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Functionalized graphene oxide as reinforcement in epoxy based nanocomposites

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ABSTRACT

The effects of amine-modified graphene oxide on dispersion and micro-hardness of epoxy based nanocomposites are reported. Graphene oxide was prepared by the modified Hummers method followed by hexamethylenediamine functionalization. Analysis conducted through Fourier transform infrared spectroscopy, Raman spectroscopy, X-ray photoelectron spectroscopy and atomic force microscopy-based infrared spectroscopy show that the functionalization process effectively promoted a replacement of oxygen with amine groups while simultaneously creating defects in the graphitic structure. An increase in hardness was observed for the developed nanocomposites.

1. Introduction

Graphene oxide (GO) is an important carbon-based nanomaterial and it has attracted a great interest from researchers due to its unique properties; high surface area (~2630 $m^2 g^{-1}$) [1], high intrinsic mobility that can reach up to 200,000 $cm^2 V^{-1} s^{-1}$ [2], high Young modulus (~1 TPa) [3], high mechanical stiffness (> 1000 GPa) [4], and exceptionally high thermal conductivity [5]. These properties make GO a very attractive material to be used as nanofiller in polymer matrices leading to the development of a new class of nanocomposites [6–8]. These composite materials have attracted extensive attention due to observed enhancements in mechanical, thermo-physical and electrical properties resulting in a variety of promising applications [9–11]. In this context, as reported by Huang et al. [12], the reinforcement efficiency of the graphene oxide in the polymer nanocomposites is better than those of the corresponding carbon nanotubes (CNTs) or functionalized CNTs.

Graphene oxide-based composite are viable candidates for a variety of industrial applications, especially for aircraft components, in particular electronics, such as supercapacitors, transistors, etc. [13–15]. However, although graphene/polymer composites have promising applications, the agglomeration of graphene sheets due to the strong van der Waals forces among their sheets and the weak compatibility with most of polymer matrices have been fundamental roadblocks that restrict its potential as a reinforcing agent [16,17]. Surface modification of graphene by adding functional groups is an effective way to reduce the tendency to agglomerate [18]. In addition, functionalization increases the graphene compatibility with specific polymers improving the reinforcing effect [19].

Several studies have investigated the effect of carbon materials functionalization on the final properties of polymer composites [20]. Chatterjee et al. [21] observed that the fracture toughness of an epoxy increased 66% after addition of 0.1 wt.% of expanded graphene nanoplatelets modified by dodecylamine. Other researchers [22] observed an increase of 72% in Young's modulus and 143% in hardness with 0.5 wt.% of amino-modified graphene by tetraethylenepentamine. The authors attributed these results to the chemical modification of the graphene. Wan et al. [23] prepared epoxy composites filled with bisphenol-A functionalized GO (DGEBA–f–GO). They observed that the surface modification of GO with DGEBA improves the compatibility and dispersion of GO sheets in epoxy matrix, resulting in improved mechanical properties of the composites. Similar results were observed by other authors working with epoxy-based composites filled with silane functionalized GO (silane-f-GO) [24], reduced graphene oxide (TRGO) [25] and polyetheramine-functionalized graphene oxide (PEA-f-GO) [26]. Other authors [27] prepared composites chemically reduced graphene oxide (CRGO) sheets grafted with poly(methyl methacrylate) (PMMA-grafted-CRGO) by emulsion polymerization. The authors

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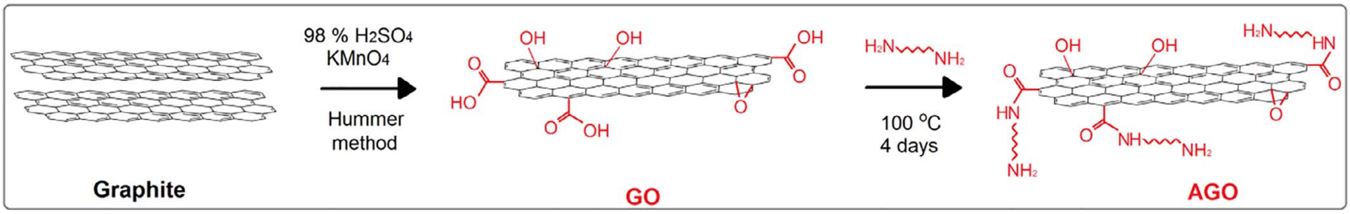

Fig. 1. Schematic of the preparation of graphene oxide by the Hummers method (GO) and surface modification using hexamethylenediamine (AGO).

observed an efficient stress transfer in the PMMA composites filled with CRGO sheets grafted with PMMA polymer molecules. Alam et al. [28] have prepared hyper branched polyester coated multi-walled carbon nanotubes (HBPCNT) by solvent evaporation technique. HBPCNT loaded unsaturated polyester (UPR) nanosuspension has been cured and investigated with differential scanning calorimetric method. The authors observed that the HBPCNT remarkably reduces the curing temperature by 13 °C during crosslinking in HBPCNT-UPR nanosuspension.

Based on the above results, the addition of hexamethylenediamine functionalized graphene (AGO) into an epoxy resin has potential to improve the mechanical properties of these nanocomposites due to amino groups introduced into the graphene sheets. These amino groups when attached to graphene sheets may increase the crosslinking process between the AGO and the polymeric matrix. Furthermore, this group may decrease graphene agglomeration resulting in an improved dispersion and distribution of the GO sheets.

To the best of the author's knowledge, the effects of graphene oxide functionalization by hexamethylenediamine (HMDE) on the thermophysical and mechanical properties of epoxy-based nanocomposites have not yet been reported. This study further contributes to the understanding of the relationships between surface modification of graphene and their interaction with polymer matrices. Results show improved properties in the modified graphene-based nanocomposites.

2. Material and methods

2.1. Materials

2.1.1. Matrix

Araldite GY 260 based on diglycidyl ether of bisphenol A (DGEBA) with Aradur 972 based on diaminodiphenylmethane, both manufactured by Huntsman were used as the base epoxy resin.

2.1.2. Preparation of graphene oxide (GO)

The graphene oxide (GO) used in this study was prepared by a modified Hummers method [29]. An amount of 1.5 g of graphite powder was added to 120 mL of concentrated sulfuric acid (H_2SO_4, Merck, 98%) and the mixture was maintained at room temperature for 24 h. These followed by addition of 0.7 g of $NaNO_3$ (Synth, 99%), the mixture was maintained under magnetic stirring at 30 °C for 2 hours. After stirring, the temperature was decreased to 0 °C and 7 g of $KMnO_4$ (Synth, 90%) were added. The mixture was magnetically stirred for 2 hours. After that, 150 mL of deionized water was added and temperature was increased to 25 °C. The reaction was terminated by slowly adding 5 mL of H_2O_2 (Synth, 30%). The resulting mixture was vacuum filtered and washed with deionized water until the filtered water reached a neutral pH. Finally, the graphene oxide was dried in a vacuum oven at 40 °C for 16 h.

2.1.3. Synthesis of functionalized graphene oxide by hexamethylenediamine (AGO)

The GO (0.3 g) was added to 150 mL of hexamethylenediamine (HMDA, $NH_2(CH_2)_6NH_2$, Aldrich, 70%). The mixture was maintained under magnetic stirring and heated at 100 °C for 4 days. The hexamethylenediamine functionalized graphene (AGO) was filtered using a polytetrafluorethylene (PTFE) membrane (0.45 µm pore size) and the excess HMDA was removed by washing with ethanol (Neon, 95%). After that, the AGO was dried in a vacuum oven at 40 °C for 16 h. Fig. 1 shows an schematic preparation of the graphene oxide and its surface modification.

2.1.4. Preparation of nanocomposites

The neat resin (epoxy) and composites (GO/epoxy and AGO/epoxy) were synthesized using a resin of diglycidyl ether of bisphenol A (DGEBA-3) and diaminodiphenylmethane (DDM). 1 wt% of GO and AGO were dispersed in acetone for 10 minutes in ultrasound baths. The acetone was chosen as pre-dispersing solvent because both GO and AGO showed good dispersion in acetone. Other authors reported that the use of pre-dispersing solvent helps in the preparation of nanocomposites with stronger interfacial interactions among filler and polymer matrix [30]. Then, the graphene/acetone mixture was added to the resin and mixed using tip sonication (UP 200S, Hielscher, 200 W) at 65 °C. The mixture was degassed under vacuum at 80 °C for 24 hours. The mixture was then heated to 90 °C and the curing agent was added with a resin-to-curing agent weight ratio of 100:27.

2.2. Characterization and measurements

2.2.1. Fourier transform infrared (FT-IR) spectra

FT-IR analysis was conducted in a FT-IR Spectrum One Perkin Elmer spectrometer (resolution 4 cm^{-1}, 40 scans) using the KBr pellet technique (0.2:400 mg), in the range of 4000-400 cm^{-1}.

2.2.2. Raman spectroscopy

The structural characteristics of the GO and AGO were investigated by Raman spectroscopy on a Renishaw 2000 Micro-Raman equipped with an argon laser (514.5 nm), in the range of 1000–2000 cm^{-1}.

2.2.3. X-ray photoelectron spectroscopy (XPS)

XPS analysis of the samples was performed on a commercial spectrometer (UNI-SPECS UHV), with Mg Kα line ($h\nu = 1253.6$ eV) and a pass energy set at 10 eV. The composition of the surface layer was determined from the ratio of the relative peak areas corrected by Scofield sensitivity factors of the corresponding elements. The width at half maximum (FWHM) varied between 1.2 and 2.1 eV and the accuracy of the peak positions was ± 0.1.

2.2.4. Atomic force microscopy-based infrared spectroscopy (AFM-IR)

Nanoscale infrared analysis (AFM-IR) was performed on a NanoIR2s Anasys Instrument. The samples were subjected to pulses at a repetition rate of 180 kHz from a tunable infrared source (Quantum Cascade Lasers - Daylight) with an 1800–1600 cm^{-1} spectral range. All AFM topographic images were obtained in contact mode with resonance frequency of 13 ± 4 kHz and a spring constant of 0.07–0.4 N/m.

2.2.5. X-ray diffraction (XRD)

X-ray diffraction patterns were recorded on a high resolution X-ray diffractometer (Philips X'Pert), equipped with CuKα radiation tube, at 45 kV and 25 mA, with 2θ scans ranging from $3^\circ \leq 2\theta \leq 90^\circ$, and a scan rate of 0.42 °/s. The distance layer ($d_{(002)}$) of the samples GO and AGO