Hybrid Nanocomposites Containing Carbon Nanotubes and Graphite Nanoplatelets

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Abstract

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

Keywords*:* Carbon Nanotube, Graphite Nanoplatelet, Hybrid Nanocomposites.

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1. Introduction

The excellent electrical conductivity and mechanical properties of carbon nanotubes (CNT) make them ideally suited as filler for conducting polymer composites, capable of dissipating electrostatic charges and shielding devices from electromagnetic radiation. Extensive researches have recently been directed towards the synthesis and fabrication of CNT/polymer nanocomposites, but the prohibitively high cost of CNT 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 excellent electrical conductivity and improved mechanical properties have been successfully developed previously [1,2]. The GNPs were subjected to a UV/O_3 treatment, which showed ameliorating effects on mechanical and thermo-mechanical properties of nanocomposites arising from the enhanced graphite-epoxy interfacial adhesion. A remarkable electrical resistivity of $7.7X10^{-4}$S/cm was achieved with only 4 wt% of GNP. However, the resistivity could not be further reduced by increasing the GNP content, because the high viscosity of the GNP and epoxy mixture made the processing of nanocomposites extremely difficult.

This paper is part of a larger project on fabrication, property characterization and applications of conducting polymers made from conductive fillers. The concept of hybrid CNT and GNP reinforcements was 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 thickness and diameter of 4.5μm and 46μm on average [1,2] were produced from graphite intercalated compound (GIC, supplied by Asbury Graphite Mills, USA). Upon rapid heating at 1050^{o}C for 30s, the GIC was expanded explosively several hundred times along the thickness direction due to the evaporation of the intercalant and thermal shock. The expanded graphite was immersed in acetone, which was subjected to ultrasonication using a temperature adjustable sonicator (Bransonic 1510-DTH with the maximum output of 70W/42KHz**)** for 8 hr to obtain GNPs. Figure 1 (a) and (b) shows the morphologies of expanded graphite and GNPs.

Multi-wall carbon nanotubes (CNT) were prepared by a chemical vapor deposition method with a purity of carbon content more than 95wt% (supplied by Iljin Nanotech Ltd., South Korea). The diameter and length ranged between 10~20nm and 10~50μm, respectively, and the specific surface area was 420m^2/g, according to the supplier's specification. The as-received CNT was immersed in acetone and sonicated for 3 hr, followed by filtering and drying at 80^{o}C overnight to purify the CNTs from foreign objects embedded on the surface, and to disentangle the CNT bundles (Figure 1(c)). Before incorporation into the epoxy resin, the CNTs and GNPs were exposed to UV light (in a Jelight 144AX-220 UV/Ozone Cleaning System) for 20min and ozone environment for 5min in order to introduce oxygen containing functional groups on the surfaces. The UV/O_3 treatment facilitated uniform dispersion with improved interfacial adhesion of carbon fillers with epoxy [1~3].

Optimised processing conditions were established to fabricate hybrid nanocomposites after an extensive trial and error. Several different combinations of CNT/GNP hybrid nano-reinforcement contents were added into the epoxy matrix. They were CNT contents of 0wt%, 0.01wt%, 0.1wt%, 0.5wt% and 1.0wt% with a total filler content of 2wt%. Treated CNTs was sonicated in acetone for 4hr, during which epoxy (Epon 828, supplied by Shell Chemical) was added and mixed via sonication for 2hr. Then the treated GNPs were added and mixed using a high shear mixer for 30

min at 3000rpm. Ultrasonication for another 1hr at 80°C was followed to further break the agglomerates. The mixture was then outgassed at 80°C for 2hr to eliminate the entrapped air. Curing agent, 1,3-Phenylenediamine (supplied by Sigma-Aldrich), was added 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 2hr, followed by post cure at 150°C for 3hr.

2.2 Mechanical/electrical tests and characterisation

The bulk electrical conductivity of hybrid nanocomposites was measured at room temperature based on the four probe method using a resistivity/Hall measurement system (Bio-Rad HL5500PC). As the highest limit of the electrical resistivity measured by the resistivity/Hall measurement system was 10^8 Ωcm, the electrical resistivity higher than this limit was measured with a programmable curve tracer (Sony Tektronix 370A).

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 12.7mm wide × 70mm long x 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. Quasi-static fracture toughness was measured using the compact tension test on a universal testing machine in accordance with the specification, ASTM D5045. The specimen dimensions satisfied the plain strain condition given in Eq(1), so that the quasi-static fracture toughness K_{Ic} was obtained directly from the stress intensity factor, K_Q , which was calculated using Eqs (2) and (3).

$$B, a, (W - a) > 2.5 * (\frac{K_Q}{\sigma_y})^2 \quad (1)$$

$$K_Q = \frac{P_Q}{B\sqrt{W}} f(x) \quad (2)$$

$$f(x) = \frac{(2+\frac{a}{W})(0.886+4.64(\frac{a}{W})-13.32(\frac{a}{W})^2+14.72(\frac{a}{W})^3-5.6(\frac{a}{W})^4)}{(1-\frac{a}{W})^{3/2}} \quad (3)$$

B is the specimen thickness, a is the crack length, W is width of the specimen, σ_y is the yield stress of the material in a uniaxial tensile test and P_Q is the maximum load. The specimen had a dimension: *B=3mm*; *a=16mm*; *W=36mm* and a pre-crack was created by tapping a brand new razor blade on the machined notch. A scanning electron microscope (SEM, JEOL-6300) was employed to exam the morphologies of hybrid nanocomposites at an accelerating voltage of 10.0 kV.

The storage modulus and glass transition temperature of hybrid nanocomposites were measured using a dynamic mechanical analyzer (DMA 7 Perkin Elmer) according to the specification, ASTM Standard D4065-90. Samples of dimensions 20mm×3mm×1mm were tested in a three point bending mode at a temperature range from 30°C to 240°C with a temperature ramp rate of 10°C/min and a frequency of 1Hz in a helium atmosphere.

3. Results and Discussion

3.1 Electrical Conductivity

The properties measured of the hybrid nanocomposites with different combinations of CNT/GNP contents with a total filler content of 2wt% were compared with those of the nanocomposite containing 2wt% GNP alone. Figure 2(a) plots the electrical conductivities of CNT/epoxy and GNP/epoxy nanocomposites as a function of filler content. The electrical conductivity increased abruptly at a critical filler concentration, i.e. percolation threshold, where the conductive fillers formed a conducting network. The percolation thresholds were found 0.25~0.3wt% and 1.0wt% respectively, confirming a much higher efficiency of CNTs in forming the electrical conducting

network than GNPs**.** High electrical conductivity along the tube axis [4], high aspect ratio and one dimensional reinforcement of CNTs are the main reasons for higher efficiency in increase the electrical conductivity of nanocomposites than GNPs. The hollow nature of CNTs further reduced the percolation threshold compared to GNPs when measured in wt%. However, the much higher cost of producing CNTs is a major drawback, severely limiting its applications as conductive fillers. The corresponding results for the hybrid CNT/GNP nanocomposites shown in Figure 2(b) clearly indicate that the electrical conductivity increased consistently with CNT content. The conductivity of the hybrid nanocomposite containing 1wt% each of CNT and GNP reached a remarkable 4.7×10^{-3} S/cm, which was more than 100 time higher than that of the nanocomposite with 2wt% GNP alone, and 7 times of the corresponding value for the nanocomposite with 1wt% CNT alone.

The SEM photograph presented in Figure 3(a) for the nanocomposite with 2wt% GNP alone indicates that electrical conducting networks were formed by the well-dispersed GNPs. Incorporation of 0.1wt% CNT did not make much difference in the morphology (Figure 3(b)), with some isolated individual CNTs. There was only small improvement in electrical conductivity (Figure 2(b)) because the GNPs were the main contributor for the formation of networks. For the hybrid nanocomposites reinforced with 1wt% each of CNTs and GNPs, both well-dispersed GNPs and mainly CNT agglomerates were observed (Figure 3(c)). Because strong conducting networks were already formed by 1wt% GNPs alone, the percolation threshold of GNP nanocomposite, incorporation of 1wt% CNT could provide an added benefit of further improving the electrical conductivity through synergy between the GNPs and CNTs. It was shown previously that once the filler content exceeded the percolation threshold, agglomerates could better improve the electrical conductivity than well dispersed fillers in CNT-epoxy nanocomposites [5]

3.2 Mechanical and fracture properties

Mechanical properties of the nanocomposites measured from the flexural test are presented in Figure 4. It is well known that the modulus of fibre or particulate reinforced composites is dependent mainly on the moduli and volume fractions of the composite constitutes. 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 (Figure 4) although there were some data scatters due probably to different dispersion states. These values were some 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 apart from the strength and volume fraction of composite constituents, amongst which the interfacial adhesion between the reinforcements and matrix is a predominant factor [6]. For nanocomposites, the dispersion state and the orientations of nano-reinforcements become very important. The similar flexural strength values for all combinations of CNT/GNP contents (Figure 4) indicate that the interfacial adhesion was similar for these hybrid nanocomposites because both the CNTs and GNPs oxidized by UV/O_3 treatment. Assuming that the CNT is only marginally stronger than the GNP (i.e. 10~60 GPa vs 10~20GPa), increasing the CNT content from 0 to 1.0wt% did not much enhance the strength of hybrid nanocomposites because of the increasing difficulty in dispersing CNTs.

Although the hybridization had minor effects on flexural properties, it affected significantly the quasi-static fracture toughness, as shown in Figure 5. The fracture toughness increased with CNT content, resulting in 21% improvement after hybridization with 1wt% CNT, compared to the nanocomposites containing 2wt% GNP alone. Compared to neat epoxy, whose fracture toughness was 1.22 MPa·$m^{1/2}$, the improvement was remarkable 57%. The toughening mechanisms of GNP

nanocomposites were identified crack tip pinning and bifurcation, similar to organoclay reinforced epoxy nanocomposites [7]. Apart from these mechanisms, additional toughening mechanisms arising from CNTs in the hybrid nanocomposites are tube pull-out and crack tip bridging [8], as revealed in our fracture analysis.

The storage moduli and the glass transition temperatures, T_g, determined by the peak position of loss modulus for the CNT/GNP hybrid nanocomposites are presented in Figure 6. The storage moduli at room temperature for all hybrid nanocomposites were barely different, resembling the flexural moduli shown in Figure 5. The T_g showed an upward trend with increasing CNT content, with an initial jump at a low CNT content of 0.01wt% from a low 124^{o}C at 0wt% CNT. A maximum of 155 ^{o}C was achieved at 0.5wt% CNT, followed by a small reduction to 142^{o}C at 1.0wt% of CNT. The large gains of T_g with small CNT contents can be attributed to an increase in thermostability as a consequence of the reduction of the mobility of the polymer molecules around the CNTs by the strong interfacial interactions. As described in Section 2, the CNTs were subjected to UV/O_3 treatment before they were incorporated into an epoxy matrix. The UV/O_3 treatment introduced oxygen containing functional groups on the CNT surface, such as hydroxyl group and carboxyl group [3], which can react with epoxide group of matrix and form strong covalent bonds. The strong covalent bonds limited the cooperative motions of epoxy molecular at high temperatures and thus increased the T_g. Meanwhile, GNPs were produced by exfoliating graphite intercalated compounds, and there may be some unexfoliated, loosely attached layers on the GNP surface. The loose attachments may introduce some free volume into the nanocomposites, counterbalancing the benefits arising from the completely exfoliated GNPs. It was also observed [1] that increasing the UV/O_3 treatment duration further enhanced the T_g of GNP nanocomposites.

4. Conclusion

Hybrid CNT/GNP nanocomposites with a total reinforcement of 2wt% were fabricated and the effects of varying individual CNT/GNP contents on electrical, mechanical and fracture properties are evaluated. The electrical conductivity of hybrid nanocomposite containing 1wt% CNT exhibited the highest value of 4.7×10^{-3} S/cm, which is more than two orders of magnitude higher than that of 2wt% GNP alone. Synergistic effects were found between the different form of nano-reinforcements not only on electrical conductivity but also on fracture and thero-mechanical properties. While the flexural properties did not change much due to the hybridization, the fracture toughness increased by 21% compared to the nanocomposite with 2wt% GNP alone, or 57% compared to the neat epoxy. Crack tip bridging and pull out of CNTs were identified as main toughening mechanisms of hybrid nanocomposites, additional to the existing crack tip pinning and bifurcations by GNPs. The glass transition temperature increased with increasing CNT content due to the reduced mobility of the epoxy matrix around the CNTs by the strong interfacial interactions.

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Figure Captions

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

Fig. 2. Electrical conductivity of (a) CNT or GNP nanocomposites as a function of filler content; (b) 2wt% CNT/GNP hybrid nanocomposites as a function of CNT content.

Fig. 3. SEM photographs of 2wt% CNT/GNP hybrid nanocomposites with (a) 0wt% CNT; (b) 0.1wt% CNT and (c) 1wt% CNT.

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

Fig. 5. Quasi-static fracture toughness of 2wt% CNT/GNP hybrid nanocomposites as a function of CNT content.

Fig. 6. (a) Storage modulus variations as a function of temperature and (b) T_g as a function of CNT content which was determined by loss modulus peaks for 2wt% CNT/GNP hybrid nanocomposites.

(a) (b) (c)

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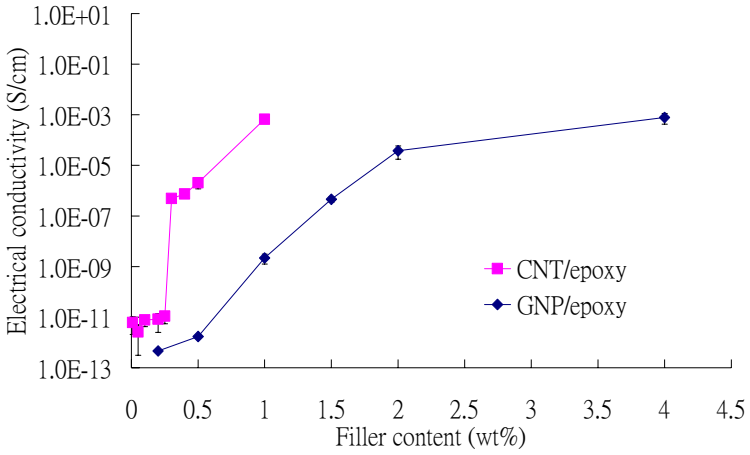
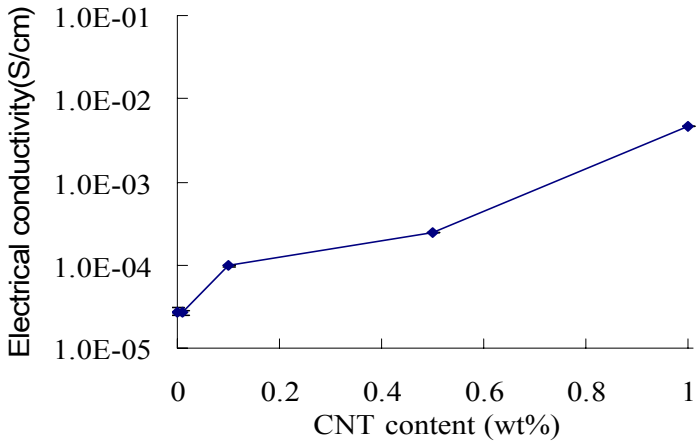


(a)



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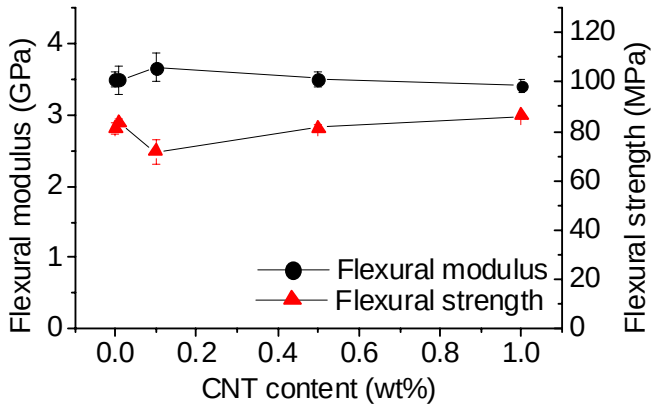

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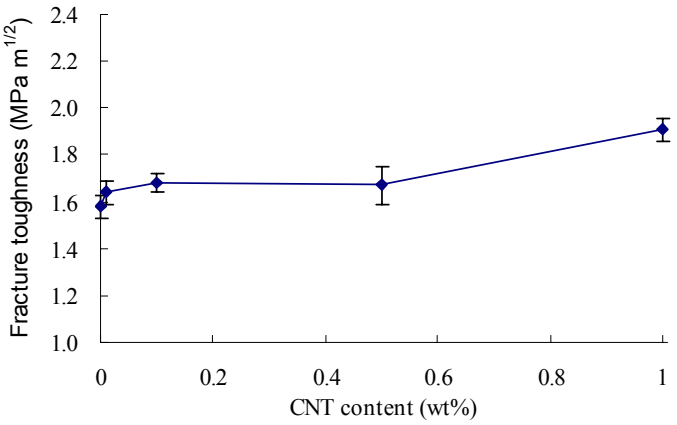
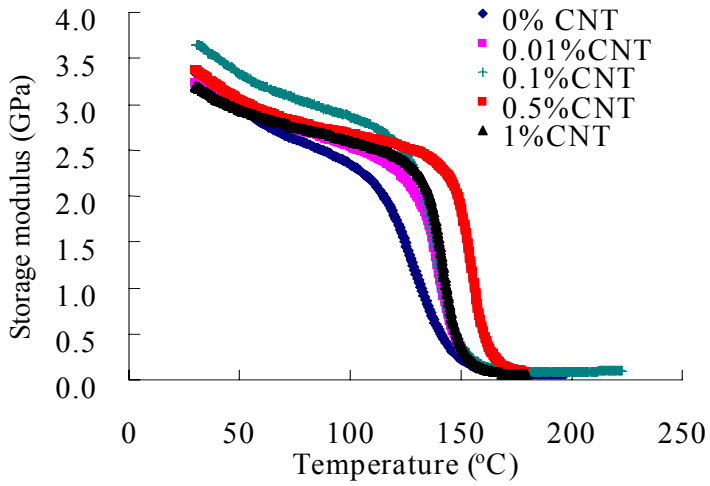
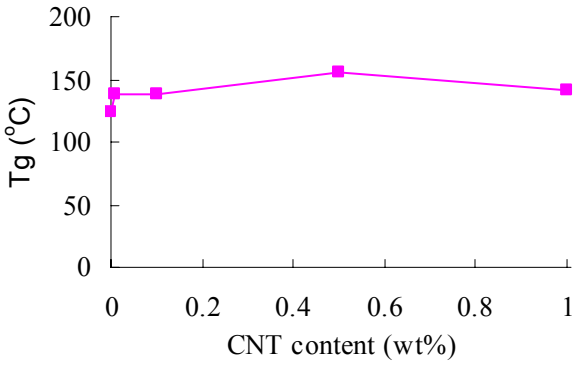


Fig. 5. Quasi-static fracture toughness of 2wt% CNT/GNP hybrid nanocomposites as a function of CNT content.



(a)



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