMMA [19]. The alkyl chain of the alkyl group-modified graphene acts as a very good compatiblizer for the fabrication of high-performance graphene polystyrene nanocomposites [20]. Non-covalently-functionalized graphene with sulphonated polyether ether ketone (SPEEK)/polyvinylidene fluoride (PVDF) nanocomposite were fabricated utilizing the compatibilizing property of SPEEK with PVDF [21]. Though there are few reports of graphene-based polymer nanocomposites using suitable compatibilizer-functionalized graphene, scientists are still facing challenges to disperse individual graphene sheet uniformly into the polymer matrix to produce excellent interfacial stress transfer [22,23].

Polyacrylonitrile (PAN) is a technologically important polymer and a major precursor for the production of carbon fibers. It has significant commercial utility and potential applications in a wide variety of fields. A large number of research efforts have been devoted to various aspects of nanocomposite processing and property development which may have potential application in the fabrication of engineering composites for industrial application. PAN is also used for the construction of packaging and fire-retardant material via nanocomposite fabrication [24].

Herein, we prepared graphene-based PAN composites via a solution mixing approach using polyvinyl phenol (PVP) as a compatiblizer to enhance the physical and mechanical properties of the composite films. The rGO shows inhomogeneous dispersion in N, N-dimethylformamide (DMF) and forms an incompatible composite with PAN. Hence, we utilized polyvinyl phenol (PVP) as a compatiblizer to enhance the dispersion of rGO sheets in the PAN matrix. PVP was chosen as a compatiblizer; because it can be interact with rGO via π-π interaction, while phenolic −OH groups of PVP help to interact with PAN to produce high-performance rGO/PAN nanocomposites. The enhancement of thermal and mechanical properties of graphene/PAN nanocomposite may have potential application in production of high-performance lightweight composite materials.

2. Experimental section

2.1. Materials

Natural flake graphite was purchased from Sigma–Aldrich Co. (Germany). Sulfuric acid (Showa Chemical Co. Japan, 98 wt %), hydrogen peroxide (Samchun Pure Chemical Co. Ltd, Korea, 35%), and hydrochloric acid (Showa Chemical Co. Japan, 35 wt.%) were used as received. Potassium permanganate (Junsei Chemical Co. Ltd, Japan) and hydrazine monohydrate (TCI, Japan) were used as oxidizing and reducing agents, respectively. PVP and PAN were purchased from Sigma–Aldrich, USA and used as received. DMF was received from Showa Chemical Co, Japan and used without purification.

2.2. Preparation of graphite oxide (GO) from natural flake graphite

GO was synthesized by the oxidation of natural graphite flake using a modified Hummers method [25]. In this typical preparation method, 46 mL of concentrated H_2SO_4 (95%) was added to a round bottom flask, which was placed in an ice bath to maintain the temperature at 0–5 °C during the reaction. Subsequently, 2 g of graphite flake was added slowly into the round bottom flake with constant stirring. Then, 6 g of potassium permanganate was very slowly added to the reaction mixture. After $KMnO_4$ addition, the mixture was removed from the ice bath and was stirred at 35 °C for 6 h. With time, the reaction mixture changed color from black to light brown and formed a thick paste. Then, 92 mL of water was slowly added into, during which the temperature of the reaction mixture increased rapidly. Subsequently, 10 mL of 30% H_2O_2 was added to the reaction mixture, producing a brown to light yellow color change. The GO was purified by centrifugation with 5% HCl. Finally, GO was obtained by repeat re-dispersion in water and centrifugation and was collected by drying the pellet after centrifugation under vacuum.

2.3. Preparation of rGO

0.1 g GO powder was dispersed in 150 mL water and sonicated for 30 min to make a homogeneous brown solution. Then, hydrazine monohydrate (1 mL) was added drop wise into this aqueous GO solution, which was immersed into an oil bath at 80 °C. Then, the reaction mixture was allowed to stir for 12 h. Within a few minutes, the color of the solution changed from brown to black and black particles precipitated from the solution. The resulting black powder was collected by vacuum filtration and drying in a vacuum oven at 60 °C for 24 h.

2.4. Preparation of rGO/PVP hybrid PAN nanocomposite (PMG)

The nanocomposites were prepared using a solution mixing method. In this typical procedure, 1 g of PAN was dissolved in 10 mL of DMF at 90 °C in a culture tube. In another culture tube, an rGO/PVP hybrid solution was prepared by dispersing the required amount of rGO in the presence of a measured amount of PVP via ultrasonication. The resulting rGO/PVP hybrid solution was mixed with PAN solution with constant stirring and allowed to sonicate for 30 min to form a homogeneous solution. Finally, the solution mixture was poured in a Petri-dish and allowed to evaporate at 50 °C to produce the PMG films. The films were placed under vacuum at 60 °C for 24 h to remove any trapped solvent. The resulting materials were designated as PMG1, PMG3, PMG5, and PMG6, respectively, where the numbers indicates the weight % of rGO/PVP hybrid with respect to polymer. Pure PAN film was also prepared by dissolving the PAN in DMF and evaporating the solvent at 60 °C.

2.5. Characterization

Ultra violet-visible (UV–vis) spectroscopy of the GO, rGO, and rGO/PVP hybrid was carried out by dispersing the materials in DMF and recording data using a UVS-2100 SCINCO spectrophotometer. Fourier transform infrared (FT-IR) spectra of the samples were recorded over a wavenumber range of 500–4000 cm^{-1} using a Nicolet 6700 spectrometer (Thermo Scientific, USA). Raman spectra of the samples were recorded at room temperature using a Nanofinder 30 (Tokyo Instruments Co., Osaka, Japan) over the range of 500–3000 cm^{-1}. Thermogravimetric analysis (TGA) was carried out at a heating rate of 5 °C min^{-1} from 50 to 800 °C in a nitrogen atmosphere using a Q50 TGA (TA Instruments, New Castle, Delaware, USA). The cross-sectional morphology of the composite films was observed through field emission scanning electron microscopy (FE-SEM) (JSM-6701F, JEOL, Japan), after each sample was coated with osmium. Wide angle x-ray diffraction (WAXS) analysis of all samples was carried out at room temperature using a D/Max 2500 V/PC (Rigaku Corporation, Tokyo, Japan) from $2\theta = 5–40°$ with a scan rate of 2 s/step. The cyclization temperatures were investigated using differential scanning calorimetry (DSC) (Perkin Elmer Pyris1). The tensile properties of the pure PAN and composite films were measured using a universal