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Development of polymer composites using modified, high-structural integrity graphene platelets

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ABSTRACT

Previous studies on polymer/graphene composites have mainly utilized either reduced graphene oxide or graphite nanoplatelets of over 10 nm in thickness. In this study we covalently modified 3-nm thick graphene platelets (GnPs) by the reaction between the GnPs' epoxide groups and the end-amine groups of a commercial long-chain surfactant ($M_w = 2000$), compounded the modified GnPs (*m*-GnPs) with a model polymer epoxy, and investigated the structure and properties of both *m*-GnPs and their epoxy composites. A low Raman I_D/I_G ratio of 0.13 was found for *m*-GnPs corresponding to high structural integrity. A percolation threshold of electrical conductivity was observed at 0.32 vol% *m*-GnPs, and the 0.98 vol% *m*-GnPs improved the Young's modulus, fracture energy release rate and glass transition temperature of epoxy by 14%, 387% and 13%, respectively. These significantly improved properties are credited to: (i) the low Raman I_D/I_G ratio of GnPs, maximizing the structural integrity and thus conductivity, stiffness and strength inherited from its sister graphene, (ii) the low thickness of GnPs, minimizing the damaging effect of the poor through-plane mechanical properties and electrical conductivity of graphene, (iii) the high-molecular weight surfactant, leading to uniformly dispersed GnPs in the matrix, and (iv) a covalently bonded interface between *m*-GnPs and matrix, more effectively transferring load/electron across interface.

1. Introduction

Since its discovery by Novoselov and Geim in 2004 [1,2], graphene has attracted increasingly paramount interest from both academia and industry, because it is one-atom thick and consists of sp^2 carbon atoms arranged in a honeycomb lattice structure leading to exceptional in-plane functional and mechanical properties. The major fabrication methods of graphene include micromechanical cleavage, chemical vapour deposition (CVD) and the oxidation, exfoliation and reduction of graphite. The first two methods are inappropriate to polymer composites, since they associate with difficulties either in the yield or in controlling the graphene lateral dimensions [3–5]. The third method uses graphite oxide (C:O ratio ≈ 2:1) to synthesis graphene oxide, creating a far higher yield, but graphene oxide is electrically insulative and its strength is just one fourth of graphene due to the high defect concentration [6]. In spite of the convenience of surface modification to engineer nanoparticles on graphene surface [7,8], these defects may cause a negative effect on the performance of polymer composites. The subsequent chemical or thermal reduction removes these oxygen-related defects, which unfortunately adds on a new type of defects – voids. For example, thermal reduction produced an electrical conductivity of 350 S/cm for graphene oxide in comparison with the CVD-grown graphene's conductivity – 2000 S/cm [9,10].

Although either unmodified or modified graphene oxide showed encouraging performance in improving the fracturing toughness of epoxy resins [11,12], more graphene derivatives such as graphene nanoplatelets and even graphite nanoparticles have been explored [13,14]. We have recently developed graphene platelets (GnPs) [15]. Fabricated from a commercial, far less oxidized graphene intercalation compound, these GnPs feature low cost (10–20 US$/kg), a thickness of 2–4 nm, covalently modifiable surface and high structural integrity as shown by the D-band to

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G-band ratio of ~0.06 [16]. Since thermal expansion was reported to produce single layer graphene of ~1 nm in thickness due to the corrugated structure of graphene caused by the expansion [17,18], each GnP of 3 nm in thickness may contain ~3 graphene layers. With increasing the number of graphene layers from 1 to 3, stiffness does not change and fracture strength reduces 23% from 130 GPa to 101 GPa [19]. Given that the fracture strength of most polymers ranging from 1 to 100 MP, these GnPs are indeed sufficiently robust to toughen or reinforce polymers.

Of major engineering materials, polymers have seen the rapidest increase in applications owing to their ease of fabrication and high specific strength. However, the properties of most polymers need improvement by using additives, which leads to development of composites and nanocomposites [20–22]. Nanoadditives often create significant property improvements at low fractions due to their superior specific surface area and low surface–surface interparticle distance [23–26]. Layered nanoadditives, such as clay, have been extensively studied due to its significant specific surface area. Our previous work showed that the interface modification of polymer/clay nanocomposites is essential to the dispersion and exfoliation of clay in matrixes and the resulting composite properties [27–31]. Graphene platelets (GnPs), a new type of two-dimensional, carbon-based nanoadditive, are compatible with epoxy. Even without surface modification, their dispersion in epoxy is far better than unmodified clay. At 0.984 vol% unmodified GnPs, the fracture energy release rate of epoxy cured by Jeffamine D230 was found to increase 160%, and a percolation threshold of electrical conductivity was recorded at 1.333 vol% [15]. Hypothesis made in this study was that GnPs upon modification may disperse better in polymers leading to more increments in functional and mechanical properties.

Modification of graphene surface in general can be made either by covalent bonding or non-covalent interactions. The former, usually achieved through the reaction between the graphene surface functional groups and surfactants' groups, is always adopted when a strong interface is desired between graphene and polymers. The latter includes π–π stacking interactions and van der Waals force, both of which may weaken or disappear with increase in temperature. Thus, this study employs covalent bonding to produce a strong interface for graphene composites.

We in this study modify the GnP surface by the reaction between the graphene's epoxide groups and surfactant's end-amine groups. By using epoxy as a representative polymer, we build up a covalently bonded interface between GnPs and matrix, and investigate the structure–property relations of these nanocomposites.

2. Experiments

2.1. Materials and preparation

Graphene platelets (GnPs) were prepared according to a previous procedure [16]. In brief, 0.1 g of a graphite intercalation compound (GIC, Ashbury 3494, 3–4 US$/lb) was thermally expanded in a common furnace at 700 °C for 1 min. The expanded product was then dispersed in 60 g *N*-methyl-*2*-pyrrolidone (NMP) and sonicated for 30 min below 30 °C to produce graphene platelets (GnPs) of 2.51 ± 0.39 with C:O ratio at 93:7 [16]. During the sonication, the layer spacing between GnPs increased significantly and created a homogenous dispersion in the solvent, as verified by no precipitation observed within 4 h of storage. 3.6 g Of surfactant J2000 (polyoxypropylenediamine, Huntsman) and 4.2 g of catalyst triisopropanolamine (Sigma–Aldrich) were added to the mixture, followed by mixing and sonication below 30 °C for 1 h. The suspended GnPs were then transferred to a round-bottom flask equipped with a condenser, followed by stirring at 150 °C for 48 h. This produced covalently modified GnPs (*m*-GnPs). Fig. 1 schematically shows the modification.

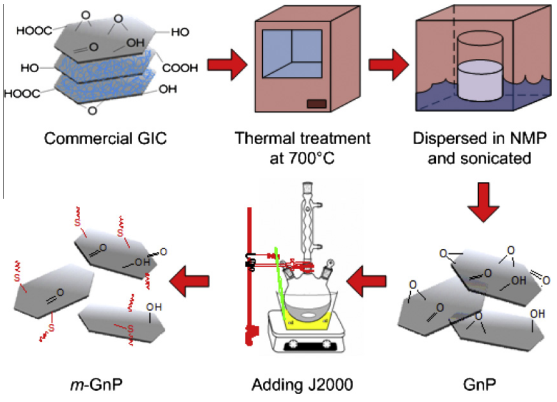

Fig. 1. Schematic of covalent modification of graphene platelets.

2.2. Synthesis of epoxy/graphene platelet nanocomposites

We dispersed a calculated amount of *m*-GnPs in tetrahydrofuran (THF) at 0.1 wt% in a metal container, followed by mechanically mixing for 10 min and sonicating for 30 min. The ultrasonic bath (200 W and 42 kHz) was set below 30 °C by connecting to a freezer, since our previous study [32] proved that the low-temperature sonication (<30 °C) is more effective in creating a better dispersion and longer suspension than sonication at higher temperatures. A calculated quantity of epoxy (DGEBA, Araldite-F) was added to the mixture, followed by 30-min mechanical stirring and then 1-h sonication below 30 °C. The mixture was then transferred into a round-bottom flask where stirring continued at 150 °C for 4 h. The solvent was evaporated through mechanical mixing at 120 °C for 1 h. When the mixture was cooled to below 50 °C, hardener Jeffamine D230 (J230) was added and mixed for 2 min. The resultant mixture was then poured into a pre-heated mould, and degassed in an oven for 5 min. This was followed by curing at 80 °C for 3 h and at 120 °C for 12 h.

2.3. Characterization

The surface groups of GnPs were identified by a Perkin Elmer 65 FT-IR spectrometer, using a Miracle Single Reflection ATR Sample Accessory. The IR spectra were collected from 700 to 4000 cm^{-1}. XRD was performed using a Diffraction Technology Mini-Materials Analyser (MMA) with a diffractometer, equipped with curved graphite monochromators and tuned to Cu Kα radiation (λ: 1.5419 Å). The diffraction spectra were collected in a reflection mode geometry between $2\theta = 2–50°$ at 1°/min.

AFM images were taken of GnPs by a NT-MDT NTEGRA SPM instrument with NSG03 non-contact "golden" cantilevers. The magnitude of oscillation was 15 nm and the scan rate for 2 μm × 2 μm images was typically 0.5 Hz. The samples were prepared by suspending GnPs in *N*-methyl-*2*-pyrrolidone (NMP) at 0.0004 wt% by 30-min ultrasonication below 30 °C and then dropping the solution on a silicon wafer followed by drying. The scanner used was a 100 μm scanner calibrated using 1.5 μm grids with a height of 22 nm. Raman spectra were recorded at room temperature by a Renishaw inVia Raman microspectrometer with 633 nm laser excitation and notch filters cutting at ~100 cm^{-1}. Extreme care was taken to avoid sample damage or laser induced heating. Measurements were performed from ~4 to ~0.04 mW incident power.