Composites Science and Technology 146 (2017) 161–168

Contents lists available at ScienceDirect

Composites Science and Technology

journal homepage: http://www.elsevier.com/locate/compscitech

Preparation of epoxy nanocomposites containing well-dispersed graphene nanosheets

Haiqing Yao [a, b], Spencer A. Hawkins [a, b], Hung-Jue Sue [a, b, c, *]

[a] Department of Materials Science and Engineering, Texas A&M University, College Station, TX 77843, United States
[b] Polymer Technology Center, Texas A&M University, College Station, TX 77843, United States
[c] Department of Mechanical Engineering, Texas A&M University, College Station, TX 77843, United States

ARTICLE INFO

Article history:
Received 9 December 2016
Received in revised form
5 April 2017
Accepted 20 April 2017
Available online 23 April 2017

Keywords:
Graphene
Epoxy nanocomposites
Dispersion
Tensile properties
Thermal conductivity

ABSTRACT

To take full advantage of the potential of graphene nanosheets as reinforcing agents for polymer nanocomposites, good exfoliation, homogenous dispersion, and strong affinity of graphene nanosheets in a polymer matrix are needed. In this research, homogeneous dispersion of graphene nanosheets in epoxy is achieved via chemical functionalization of graphene oxide with 4-nitrobenzenediazonium salt. Optical microscopy and transmission electron microscopy demonstrate that graphene nanosheets are well-exfoliated in organic solvents and in epoxy. While only a marginal increase in Young's modulus is observed, significant improvements in tensile strength (>30%) and elongation at break (>50%) for epoxy nanocomposites with a graphene concentration of 0.8 wt.% are achieved. The thermal conductivity of an epoxy nanocomposite with modified graphene nanosheets at 5 wt.% increases to 0.56 W/mK, approximately 2.5 times that of the neat epoxy. The possible mechanisms that account for the observed improvements in tensile properties and thermal conductivity are discussed.

1. Introduction

Graphene, a single-atom-thick layer of carbon atoms bonded together in a hexagonal lattice, has received significant attention due to its attractive electrical, thermal, and mechanical properties [1–7]. Graphene and graphene derivatives have been widely used as nanofillers to prepare polymer nanocomposites. These nanocomposites exhibit tremendous potential for mechanical property enhancement due to their combination of high specific surface area, strong nanofiller–matrix adhesion, and the outstanding mechanical properties of the planar sp2 carbon bonding network in graphene [7–9].

Until now, four approaches have been shown to successfully produce graphene nanosheets [10] including: mechanical cleavage of graphite [11], epitaxial growth [12], chemical vapor deposition (CVD) [13] and chemical exfoliation of graphite [14]. Among these methods, chemical exfoliation is the most economical and promising method for preparing polymer nanocomposites because of the large yield of graphene generated and its easy functionalization thereafter for targeted applications [10]. For chemical exfoliation, the first step involves chemical oxidation of graphite into graphene oxide (GO) [15]. In contrast to pristine graphite, GO is heavily oxidized, containing hydroxyl and epoxide functional groups on its basal plane and carboxyl groups at the sheet edges [16,17]. The presence of these functional groups causes GO to readily swell and exfoliate in water. Unfortunately, the coexistence of oxygen containing species at the edges and polyaromatic rings on the surface of the nanosheet make GO amphiphilic and difficult to disperse in organic media [18]. In addition, the formation of large amounts of sp3 carbon during oxidation greatly decreases the inherent electrical, thermal and mechanical properties of graphene. Thus, further chemical modification of GO to restore these sp3 carbons back to sp2 carbons is needed to partially recover the electrical and mechanical properties [19–21].

To enhance the solubility of GO in organic solvents and to achieve better compatibility between GO and a polymer matrix, chemical modification of GO is essential to prepare good quality polymer nanocomposites [22]. For example, phenyl isocyanate-treated GO was reported by Stankovich and his coworkers as an effective route to successfully prepare polystyrene nanocomposites [13]. This isocyanate treatment reduces the hydrophilic characteristic of GO by forming amide and carbamate ester groups. The

---

[*] Corresponding author. Department of Materials Science and Engineering, Texas A&M University, College Station, TX 77843, United States.
E-mail address: hjsue@tamu.edu (H.-J. Sue).

http://dx.doi.org/10.1016/j.compscitech.2017.04.026

resulting GO derivative is uniformly dispersed in polystyrene. More recently, Wan et al. reported GO sheets functionalized with low-cost diglycidyl ether of bisphenol-A epoxy chains to enhance its compatibility with epoxy [3]. Improved dispersion and exfoliation of functionalized GO sheets in epoxy were achieved when compared to epoxy nanocomposites prepared with as-prepared GO sheets. To remove the defects in GO and to restore the inherent electrical and thermal conductivities of graphene, a chemical/thermal reduction step is needed [19,23]. One accompanying problem with the reduction process is the irreversible re-aggregation and restacking of exfoliated graphene sheets due to strong van der Waals interactions among the recovered sheets [10]. One way to prevent re-aggregation of graphene is to stabilize GO with surfactants during the reduction process, which makes the re-dispersion of reduced GO in solvents more feasible [14].

In this work, the chemical reduction of GO using hydrazine and subsequent chemical modification of reduced GO using 4-nitrobenzenediazonium salt are reported. The diazonium reaction occurs via an aryl radical reaction with GO to anchor onto the graphene surface by forming covalent aryl bonds [24]. The nitrobenzene groups form covalent bonds with the basal carbon atoms of GO. The modified graphene nanosheets form a homogeneous dispersion in organic solvents and in epoxy due to the polar nature of the nitrobenzene groups. The effect of modified graphene on the thermal and tensile properties of epoxy/graphene nanocomposites is reported to understand their structure-property relationship.

2. Experimental

2.1. Materials

Graphite (SP-1, average particle size 45 μm) was donated by Bay Carbon Inc., USA. 4-nitrobenzenediazonium tetrafluoroborate was purchased from TCI, USA. Sodium dodecylbenzenesulfonate, hydrazine and all solvents were purchased from Sigma-Aldrich and used as received. The epoxy resin and curing agent used in this study are diglycidylether of bisphenol F, DGEB-F (D.E.R.® 354) and DETDA (diethyl toluenediamine), which were donated by the Dow Chemical Company and Momentive Company, respectively.

2.2. Experimental methods

2.2.1. Synthesis of GO

GO was synthesized according to a modified Hummers' method [15]. Graphite powder (0.5 g) was first treated by a solution containing concentrated H_2SO_4 (50 mL) and $NaNO_3$ (0.5 g) and kept below 5 °C. $KMnO_4$ (3 g) was added gradually into the mixture while stirring. After stirring for 2 h, the temperature of the mixture was increased to 35 °C and kept for another 2 h. The mixture was then carefully diluted with deionized (DI) water (23 mL). An additional 71 mL of DI-water and H_2O_2 (10 mL, 30%) were added after 15 min. The color of the mixture changed from black to brilliant yellow. The mixture was then washed with DI water and HCl several times to purify the GO.

2.2.2. Synthesis of diazonium-functionalized graphene (DG)

In a typical functionalization procedure (Fig. 1), GO (100 mg) was dispersed in aqueous solution containing 1 wt.% sodium dodecylbenzenesulfonate (SDBS) surfactant (200 mL). The resulting GO dispersion was reduced by hydrazine hydrate (1 mL) at 80 °C for 24 h. Without further treatment, the reduced GO solution was reacted with 4-nitrobenzenediazonium tetrafluoroborate (molar ratio of diazonium salt to GO was 4:1) for 2 h at RT. The mixture was then diluted with 100 mL of acetone and filtered. The filter cake was washed with water and acetone several times until the filtrate became colorless, indicating the excess diazonium salts had been totally removed. The resulting filter cake was re-dispersed in acetone.

2.2.3. Preparation of epoxy/DG nanocomposites

Functionalized graphene was mixed with epoxy and curing agent in acetone to achieve a final graphene concentration of 0.4 and 0.8 wt.%. The solvents were then removed via rotary evaporation in a water bath at 60 °C until no bubbles are observed. The mixture was poured into a preheated glass mold with pretreated mold release agent. The epoxy nanocomposites were then cured in an oven at 121 °C for 3 h, followed by a 3 h post-cure at 177 °C. For comparison purposes, a neat epoxy sample was also prepared using the same curing procedure.

2.2.4. Preparation of thin film composites

Epoxy/curing agent mixtures containing 2 wt.% and 5 wt.% of graphene were B-staged in a preheated oven at 121 °C for 30 min to increase its viscosity for thin film processing. Once B-staged, the mixture was poured onto an Elcometer 4340 thin film coater preheated to 80 °C and cast at 5 mm/s to obtain a thickness of ~140 μm. Next, the film was placed in a preheated oven at 121 °C and cured for 2.5 h followed by a post-cure at 177 °C for 3 h.

2.3. Characterization

Fourier transform infrared spectroscopy-attenuated total reflectance (FTIR-ATR) spectra were acquired using a Nicolet 380 (Thermo Fisher Scientific) in conjunction with an ATR accessory (AVATAR OMNI Sampler, Germanium crystal) under ambient conditions. XPS spectra of functionalized graphene were obtained with a Kratos Axis Ultra using a nonmonochromatic MgKa photon source (1486 eV) for measurements. The spectra were fit using XPSPEAK 4.1 by applying a linear-type background correction. For thermogravimetric analysis (TGA), powdered graphene samples (2–3 mg) were tested. The tests were performed using a TGA (Q500, TA Instruments) by ramping the sample temperature from 30 °C to 900 °C at a ramp rate of 10 °C/min in air.

The dispersion state of graphene in acetone was directly observed with an Olympus BX60 optical microscope (OM) in transmission mode under ambient temperature. Graphene solution was dropped onto a glass slide and covered with another glass slide before the solvent evaporated. The focus was adjusted to observe the solution dispersion state between the two glass slides. The thickness of exfoliated graphene was determined by an atomic force microscope (AFM, Digital Instruments Nanoscope AFM/STM). To observe the nature of DG bonding to epoxy, pre-notched samples were quenched in liquid nitrogen and then broken to obtain fresh fracture surfaces. The fracture surfaces of the nanocomposites were sputter-coated with a thin layer (5 nm) of Pt prior to imaging with a field emission scanning electron microscope (SEM) (JSM-7500F, JEOL). TEM was performed using a JEOL 2010 transmission electron microscope operated at 200 kV. A Reichert-Jung Ultracut-E microtome was used to prepare thin sections of the nanocomposites with a thickness of 60–70 nm for TEM.

Thermal conductivity was measured according to ASTM D5470-12. The dimensions of the thin film samples are $52 \times 26 \times 0.14\ mm^3$. Tensile properties were measured according to ASTM D638-98. The tests were performed using an MTS universal testing machine at a crosshead speed of 5 mm/min at ambient temperature. The Young's modulus, tensile strength, and elongation at break of each sample were calculated based on at least five specimens per sample with the average values and standard deviations reported. Dynamic mechanical analysis (DMA) was conducted using an ARES-G2 dynamic mechanical analyzer (TA