Materials and Design xxx (2014) xxx–xxx

Contents lists available at ScienceDirect

Materials and Design

journal homepage: www.elsevier.com/locate/matdes

Effect of functionalization of graphene nanoplatelets on the mechanical response of graphene/epoxy composites

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ARTICLE INFO

Article history:
Received 17 June 2014
Accepted 18 October 2014
Available online xxxx

Keywords:
Functionalization
Graphene nanoplatelets
Mechanical properties
Chemical analysis

ABSTRACT

This study introduces a new strategy for functionalizing graphene nanoplatelets (GNPs) by bonding a silane agent to its structure. In order to evaluate the efficacy of the proposed method, epoxy resin specimens reinforced with silane modified GNPs (G-Si) are prepared at different weight contents of nanoparticles along with three other types of GNPs (unmodified GNP, graphene oxide GNP [GO], and amino functionalized GNP [G-NH_2]). The nanocomposites' mechanical properties, such as the elastic modulus, ultimate strength, modulus of toughness and fracture toughness are evaluated and compared for different types of functionalization. Raman spectroscopy, thermo-gravimetric analysis (TGA) and Fourier transform infrared spectroscopy (FTIR) are employed to characterize the chemical and structural changes of the functionalized GNPs. The results show that nanocomposites containing G-Si and G-NH_2 provide the best results for most of the mentioned properties. The functionalization of GNPs gives the most promising results for fracture toughness of epoxy, showing an 82% increase, and scanning electron microscopy (SEM) micrographs and XRD analysis reveal that an improved dispersion status is obtained by GNP functionalization.

1. Introduction

Graphene nanoplatelets (GNPs) are the new generation of carbon-based nanoparticles that feature remarkable mechanical, electrical and thermal properties [1], along with lower production costs than carbon nanotubes (CNTs) [2]. These characteristics have prompted numerous researchers to focus their efforts on investigating the enhancement of several physical properties of polymers reinforced with GNPs [3–5].

Similar to other types of carbon nanoparticles, the main challenges in the fabrication of GNP-based nanocomposites are achieving a homogeneous dispersion of GNPs in epoxy resin without damaging its structure and improving the quality of the interface between the GNPs and matrix. To address the former issue, the authors previously proposed an optimum and cost-effective dispersion method for GNP/epoxy nanocomposites by taking into account the structural differences between GNP and CNT [6].

In addition to the dispersion method, the functionalization of carbon nanoparticles has been established as an efficient means to achieve superior dispersion of nanoparticles in polymers [7–10]. The functional groups bonded to the surface of nanoparticles are usually chemically compatible with the host resin, thus providing a stronger interface between each nanoparticle and some polymeric matrices. For instance, Reed [11] recently reviewed the interface properties of functionalized CNTs and their matrix, showing that the main reason for selecting a functional group is to match the surface energy of the filler materials to the polymer matrix.

Although there are a few studies on the functionalization of GNP in the literature, they mainly focused on the electrical and thermal properties of the resultant nanocomposites [12–14], while little attention has been given to their effect on the mechanical response of GNP-based nanocomposites [15,16]. Moreover, while several attempts have been made toward the functionalization of CNTs, the literature suffers from a lack of a suitable functionalization technique for GNPs. To the best of the authors' knowledge, there has been no study on the functionalization of GNPs by a silane coupling agent (i.e., [3-glycidyloxypropyl] trimethoxysilane).

In this research, a new method is introduced for the functionalization of GNPs that uses a silane agent to increase GNPs' reinforcement efficiency for polymers. To investigate the structural and chemical changes of GNPs due to the functionalizing process, thermo-gravimetric analysis (TGA) and Raman spectroscopy were

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http://dx.doi.org/10.1016/j.matdes.2014.10.047
0261-3069/

utilized. To compare the competency of the proposed silane function, nanocomposites reinforced with silane-functionalized GNPs (referred to as G-Si hereafter), along with three other types of GNPs, namely, unmodified GNPs (referred to as UG hereafter), graphene oxide GNP ((referred to as GO hereafter), and amino functionalized GNP (referred to as G-NH_2 hereafter). Nanocomposites with different weight contents (i.e., 0.25, 0.5 and 1 wt%) of nanoparticles were prepared and their mechanical properties, including the tensile properties and fracture toughness, were assessed. Moreover, the effects of functionalization on the dispersion status of GNPs and the morphology of fracture surfaces were qualitatively investigated using scanning electron microscopy (SEM).

2. Methodology

2.1. Materials

The unmodified GNPs (UG) with an average thickness of 7 nm and average particle diameter of 25 μm, supplied by the XC Science (Lansing, MI), were used in this research. G-NH_2 with an average thickness of 5 nm and average diameter of 8 μm were obtained through Cheap Tubes Inc. (Battleboro, VT). Araldite LY1564 (Bisphenole-A) epoxy resin was used throughout this study along with Aradur 2954 (cycloaliphatic polyamine) hardener, which is available through Huntsman Co. (West Point, GA). A purified silane coupling agent, (3-glycidyloxypropyl) trimethoxysilane, used for functionalizing the GNPs, was obtained from Sigma–Aldrich Canada Co. (Oakville, ON).

2.2. GNP functionalization method

To fabricate the G-Si, the first step was to reflux 1.0 g of UGs with 200 ml of 40% nitric acid for 4 h at 80 °C. The GNPs were then thoroughly washed with distilled water to remove untreated acid until the pH became neutral, resulting in GO. Next, 15.0 g of 98% purified silane coupling agent, 15.0 g of methanol, 0.15 ml glacial acetic acid and 0.75 ml distilled water were mixed together, after which 20 ml of this mixture and 1.0 g of the GO obtained through the previous step were added to 200 ml of toluene and stirred at room temperature for 64 h. The mixture was filtered and then washed first with toluene and subsequently with methanol to obtain G-Si. Finally, the G-Si was dried for 4 h at 80 °C.

2.3. Nanocomposite preparation

As stated, GNPs with four different surface modifications (namely, UG, G-NH_2, GO, and G-Si) were used in the present study. The same manufacturing method was utilized for nanocomposites reinforced with all types of GNPs. Firstly, nanoparticles were dispersed in the epoxy resin according to an established method using a three-roll mill [6] with different GNP weight contents (i.e., 0.25, 0.5 and 1 wt%). Then, the hardener was added to the GNP-resin slurry and mixed for 15 min using a mechanical stirrer at 150 rpm. The mixture was subsequently degassed, poured into molds, and cured at 60 °C for 1 h, followed by post-curing at 120 °C for 8 h.

2.4. Characterization

The untreated GNPs, and modified GNPs (GO and G-Si) were subjected to chemical analysis using TGA by a TG-209-F1-Libera thermogravimetric analyzer (NETSCH, Burlington, MA), Raman spectroscopy analysis by a DEXR Smart Raman Spectrometer (Thermo Scientific, Waltham, MA) and also FTIR analysis by Bruker Tensor 27 FTIR (Bruker, Madison, WI) to verify the effective bonding between the silane coupling agents and the GNPs.

Tensile tests were carried out according to the ASTM-D638 standard to assess the materials' tensile properties (i.e., the elastic modulus, ultimate strength, ultimate strain, and strain energy). In addition, the fracture toughness of pure epoxy and nanocomposites was evaluated according to ASTM-D5045. All mechanical tests were performed at room temperature using a MTS servo-hydraulic test machine (model 312.21) with a 100 kN load cell.

To further explore the influence of functionalization on the structure of GNPs, the dispersion quality of GNPs in nanocomposites and failure mechanisms, the fracture surfaces of pure epoxy and nanocomposites were thoroughly examined using the field emission SEM S-4700 (Hitachi, Dallas, TX). In addition, a high speed Bruker D8 Advanced XRD system (Bruker, Madison, WI) was used to extract the XRD signals of nano particles and nanocomposites to evaluate the dispersion quality of GNPs in nanocomposite.

3. Results and discussion

3.1. Chemical analysis

The Raman spectra of UG, GO and G-Si excited with a 532 nm laser are shown in Fig. 1. The spectra of unmodified GNPs consists of the G-band at about 1580 cm^{-1} and a weak defect band (known as the D-band) at about 1370 cm^{-1}. The G-band and D-band have different intensities and are shifted by functionalizing GNPs The G-band shift could be indicative of a change in the amount and type of chemical groups attached to GNPs and/or increased oxygen content in the GNP structure [17]. It has been observed that when a GNP's thickness is increased, the G-band position shifts to a lower energy [18]. Although the D-band is normally very weak in both graphite and graphene in comparison to carbon nanotubes [18], the intensity of the D-band (I_D) is directly proportional to the level of defects in the sample. In other words, the larger the I_D, the higher is the intensity of atomic-scale defects. The shift in the D-band after the functionalization process is negligible compared to the UGs, which could indicate that this process did not introduce extensive defect and damage to the GNPs' structure.

The ratio of I_D/I_G was increased by functionalization of GNPs with I_G being the intensity of the G-band (see Table 1). This may be attributable to the functionalization process that increases the GNPs' structural disorder intensity by formation of covalent bonds [19]. The increasing trend of I_D/I_G was also reported by Cho et al. [15] for other groups of chemical functions of GNPs.

TGA analysis was also conducted to obtain further information with respect to the degree of functionalization achieved for the

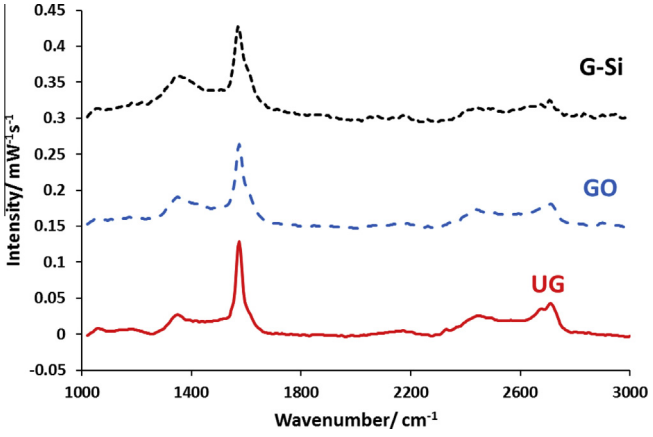

Fig. 1. The Raman spectra of as-received and functionalized GNPs.

Please cite this article in press as: Ahmadi-Moghadam B et al. Effect of functionalization of graphene nanoplatelets on the mechanical response of graphene/epoxy composites. J Mater Design (2014), http://dx.doi.org/10.1016/j.matdes.2014.10.047