Hybrid nanocomposites containing carbon nanotubes and graphite nanoplatelets

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Abstract

The effects of hybrid carbon nanotubes (CNT) and graphite nanoplatelets (GNPs) on the mechanical and electrical properties of epoxy nanocomposites were studied. When the total reinforcement contents is fixed at 2 wt.%, the nanocomposite containing 1% GNP and 1% CNT achieves the highest electrical conductivity of 4.7×10^{-3} S/cm, which is more than two orders of magnitude higher than that of nanocomposites with 2 wt.% GNP alone. Although the flexural properties are only marginally changed by hybridization, the quasi-static fracture toughness can be enhanced significantly by increasing the CNT content.
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1. Introduction

The excellent electrical conductivity and mechanical properties of carbon nanotubes (CNTs) make them ideally suited as filler for conducting polymer composites, capable of dissipating electrostatic charges and of shielding devices from electromagnetic radiation. Extensive researches have been directed towards the synthesis and fabrication of CNT/polymer nanocomposites, but the prohibitively high cost of CNTs limits wider applications. Graphite nanoplatelets (GNPs) produced by exfoliating natural graphite flakes have been used as a cheap conductive alternative. The high aspect ratio and large surface area of GNPs allow the formation of electrical conductive network at filler content much lower than conventional metallic powders, carbon fibres or carbon black. The GNP/epoxy nanocomposites with an excellent electrical conductivity and an improved mechanical property have been successfully developed [1,2] based on the UV/O₃ treatment of GNP with much enhanced graphite-epoxy interfacial adhesion. Although a very low electrical resistivity of 7.7×10^{-4} S/cm was achieved with only 4 wt.% of GNP, a further reduction was not feasible because of the difficulty in processing the composites with

a higher GNP content. In this paper, the concept of hybrid CNT and GNP reinforcements is devised in an effort to further improve the electrical conductivity of nanocomposites while maintaining balanced mechanical and fracture properties.

2. Experiments

2.1. Materials and nanocomposite fabrication

GNPs with average thickness and diameter of 4.5 and 46 μm, respectively [1,2] were produced from graphite-intercalated compound (GIC). Upon rapid heating at 1050 °C for 30 s, the GIC was expanded explosively several hundred times along the thickness direction (Fig. 1(a)) due to the evaporation of the intercalant and thermal shock. The expanded graphite was immersed in acetone and sonicated for 8 h to obtain GNPs.

Multi-wall CNTs were prepared by a chemical vapor deposition method with a purity of carbon content more than 95 wt.%. The diameter and length ranged between 10–20 nm and 10–50 μm, respectively. The as-received CNTs were immersed in acetone and sonicated for 3 h, followed by filtering and drying at 80 °C overnight to purify and disentangle the CNT bundles (Fig. 1(b)). Before incorporation into the epoxy resin, the CNTs and GNPs were exposed to UV light for 20 min and ozone environment for 5 min to introduce

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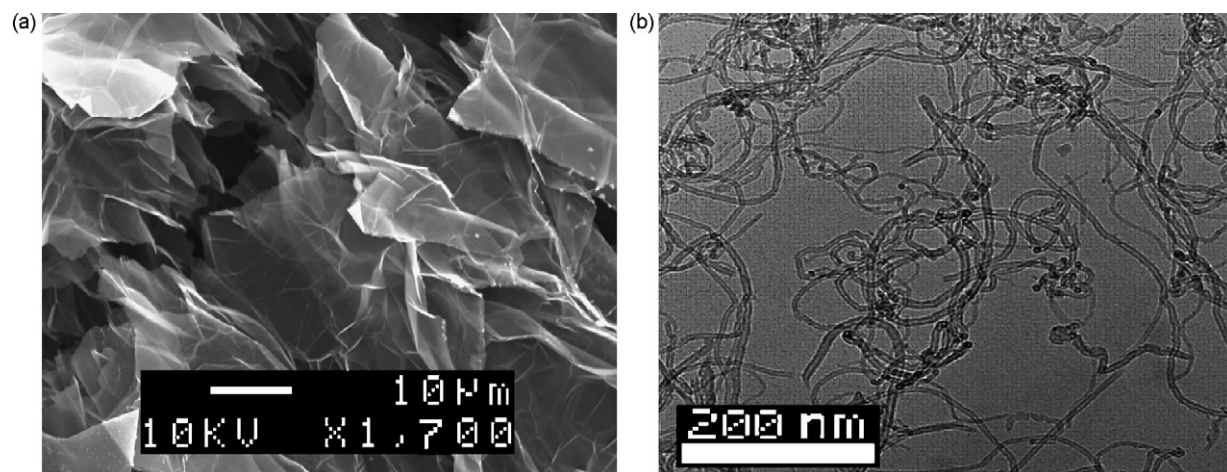 *E-mail address:* mejkkim@ust.hk (J.-K. Kim).

Fig. 1. Morphologies of (a) expanded graphite and (b) CNTs after dispersion by sonication in acetone.

oxygen containing functional groups on their surfaces. The UV/O_3 treatment facilitated uniform dispersion and improved the interfacial adhesion of carbon fillers with epoxy resin [1–3].

Optimised processing conditions were established to fabricate hybrid nanocomposites after an extensive trial and error. Several different combinations of CNT/GNP hybrid nanoreinforcement contents were added into the epoxy matrix, with the CNT contents ranging 0–1.0 wt.% while the total filler content was maintained 2 wt.%. Treated CNTs was sonicated in acetone for 4 h, during which Epon 828 epoxy was added and mixed via sonication for 2 h the treated GNPs were subsequently added and mixed using a high shear mixer for 30 min at 3000 rpm. Ultrasonication for 1 h at 80 °C was followed to further break the agglomerates. The mixture was outgassed at 80 °C for 2 h to eliminate the entrapped air, followed by adding a curing agent, 1,3-phenylenediamine, into the mixture in the ratio of 14.5/100 by weight. The composite was moulded into a flat plate and cured at 80 °C for 2 h, followed by post-cure at 150 °C for 3 h.

2.2. Mechanical/electrical tests and characterization

The bulk electrical conductivity of hybrid nanocomposites was measured at room temperature based on the four probe method using a resistivity/Hall measurement system Three-point flexure test was performed to measure the mechanical properties of neat epoxy and hybrid nanocomposites according to the specification, ASTM standard D790-96. The moulded nanocomposite plates were cut into 12.7 mm wide × 70 mm long × 3 mm thick samples, which were subjected to bending with a support span of 50 mm 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 quasi-static fracture toughness was measured using the compact tension test on a universal testing machine in accordance with the specification, ASTM D5045. Further details of specimen dimensions and geometry, and calculation of the critical stress intensity factors are given elsewhere [4].

3. Results and discussion

3.1. Electrical conductivity

The properties of the hybrid nanocomposites with different combinations of CNT/GNP contents with total filler content of 2 wt.% are compared with those of the nanocomposite containing 2 wt.% GNP alone. Fig. 2(a) plots the electrical conductivities of CNT/epoxy and GNP/epoxy nanocomposites, showing that the electrical conductivity increases abruptly at a critical filler concentration, i.e. the percolation threshold,
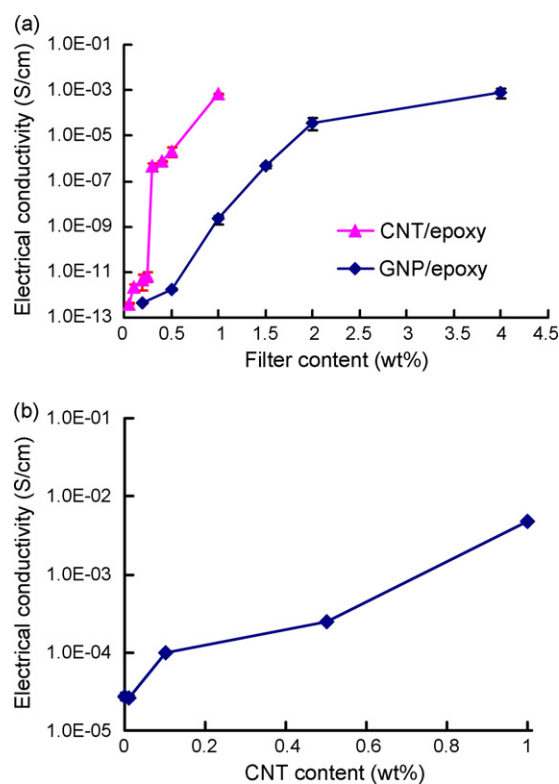

Fig. 2. Electrical conductivity of (a) CNT or GNP nanocomposites as a function of filler content and (b) 2 wt.% CNT/GNP hybrid nanocomposites as a function of CNT content.
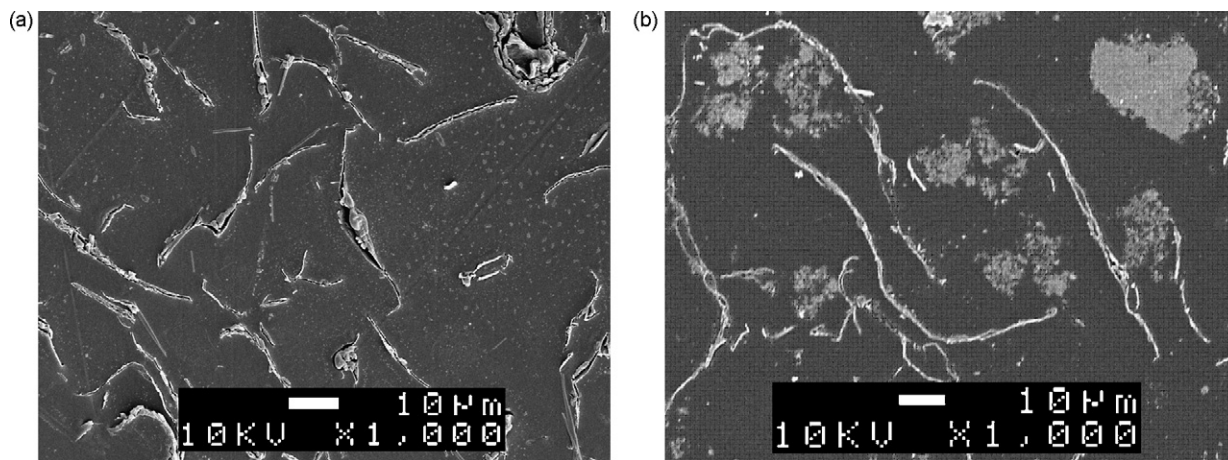
Fig. 3. SEM images of 2 wt.% CNT/GNP hybrid nanocomposites with (a) 0 wt.% CNT and (b) 1.0 wt.% CNT.

where the conductive fillers form a conducting network. The percolation thresholds amount to 0.25–0.3 wt.% and 1.0 wt.%, respectively, confirming a much higher efficiency of CNTs in forming the electrical conducting network than GNPs. A high electrical conductivity along tube axis [5], a high aspect ratio and the one-dimensional reinforcement of CNT are mainly responsible for the above observations. The hollow nature of CNTs further reduces the percolation threshold when measured in wt.%. However, the much higher cost of producing CNTs is a major drawback, severely limiting its applications as a conductive filler. The corresponding results for the hybrid CNT/GNP nanocomposites shown in Fig. 2(b) clearly indicate that the electrical conductivity increases consistently with the CNT content. The electrical conductivity of the hybrid nanocomposite containing 1 wt.% each of CNT and GNP reaches a remarkable 4.7×10^3 S/cm, which is more than 100 times higher than that of the nanocomposite with 2 wt.% GNP alone, and seven times that the corresponding value for the nanocomposite with 1 wt.% CNT alone.

The SEM image (Fig. 3(a)) for the nanocomposite with 2 wt.% GNP alone indicates that electrical conducting networks are comprised of well-dispersed GNPs. For the hybrid nanocomposites with 1 wt.% each of CNTs and GNPs, both well-dispersed GNPs and CNT agglomerates are observed (Fig. 3(b)). Because, conducting networks have already been formed by 1 wt.% GNPs alone (the percolation threshold of GNP), 1 wt.% CNT can provide multiple electron pathways through a synergy between the GNPs and CNTs. Once the filler content exceeds the percolation threshold, agglomerates can better improve the electrical conductivity than well-dispersed CNTs [6].

3.2. Mechanical and fracture properties

Mechanical properties of the nanocomposites measured from the flexural test are presented in Fig. 4. It is well known that the modulus of fibre- or particulate-reinforced composites depends mainly on the moduli and volume fractions of the composite constituents. Because, CNT and GNP have similar moduli,

of approximately 1 TPa, the CNT/GNP hybrid nanocomposites should have a similar modulus as far as the total filler contents are the same. The same explanation applies to the flexural modulus although the data exhibit some scatter due to different dispersion states. These values are somewhat 15–21% higher than the corresponding value of 3.04 GPa for the neat epoxy.

Unlike the modulus, however, the strength of nanocomposites depends on many factors in addition to the strengths and volume fractions of the composite constituents, amongst which the interfacial adhesion between the reinforcements the and matrix is a predominant factor [7]. For nanocomposites, the dispersion state
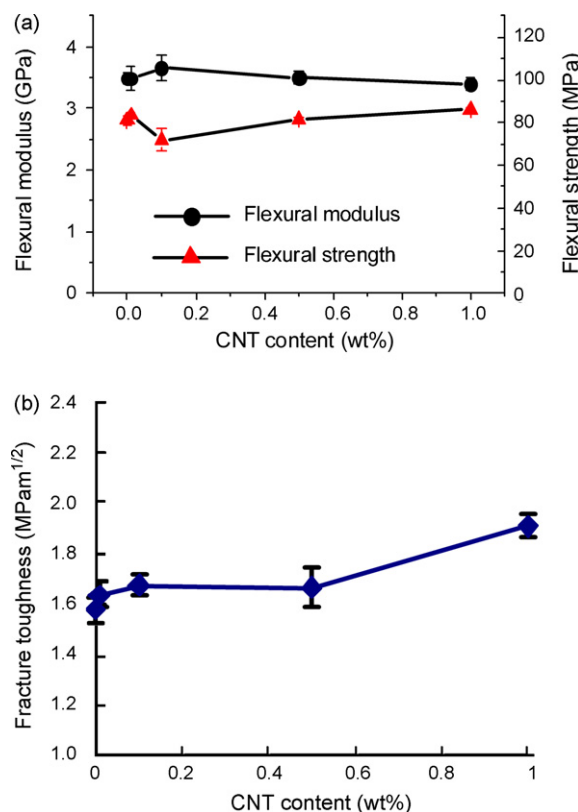

Fig. 4. (a) Flexural modulus and strength and (b) fracture toughness of 2 wt.% CNT/GNP hybrid nanocomposites as a function of CNT content.

is also very important. The fact that the flexural strength is the same for all combinations of CNT/GNP contents indicates that the interfacial adhesion is similar for these hybrid nanocomposites because both the CNTs and GNPs were oxidized by UV/O$_3$ treatment. Assuming the CNT is marginally stronger than the GNP (i.e., 10–60 GPa versus 10–20 GPa), increasing the CNT content from 0 to 1.0 wt.% does not enhance much the strength of hybrid nanocomposites because of the increasing difficulty in dispersing CNTs than GNPs.

Although the hybridization has marginal effects on flexural properties, it significantly affects the quasi-static fracture toughness (see Fig. 4(b)). The fracture toughness increases with the CNT content, resulting in 21% improvement after hybridization with 1 wt.% CNT, compared to the nanocomposites containing 2 wt.% GNP alone. Compared to neat epoxy, whose fracture toughness is 1.22 MPa m$^{1/2}$, the improvement by 57% is remarkable. The toughening mechanisms of GNP nanocomposites proceeds via crack tip pinning and bifurcation, similar to organoclay reinforced epoxy nanocomposites [4]. Additional toughening mechanisms arising from CNTs in the hybrid nanocomposites are tube pull-out and crack tip bridging [8], as revealed by our fracture analysis.

4. Conclusions

Hybrid CNT/GNP nanocomposites with a total reinforcement of 2 wt.% were fabricated and the effects of varying individual CNT/GNP contents on electrical, flexural and fracture properties were evaluated. The electrical conductivity of hybrid nanocomposite containing 1 wt.% CNT exhibits the highest value of 4.7×10^3 S/cm, which is more than two orders of magnitude higher than that of 2 wt.% GNP alone. While the flexural properties do not change much due to the hybridization, the fracture toughness increases by 21% compared to the nanocomposite with 2 wt.% GNP alone, or 57% compared to neat epoxy. Crack tip bridging and pull out of CNTs are identified as the main toughening mechanisms of hybrid nanocomposites, in addition to the existing crack tip pinning and bifurcations by GNPs.

Acknowledgement

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