Conductive graphite nanoplatelet/epoxy nanocomposites: effects of exfoliation and UV/ozone treatment of graphite

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Abstract

The effects of ultrasonication and UV/ozone treatment of graphite on electrical conductivity of epoxy-based nanocomposites containing graphite nanoplatelets are investigated. Ultrasonication applied at various stages of composite fabrication enhanced the exfoliation and dispersion of graphite within the matrix. A porous multi-layer graphite structure resulted in a higher electrical conductivity and poorer mechanical properties than the completely exfoliated graphite. UV/ozone treatment improved both the electrical conductivity and mechanical properties by improving the graphite–epoxy interfacial adhesion, which is attributed to ameliorating changes in graphite surface chemistry and morphology.

Key words: graphite; nanocomposite; electrical conductivity; UV/ozone treatment

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1. Introduction

Graphite has been widely used as a conducting filler in fabricating conductive polymer composites. Conventional fillers are usually micrometer-scale metal powder, carbon black, or carbon fibres. To achieve satisfactory electrical conductivity, the filler content needs to be as high as 15 to 50 wt.%, resulting in poor mechanical properties and high density of composite. The corresponding percolation threshold of graphite nanoplatelet (GNP) polymer nanocomposites is very low — often below 2 wt.%. This unique property is attributed to the extremely large surface area and aspect ratio of the GNPs, allowing the formation of an uninterrupted conducting network for electrons within the polymer [1, 2].

GNPs are produced from graphite flakes intercalated with highly concentrated acids, which can be expanded up to a few hundred times over their initial volume at a high temperature. The expansion results in a separation of the graphite sheets into nanoplatelets with very high aspect ratio. Unlike other types of nanoparticles, graphite has unique properties, with a very high modulus along its graphene plane, and has excellent electrical and thermal conductivity due to its layered structure. These useful properties combined with very low cost make it an attractive filler to produce conducting polymers for applications in electromagnetic interference (EMI) shields and thermal conductors.

A major issue encountered in fabricating GNP polymer nanocomposites is the low compatibility between graphite and polymers, as manifested by the poor mechanical properties, especially the strength compared to the neat polymer. Another related issue is the difficulty of dispersing the GNP aggregates within the polymer to achieve uniform properties. While there have been a great deal of studies on the manufacturing of nanocomposites based on layered silicates or carbon nanotubes [3], very few studies have so far been successful in improving the interfacial interaction, and the dispersion of GNP aggregates. Like carbon fibres after production, graphite in its layered structure has little surface functionality. Various

surface treatment methods have been developed for carbon fibers [4], and most of these techniques can in principle be applied to GNP/epoxy nanocomposites [5]. Among them, plasma treatment has been used to modify the surface of GNP [6, 7]. However, plasma treatment is inconvenient for powders because powders will volatilize and contaminate the plasma chamber during vacuum pumping and venting. A new surface treatment method is proposed and its effect on the properties of GNP/epoxy nanocomposite is studied in this paper. In addition to GNP surface treatment, the effect of GNP exfoliation produced by sonication is also specifically evaluated.

2. Experiments

2.1 Materials and Fabrication of Nanocomposites

The as-received graphite intercalated compounds (GICs, supplied by Asbury Graphite Mills, USA) containing 2.8 wt.% of sulfur as the intercalant were heat treated at 1050°C for 30s to exfoliate into expanded graphite. Upon rapid heating the GICs were expanded explosively several hundred times along the thickness direction due to the evaporation of the intercalant. The expanded graphite (EG) presents a loosely-bonded, porous and worm-like rod, consisting of numerous preferentially-oriented graphite layers, as shown in Figures 1(a) and 1(b). The expanded graphites were immersed in acetone and sonicated using an ultrasonicator at 70 W for 8 hr to exfoliate into individual or bundles of GNPs, as shown in Figure 1(c). The extent of exfoliation was controlled by changing the sonication time in two groups: group A for 2 hr and group B for 8 hr.

Figure 1. (a) SEM photograph of bundle form of expanded graphite after heat treatment; (b) magnified view; and (c) individual graphite nanoplatelet after sonication.

The exfoliated graphite surface was treated using an UVO Cleaner (Jelight Co., Inc.) at room temperature and atmospheric pressure to improve the surface reactivity with polymer. The changes in graphite surface chemistry after UV/ozone treatment were analysed using an X-ray photoelectron spectroscope (XPS, Surface analysis PHI5600) with a monochromated Al- α (1486.6eV) X-ray source operating at 350W (14kV, 25mA) in a residual vacuum of 5×10^{-9} Torr. A scanning electron microscope (SEM, JEOL-6300) was used to examine the changes in surface morphology after the treatment.

The composites were made from epoxy, a diglycidyl ether of bisphenol A (Epon 828, supplied by Shell Chemical), and a curing agent, 1, 3-phenylenediamine (mPDA, supplied by Sigma-Aldrich). To allow uniform dispersion of GNPs within the epoxy resin, the monomer epoxy was diluted with acetone before adding a constant 2 wt.% of GNPs. The epoxy–acetone–GNP mixture was stirred mechanically for 30 min, followed by sonication using an ultrasonicator at 70 W, 42 kHz for 30 min. The mixture was then outgassed at 80°C for 2 hr in a vacuum oven and mPDA curing agent was added into the mixture in the ratio of 14.5/100 by weight. The composite mixture was moulded into a flat plate and cured at 80°C for 2 hr, followed by post cure at 150°C for 3hr in air.

2.2 Measurements of Mechanical Properties and Electrical Conductivity

A three-point flexure test was performed to measure the flexural properties of neat epoxy and nanocomposites according to ASTM standard D790-96. The moulded nanocomposite plates were cut into 12.7mm wide $\times$ 70mm long $\times$ 3mm thick samples, which were subjected to bending with a support span of 50mm at a constant cross-head speed of 1.3 mm/min on a universal testing machine. Five specimens were tested for each set of conditions. The bulk electrical resistivity of nanocomposites was measured using a resistivity/Hall measurement system which has a limit of $10^8 \Omega\cdot\text{cm}$. The moulded plates were cut into 10 mm square $\times$ 1 mm thick specimens, which were probed at four corners.

Table 1. Bulk electrical resistivity of nanocomposites and surface area of graphite with different graphite structures.

Graphite structure		Group A Expanded graphite	Group B Exfoliated GNP
Electrical resistivity ($\Omega\cdot\text{cm}$)	Top	3.0×10^3	5.2×10^5
	Bottom	3.2×10^3	5.3×10^5
Surface area (m^2/g)		34.5	338

3. Results and Discussion

3.1 Effects of Ultrasonication

Two different graphite structures were obtained within the polymer by varying the sonication time: namely the multi-layer structure (2hr, group A) with the pores in between expanded layers filled by matrix resin; and the well-dispersed exfoliated, individual GNPs (8hr, group B), as shown in Figure 2. It is noted that the group A samples showed a higher electrical conductivity than the group B nanocomposites made from exfoliated GNPs, with the difference being about two orders of magnitude, Table 1. The porous EGs in the group A samples maintained their original, expanded shape, capable of forming a conductive network better than group B. This result is in spite of the much smaller effective surface area of group

A samples than group B. The negligible difference in electrical conductivity between the top and bottom sample confirms that regardless of the final morphology of graphite after sonication, particle sedimentation did not take place during curing.

The higher electrical conductivity for group A nanocomposites, however, was at the expense of poorer mechanical properties, Figure 3. The bundles of poorly exfoliated graphites in group A were mainly responsible for the lower flexural strength and modulus than group B because cracks can easily initiate and propagate through the area where there is virtually no bond with the epoxy matrix. It is also noted that the flexural strengths of GNP–epoxy nanocomposites were much lower than the neat epoxy regardless of the degree of exfoliation of graphite.

Figure 2. SEM photographs of (a) group A and (b) group B nanocomposites.

Figure 3. Flexural properties of neat epoxy and nanocomposites with different structures. (Error bars represent one standard deviation of five specimens.)

3.2 Effect of UV/ozone Treatment

The bulk electrical resistivity of group B GNP/epoxy nanocomposites is plotted as a function of UV/ozone treatment time in Figure 4. The electrical resistivity decreased with increasing treatment time, and approached a saturation value of $2 \times 10^4 \Omega\cdot\text{cm}$ after 20 min treatment, which compares well with the value reported recently, $5 \times 10^7 \Omega\cdot\text{cm}$ [6], for a similar GNP/epoxy nanocomposites with the same 2 wt.% GNP content.

Figure 4. Bulk electrical resistivity of nanocomposite with different UV exposure times. (Error bars represent one standard deviation of five specimens.)

Along with the improved electrical conductivity, the UV/ozone treatment also increased both the flexural modulus and strength, as shown in Figure 5. The improvement of flexural strength was more pronounced than that of the modulus, an indication of enhanced graphite–epoxy interfacial adhesion. It is well known [4] that the fibre–matrix interfacial adhesion has significant effects on strength measured at various loading conditions, whereas it has relatively little influence on longitudinal modulus because the composite modulus is more dependent on the moduli and volume fraction of the composite constituents than the interfacial adhesion.

Figure 5. Flexural properties of nanocomposites as a function of UV/ozone exposure time.

Several characterization techniques were employed to identify the mechanisms behind the improvements in electrical and mechanical properties, including SEM and XPS analysis. The fracture surface morphologies in Figure 6 present a major difference between the untreated and treated GNPs: interfacial debonding is predominant between the untreated GNPs and epoxy matrix, as the cracks along the graphite layers indicate (Figure 6(a)), whereas a strong bond with the matrix is evident for the treated GNPs.

Figure 6. SEM photographs of fracture surface of nanocomposites with (a) untreated and (b) UV/ozone treated GNPs (for 70 min).

The atomic concentrations of elements obtained from the XPS analysis of GNPs in Table 2 indicate that the oxygen content on the GNP surface increased significantly after UV/ozone treatment, although the oxygen to carbon ratio still remained less than about 5%. This value is

much lower than that (over 100%) often observed on the electrolytically treated graphite fibre surface [8]. This is because the oxygen containing surface compounds can only be found at the graphene edges and/or lattice defects of GNP [9]. Unlike graphite fibers that may have many lattice defects, edges and impurities exposed on the surface, the graphite nanoplatelets are relatively pure and flat with far fewer exposed graphene edges.

Table 2. Atomic concentrations of GNP surface for varying UV/ozone treatment time (min).

Elements	UV0	UV20	UV30	UV50	UV70
C	98.2	95.1	96.8	95.5	96.9
O	1.7	4.8	3.2	4.5	3.1
Si	0.15	0.15	0	0	0
O/C ratio	1.7%	5.0%	3.3%	4.7%	3.2%

Table 3. Functional groups of GNP surface for varying UV/ozone treatment time (min).

Functional groups	Position (eV)	0	20	30	50	70
C	284.6	91.0%	85.8%	85.5%	84.9%	85.5%
C-OH or C-O-C	286.5	4.9%	7.7%	7.3%	8.0%	7.7%
C=O	287.9	2.2%	2.4%	2.9%	2.6%	2.6%
HO-C=O	289.3	2.0%	4.2%	4.3%	4.5%	4.2%

The surface functional groups obtained from the convolution curve fitting of XPS spectra are hydroxyl and ether, carboxyl and carbonyl groups, as shown in Table 3 [10]. The UV/ozone treatment increased the contents of all these functional groups, although these increases appear to be marginal in accounting for the significant improvement in electrical conductivity. Similar increases in hydroxyl, carbonyl and carboxyl groups on graphite surface were reported after a plasma treatment, with a corresponding improvement in flexural strength of the epoxy composites containing treated GNPs [7].

The SEM examinations of the GNP surfaces revealed an interesting change in surface morphology after UV/ozone treatment, as shown in Figure 7. The treated graphite exhibited a rougher surface along with clearer boundaries between the individual basal planes than the untreated graphite, indicating that loosely-bonded materials and organic contaminants present

on the surface were removed through the etching process by ozone. Removal of loose, weak material is a well established, major effect of surface treatment of graphite fibres [11].

Figure 7. SEM photographs of GNP surfaces (a) before and (b) after UV/ozone treatment (for 50 min).

Based on the above observations from various characterization methods, it can be summarized that the UV/ozone treatment cleansed the graphite surface, and embedded functional groups containing oxygen on the graphite surface through the oxidation process, facilitating improvement in the interfacial bond with the epoxy matrix, and in the corresponding bulk mechanical properties of nanocomposites. The hydroxyl and carboxyl groups on the graphite surface are reactive with epoxy [5], forming strong chemical bonds, as described in Eq. (1), where R' is the carbon atom in GNP. Although the total amounts of functional groups generated through UV/ozone treatment were only marginal, they had obvious, positive effects on the properties of nanocomposites because of the extremely large surface area of GNPs used in this study. Using a particle analyzer, unit surface area $338\text{m}^2/\text{g}$ and aspect ratio 1.5×10^4 were estimated for the GNPs. The improved mechanical interlocking between the well-defined graphite surface and the matrix resin was also partly responsible for the improved interfacial adhesion. Unfortunately, no reliable techniques have hitherto been developed to measure directly the interfacial adhesion between the nanoscopic reinforcements and polymeric resins.

It is more difficult to establish the correlations between the surface treatment and the electrical conductivity of nanocomposites. It is proposed here that the removal of surface (organic) contaminants and weak materials from the graphite surface through the UV/ozone treatment may have an ameliorating effect on the formation of stronger conductive network. The organic contaminant and loosely bonded weak material may possess an electrically insulating character as the electron scatterer. The chemical interactions between the functional groups present on the graphite surface and epoxy also contributed to improving electrical conductivity by eliminating unbonded gaps or micro-voids that have high resistivity, detrimental to the formation of the conductive network with a very low volume of conductive reinforcements. Moreover, the steric and electrostatic repulsion of the functional groups may facilitate the dispersion of the GNP, which is also beneficial to the formation of the conductive network. A similar result was shown for carbon fibre reinforced cement composites [12], where ozone treatment increased the interfacial bond strength while reducing the volume electrical resistivity.

4. Conclusion

The high aspect ratio and excellent electrical conductivity of GNPs makes them an effective reinforcement for polymer composites in providing high electrical conductivity. The main issues in fabricating useful GNP/polymer nanocomposites are (i) exfoliation of expanded graphites into GNPs and their uniform dispersion in the polymer matrix and (ii) proper surface treatment of GNPs to ensure sufficient interfacial adhesion with the matrix. In this

study, ultrasonication was used at various stages of nanocomposite fabrication and the GNPs were cleaned by UV/ozone treatment to address the above issues and successfully produce epoxy-based nanocomposites with balanced properties. The UV/ozone treatment improved both the electrical conductivity and the mechanical properties of the nanocomposites by increasing the surface roughness and creating functional groups on the graphite surface. These changes were beneficial in enhancing the graphite–epoxy adhesion, which showed some correlations with electrical conductivity and the mechanical properties of the nanocomposites.

Acknowledgements

This project was supported by the Research Grant Council of Hong Kong SAR.

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