Graphene-like nanocarbon: An effective nanofiller for improving the mechanical and thermal properties of polymer at low weight fractions

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ARTICLE INFO

ABSTRACT

Epoxy composites were prepared with graphene-like nanocarbon sheets (GNCs) at weight fractions between 0.005 and 2 wt%. At these weight fractions, the composites showed substantial improvements in the mechanical, physical and thermal properties. However, above 0.01 wt%, GNCs formed micron-size aggregates in the matrix as revealed by optical microscopy likely due their high aspect ratio and the density of aggregates increased with weight fraction and followed a power law curve. For 0.01 wt% composite, the mechanical properties, notably fracture toughness (K_{IC}) and critical strain energy release rate (G_{IC}) are found to increase by ~51% and ~140%; while flexural strength and modulus increased by 22% and 23%, respectively as compared to pristine epoxy. The unprecedented enhancements in the mechanical properties at such a low weight content of GNCs (0.01 wt%) is attributed to the excellent dispersion of these high aspect ratio functional fillers in the matrix as revealed by spectral Raman mapping. Further the nanocomposites showed improved thermal degradation and, asymmetric and broad loss tangent peaks as against symmetric narrow peak for neat epoxy, obtained from dynamic mechanical analysis. These curves suggest significant alteration of glass transition temperature upon GNC incorporation. Fracture mechanisms in the nanocomposites were predominantly governed by formation of a large number of micro-cracks and their path deflection and higher extent of plastic deformation at the notch tip. The mutual effects of these phenomena resulted in higher fracture toughness of composites as compared to that of pure epoxy. On account of their ability to enhance various key mechanical properties, GNC may also be used as an effective reinforcing agent in other polymer matrices.

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1. Introduction

Graphene is two-dimensional single-atom-thick sheet like material with exceptionally high in-plane elastic modulus (~1 *TPa*), high strength (~130 *GPa*) [1] and high specific surface area (>2000 m^2/g) [2]. Graphene also possesses excellent thermal conductivity (~5000 *W/mK*) [3], thermal stability [4] and high electron mobility at room temperature (~2×10^5 cm^2/*Vs*) [5]. These extraordinary properties make it an ideal filler material for developing polymer composites [6,7]. These composite materials find applications in conducting composites [6], transparent electrodes [8], high strength composites [7,9], electromagnetic interference shielding [10], etc. Graphene based nanofillers; such as expanded graphite [11], graphite nanoplatelets [12,13], graphene oxide (GO) [14,15] and graphene nanoribbons (GNR) [16] have been extensively used as reinforcing agents in various polymer matrices with weight fractions up to 5 wt%. However, formation of agglomeration as a result of poor dispersion of nanofillers in polymer matrix limits transfer of its properties to polymer matrix [17]. Agglomeration of graphene platelets is attributed to strong interlayer van der Waals forces between graphene sheets and its poor interfacial bonding with matrix polymer. Hence, chemical functionalization of graphene has been carried out to address these issues [9,18].

Investigation of mechanical properties is probably one of the most studied phenomena in epoxy composites due to their wide range of applications from aerospace to wind-mill. In this context, there are consistent efforts to reduce the amount of filler content in

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epoxy matrix in order to minimize the nanoparticle agglomeration, and to achieve better dispersion and improvements in mechanical properties [7,9,19]. The overall performance of the composites is the manifestation of the combination of various mechanical parameters; such as tensile strength and modulus, flexural strength and modulus and fracture toughness etc. Fracture toughness is the most crucial parameter particularly for structural applications. Several research efforts have been attempted to improve the fracture toughness and to study the fracture behavior of epoxy composites [14,17,20]. The improvements in mechanical properties of composite material are highly influenced by the physical and chemical properties of fillers like, surface area, geometry and surface morphology [7,21], chemical functionality [22], interfacial chemistry [23], and agglomeration tendency [17]. Rafiee et al. [7] compared the mechanical properties of composites using graphene platelets (GPL), single-walled carbon nanotubes and multi-walled carbon nanotubes (MWCNT) as fillers in epoxy matrix. They found that the highest improvement in mechanical properties was obtained using GPL amongst the fillers used. The Young's modulus, tensile strength, fracture toughness (K_{IC}) and critical strain energy release rate (G_{IC}) of 0.1 wt% GPL composites were found to increase by ~31%, ~40%, ~53% and ~126%, respectively, as compared to pure epoxy. Bortz et al. [14] reported the effect of incorporation of GO on mechanical properties of epoxy. The flexural strength and modulus, K_{IC} and G_{IC} showed a monotonic increase with weight fractions between 0.1 and 1 of GO; whereas the tensile properties showed improvements, but not invariably [14]. At 1 wt% loading of GO, the flexural strength and modulus, K_{IC} and G_{IC} were found to improve by 23, 12, 63 and 111%, respectively. Tang et al. [17] investigated the effect of filler dispersion on mechanical properties of graphene/epoxy composites. In comparison with poorly dispersed reduced GO composites, highly dispersed composites showed higher improvement (~52%) in K_{IC} with 0.2 wt% filler. Both the composites showed marginal improvements in tensile and flexural modulus as compared to neat epoxy [17].

In most of the above studies, graphene and its derivatives are shown to be superior nanofillers for improving the mechanical properties of polymers compared to other carbon based fillers. Further the filler contents used in these composites were 0.05 wt% or more [13,16,17]. However, the mechanical properties and fracture mechanisms in epoxy composites at a very low content (<0.05 wt%) of graphene derivatives have not been explored and not fully understood. Further, graphene-like nanocarbon (GNC) being a new derivative of graphene, their nanocomposites have not been reported in the literature. GNC contains polar hydroxyl and epoxide groups with highly disordered graphitic backbone and with mixed hybridization (sp^2 and sp^3) [24]. Moreover, GNC has several advantages over GO; such as the former is prepared by a simpler method and from a less expensive precursor material. Similarly, GNCs have advantages over carbon nanotubes (CNTs); such as: (i) GNCs are sheet-like structure, hence offers higher surface area to interact with matrix as compared to CNTs, (ii) GNCs have polar functional groups which probably reduce the interlayer van der Waals forces between their sheets and thereby facilitate their dispersion in polymer solution by gentle sonication.

In the present study, GNCs were used as reinforcement in epoxy matrix at weight fractions between 0.005 and 2 wt%. The dispersion of GNCs in epoxy matrix is investigated by means of various characterization techniques. The bulk dispersion of GNCs in nanocomposites was investigated by interplay between dispersion-agglomeration phenomena using optical microscope. The mechanical and thermal properties were investigated in detail. Further, the toughening mechanisms and energy absorption through crack propagation were studied using fractography.

2. Experimental methods

2.1. Materials

Bisphenol A-(epichlorhydrin) epoxy resin (Araldite LY 1564 SP) and amine hardener (XB 3416) were purchased from Huntsman Inc., India. Soft wood charcoal (C) (Shree Krishna Industries LLC, India), KNO_3 (Merck, India), sulfur powder (Alfa Aesar, India), H_2SO_4 (AR grade, 98%) and HNO_3 (AR grade, 60%) (Vetec™, Sigma Aldrich, India), ethanol (Merck, India) were used as received.

2.2. GNC and nanocomposite preparation

GNC was prepared from soft wood charcoal (C) powder as per the method given in our previous work [24]. In this process, the charcoal powder, KNO_3 and sulfur powder were mixed in the stoichiometric weight ratio of ~85: 10: 05. The mixture was ground using mortar and pestle for ~30 min. The powder was made into a pallet using hydraulic press (~10 kPa). Following this, the pallet was exposed to a flame of Bunsen burner directly in atmospheric condition. As a result the pallet was transformed into powder. Subsequently, the powder was treated with a mixture of H_2SO_4 (98%) and HNO_3 (60%) in a ratio of 4:1 (v/v) for 48 h at room temperature with continuous stirring. The resulting slurry was filtered and washed with a mixture of deionized water and acetone (8:2, v/v) until the filtrate became pH ~7. The resulting powder was dried in a vacuum oven for 12 h at 100 °C followed by thermal shock at 1000 °C for 10s in argon atmosphere. The detailed characterization results for GNCs are presented in Supporting Information (SI-1). GNC was dispersed in liquid epoxy using ethanol as solvent followed by composite preparation. The details of composite preparation are presented in Supporting Information (SI-2).

2.3. Characterization

The GNCs were characterized using FTIR spectroscopy (Model No. 1605, Perkin Elmer, USA) between 400 and 4000 cm^{-1} at a resolution of 2 cm^{-1}. The electron spectroscopy for chemical analysis (ESCA) was performed using Omicron ESCA Probe (Omicron Nanotechnology, Germany) system at a vacuum of 2×10^{-9} mbar using an Al K_α ($h\nu$ = 1486.6 eV) monochromatic source at 200 W (10 kV × 20 mA). A beam size of ~1 mm cross-section with pass energy of 100 eV and energy step size of 0.1 eV was used for all the scans. For deconvolution of ESCA data, the XPS Peak Fit 4.1 software was used. The confocal Raman imaging measurements were performed on ~1 mm thick films using unpolarized Raman spectroscopy (Horiba LABRAM-HR 800) at λ = 633 nm. To record a single image, a total of 25,921 spectra with a step size of 0.5 μm were collected for each sample. LabSpec 5 software was used for data acquisition as well as for Raman mapping, which showed spectral distribution of sample composition. The agglomerates on the surface were analyzed using optical microscopy (OM, Olympus BH-2) equipped with an image analyzer software (Bio-vis Mat Plus V4.11). Fractography was studied on various specimens using scanning electron microscope (SEM) (Zeiss EVO 50) at 5 and 10 kV. Prior to imaging, the samples were gold-coated using sputtering technique. Thermogravimetric analysis (TGA) was performed on a thermal analyzer (STA 6000, Perkin Elmer, USA) in the temperature range between 20 and 600 °C for composite samples and between 20 and 800 °C for GNCs at a heating rate of 5 °C/min under N_2 atmosphere at a flow rate of 20 ml/min. Thermo-mechanical properties of epoxy and nanocomposites were studied using dynamic mechanical analyzer (DMA) (Paar MCR 301 Rheometer) equipped with Rheoplus/32 V3.40 data analyzer software. The measurements were performed between 25 °C and 150 °C at a ramp rate of 3 °C/