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Strength dependence of epoxy composites on the average filler size of non-oxidized graphene flake

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ABSTRACT

Enhancing the filler-to-matrix contact area by incorporating large graphene flakes (GFs) is considered a viable approach for improving the mechanical properties of polymer composites. Graphene oxide (GO) flakes have been initially pursued for this application owing to the advantage of producing large-sized GFs. However, the defective nature of GO makes it technically challenging to precisely assess their dimensional effect on resulting mechanical properties, limiting their versatility as reinforcing materials. Therefore, it is highly desired to fabricate GFs with minimum defects and large lateral size. In this paper, we report the fabrication of high-quality edge functionalized non-oxidized graphene flakes (f-NOGFs) by the liquid exfoliation of graphite intercalation compounds. As-prepared f-NOGFs are over 1 μm in lateral size and contain less than 6.25% of impurity oxygen. By using size-sorted f-NOGFs, we systematically studied the relationship between mechanical properties and lateral sizes in f-NOGFs-incorporated epoxies. We identify that epoxy composites containing 0.6 wt% of f-NOGFs with a lateral size of 1 μm present outstanding mechanical properties; elastic modulus of 3.65 GPa, ultimate tensile strength of 95.74 GPa and toughness of 2.52 MJ m^{-3}. The study presented in this paper could provide better understanding for optimization of the mechanical reinforcement of graphene-polymer composites.

1. Introduction

Applications of graphene fillers to polymeric composites have gained substantial attention in various industries which demand light-weight materials with robust mechanical properties [1–9]. Graphene flakes (GFs) have been intensively utilized to mechanically reinforce raw polymers owing to their high aspect ratio and excellent mechanical strength (i.e. young's modulus of 1 TPa and tensile strength of 130 GPa) originating from the sp^2 bonded single layer structure [10,11]. Their intrinsically two-dimensional structure can offer additional advantages of wider contacting area when they are interfaced with polymer matrices. Rafiee et al. demonstrated that graphene-reinforced epoxy composites could possess superior mechanical properties in comparison to carbon nanotube composites due to enhance filler-to-matrix interactions [2].

The effect of the lateral size of GFs is an important subject in designing graphene based materials. Many researches have focused on studying the size effect on resulting electrical or thermal conductivities of graphene based composites or films/papers for further optimization of performance [12–16]. Mechanical reinforcement of graphene-polymer composites is also significantly influenced by the size of GFs due to the change in filler-to-matrix contact area, as suggested by various numerical models [6,7,9,17]. Therefore, it is essential to better understand the influence of the size of GFs on resulting mechanical properties. Graphene oxide (GO) flakes and their reduced forms were initially explored to verify such size effects since they could be easily exfoliated in large size and quantities [13,18]. For example, Choi et al. showed that larger GO flakes exhibited higher stiffness than smaller ones when incorporated in polyurethane [9]. However, the structural defects inherent to pristine GO flakes make it technically challenging to exclusively elucidate such size effects as well as limit their reinforcing ability when incorporated in polymers [3–5]. These defects include covalently bonded oxygen groups and vacancies which lead to a reduced tensile modulus of 207.6 ± 23.4 GPa, far lower than

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that of pristine graphene [18–21].

On the other hand, high quality GFs exfoliated from a fabrication method involving no oxidation process are anticipated to possess less structural defects, which make it more suitable for a reinforcing material as its intrinsic size effect on reinforcing ability can be readily realized. The fabrication of high quality GFs has been pursued by various methods, such as liquid exfoliation [22,23], unzipping carbon nanotubes [24,25], and exfoliation of graphite intercalation compound (GIC) [26–31]. However, these methods tend to fabricate GFs in small lateral sizes (<1 μm), resulting in a significant decrease of contact areas between graphene and matrices when incorporated into composites. Such limitations have made it technically challenging to quantitatively verify the exclusive influence of the GF size on the resulting reinforcement of composites. Therefore, it is highly demanded to develop a viable method to fabricate high-quality GFs containing large individual flake size and to systematically explore their feasibility for reinforcing materials.

Here, we demonstrate the relationship between the lateral size of near pristine GFs and the mechanical reinforcement of epoxy nanocomposite by incorporating edge functionalized non-oxidized graphene flakes (f-NOGFs) of uniformly separated sizes (20 nm–1 μm) and extremely low defects. The f-NOGFs were liquid exfoliated from GIC, intercalated with h-salt such as potassium sodium tartrate tetrahydrate [31]. From the GIC, exfoliation of larger sized GFs could be expected because of intercalation of metal ions and tartrate molecules resulting in expansion of interlayer spacing, significantly reducing the interlayer binding of graphite [32–35]. The majority of the f-NOGFs had lateral size over 1 μm while exhibiting high crystallinity and minimum oxidation, comparable to that of source graphite. Moreover, the co-intercalated tartrate molecules simultaneously functionalize on graphene edge during exfoliation, making f-NOGFs highly compatible to various solvents and epoxy matrix. The f-NOGFs were subsequently separated into four different size ranges and incorporated into epoxy composite, revealing that the lateral size of f-NOGFs could significantly affect mechanical properties of epoxy composite in terms of stiffness, extensibility, and toughness. Such tendencies are in good agreement with a theoretical model. The graphene-epoxy composite composed of 0.6 wt% of f-NOGFs whose average size is larger than 1 μm exhibited the best mechanical properties, including elastic modulus of 3.65 GPa, ultimate tensile strength (UTS) of 95.74 MPa and toughness of 2.52 MJ m^{-3}. Owing to the high quality of incorporated f-NOGFs, our composite, compared to other reported values, exhibited exceptionally large enhancement in toughness while maintaining high stiffness, both of which often compensate one another.

2. Experimental method

2.1. Sample preparation

2.1.1. Fabrication of f-NOGFs

Graphite powder (30 mg, average diameter: 70 μm, Bay Carbon, MI, US) was mixed with potassium sodium tartrate tetrahydrate (450 mg, Sigma-Aldirch) in 1:15 ratio and at 250 °C for approximately 12 h to produce GIC. The grinding and reaction took place in an Argon filled glove box to avoid moisture. The GIC was then immersed in pyridine (30 ml, Sigma-Aldrich) in 1 mg ml^{-1} ratio. For f-NOGF_L, the solution was ultra-sonicated for 45 min and centrifuged at 800 rpm. For f-NOGF_M, the solution was ultra-sonicated for 3 h and centrifuged at 2000 rpm. For f-NOGF_S, the solution was ultra-sonicated for 12 h and centrifuged at 5000 rpm. f-NOGFs were washed with water and dried in vacuum condition.

2.1.2. Fabrication of graphene quantum dots (GQDs)

The GIC was immersed in water and ultra-sonicated for 3 h. The solution was filtered through a 20 nm pore size Al_2O_3 filter and subsequently dialyzed in a dialysis tube. Water was removed by heating the solution at 120 °C to obtain GQD powder.

2.1.3. Fabrication of pristine graphene flakes

Graphite power (30 mg) was immersed in pyridine (30 ml) in 1 mg ml^{-1} ratio. The solution was ultra-sonicated for 12 h. The solution was then centrifuged at 1500 rpm for 30 min and the supernatant was collected.

2.1.4. Fabrication of graphene-epoxy composite

The f-NOGFs powder was ultra-sonicated in acetone (30 ml, Samchun) for 20 min in 1 mg ml^{-1} ratio. Epoxy resin (diglycidyl ether of bispenol A, EPON 862) and curing agent (diethytolenediamine, SEIKA-S) were mixed in a ratio of 100:36 in weight and added to f-NOGFs-acetone solution. The mixture was sonicated for additional 30 min. The solution was loaded into a stainless steel mold in dog-bone shape, and heated at 70 °C for 12 h in dynamic vacuum condition to remove acetone. Then curing was done at 175 °C for 1 h.

2.2. Characterization

2.2.1. Characterization of f-NOGFs

The structure of GIC was examined with X-ray diffraction (XRD) (D/MAX-2500 (18 kW) with Cu Kα radiation ($\lambda = 1.518$ Å). Transmission electron microscopy (TEM) analysis was performed with F2 F20 (Tecnai) at acceleration voltage of 200 keV. Lateral size measurement of an f-NOGF was done by measuring the longest end to end point from the TEM analysis. Raman spectroscopy was done with Senterra system (Bruker). For thickness measurement, atomic force microscopy (AFM) (SPA400, SII, Japan) was used. X-ray photoelectron spectroscopy (XPS) was performed with Sigma Probe system (Thermo VG Scientific) with AlKα radiation source. Fourier transform infrared (FT-IR) spectroscopy was carried out by FT-IR-4100 type-A FT-IR spectrometer (Jasco). Thermogravimetric analysis (TGA) was performed with TG 209 F3 (Netzsch-Gerätebau GmbH) at a heating rate of 5 °C min^{-1} in Ar atmosphere. UV–Vis spectroscopy was done by using UV-3101PC spectrometer (Shimadzu). Finally, zeta-potential was performed with ELS-Z2.

2.2.2. Characterization of graphene-epoxy composite

Tensile properties were measured by using a uniaxial testing machine (INSTRON 8848 microtester) according to ASTM D638-10 with crosshead speed of 0.75 mm min^{-1} at room temperature. The dog-bone sample had width of 3.25 cm and length of 14.25 cm. The fracture surface of graphene-epoxy composite was observed with scanning electron microscopy (SEM) (S-4800, Hitachi) with field-emission source at 10 keV. The T_g was analyzed with Dynamic Mechanical Analyzer (DMA Seiko EXSTAR 6000).

3. Results and discussion

The schematic in Fig. 1 illustrates the overall fabrication process of graphene-epoxy composite. The GIC is fabricated by heating graphite and h-salt mixture at 250 °C in Argon atmosphere (Fig. 1a) [31]. The reaction results in the expansion of the graphite, induced by charge balanced insertion of metal ions and tartrate molecules, as shown in Fig. S1. SEM characterizations reveal that this intercalation process resulted in the distortion of graphite flakes with widened interlayers (Fig. S1). This structural change is further verified by XRD (Fig. 1b), which shows the shift of main graphite peaks from 26.4° to 14.1°, corresponding to 3.37 Å and 6.27 Å