

MECHANICAL PROPERTIES OF MODIFIED GRAPHENE NANOPLATELETS REINFORCED EPOXY NANOCOMPOSITES

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Abstract

Graphene nanoplatelets (GNPs) are a novel nanofillers including single or multilayers of a graphite plane which possesses exceptional functionalities, high mechanical strength (1 TPa in Young's modulus and 130GPa in ultimate strength), and chemical stability, for the following reasons: their abundance in nature and thus their cost effectiveness and their extremely high specific surface area, which carries high levels of transferring stress across interface and provides higher reinforcement than other carbon materials. Because of their high absolute strength, large surface area and cost effectiveness, graphene nanoplatelets (GNPs) have high potential for improving the material properties of polymer based composites. In this study, the graphene nanoplatelets (GNPs) modified with maleic acid (MA) were used to reinforce epoxy resin to prepare the GNPs/epoxy nanocomposite and to investigate their mechanical properties. The mechanical properties of GNPs/epoxy nanocomposite, such as ultimate tensile properties and impact strength were investigated. Significant improvement in the mechanical properties of nanocomposites containing different proportions of GNPs were increased over that of neat epoxy resin. The fracture surfaces of the neat epoxy composites (without adding GNPs) and the GNPs/epoxy nanocomposites were comparatively examined using Scanning electron microscope (SEM). The images showed that nanofillers exhibited higher solubility and compatibility in epoxy matrix. Therefore, embedding GNPs can restrain creviced growth in the GNPs/epoxy nanocomposites and prevent the expansion of these cracks.

1. Introduction

Graphene nanoplatelets (GNPs) are platelet-like graphite nanocrystals with multi-graphene layers. In general, a high contact area between polymer and nanofiller maximizes stress transfer from polymer matrix to nanofillers. Therefore, GNPs can be expected to exhibit better reinforcement than CNTs in polymer composites, due to their ultrahigh aspect ratio (600–10,000) [1-5], and higher surface constant area. The GNPs planar structure provides a 2-D path for phonon transport, and the ultrahigh surface area allows a large surface contact area with polymer resulting in enhancement of the composite thermal conductivity [6-8]. However, the large surface area between GNPs what is NGP planar nano-sheets results in large Van der Waals forces and strong π - π interactions [9-11]. Thus, the performance of graphene-based polymer composites is limited by the aggregation and stacking of NGP sheets. Since the physicochemical properties of aggregated GNPs are similar to those of graphite with its

relatively low specific surface area, the performances of GNPs will be suffer significantly reduced performance. This is an important issue if NGP potential as a polymer composite reinforcing materials is realized [12,13].

Epoxy is widely applied in advanced CFRP (carbon fiber reinforce plastic, CFRP) due to their good mechanical performance, process-ability, compatibility with most fibers, chemical resistance, wear resistance and low cost. However, these materials are relatively brittle, which is detrimental to the interlaminar properties between matrix and reinforcement. The addition of CNTs or GNPs to improve the interfacial strength of laminates has demonstrated. Besides, the great potential to increase the mechanical properties of thermoset resins and their fiber-reinforced composites as using CNTs and GNPs as fillers.

In this study, various amounts of Graphene nanoplatelets (GNPs) modified with maleic acid (MA) were uniformly dispersed in epoxy resin (i.e., 0, 0.25, 0.5, 1, and 1.5 wt%), and prepared the GNPs/epoxy nanocomposites. Mechanical properties of the nanocomposite, including ultimate tensile and impact strength were investigated.

Finally, The fracture surface of the specimen was investigated using scanning electron microscopy (SEM) to determine the dispersion of the GNPs in the nanocomposites.

2. Experimental

2.1. Preparation of GNPs/epoxy resin solution.

The unmodify graphene nanoplatelets, GNPs (Xiamen Knano Graphene Technology Co., Ltd, China) with a thickness of 5–25 nm were used for reinforcement in this study. The graphene nanoplatelets (GNPs) modified with maleic acid (MA) and the GNPs-MA/ Methyl ethyl ketone (MEK) solution was stirred for 10 minutes using a homogenizer. The solution was then vibrated by ultrasonication for 90 minutes to enable the GNPs to disperse uniformly throughout the Methyl ethyl ketone solution.

The GNPs/ MEK solution was mixed with epoxy resin (EPO-622TM Epoxy Resin, Epotech Composite Co., Ltd, Taiwan) for 90 minutes using a mechanical mixer and then vibrated by ultrasonication for 90 minutes to enable the GNPs to disperse uniformly throughout the epoxy solution. A schematic illustration of the fabrication of the GNPs/epoxy resin is shown in Fig.1(a).

2.2. Preparation of GNPs/epoxy nanocomposites.

The GNPs/epoxy resin solution was placed in a heating oven to expose at 83°C for three hours to evaporate all of the solvent and then placed in a vacuum heating oven and vacuum pumping was performed for 5 minutes to eliminate air bubbles. The resin solution was poured into molds and then placed on a hot press machine to form the GNPs/epoxy nanocomposites (pressed at 1500 psi and 150 °C for 30 minutes). The nanocomposites were then placed in a heating oven at 140°C for 3 hours to eliminate the internal stress (post-cure). The curing agent used in this research is dicyandiamide (DICY), mixing ratio of epoxy and curing agent was 18:2 (wt%). A schematic illustration of the fabrication of the GNPs/epoxy resin is shown in Fig. 1(b).

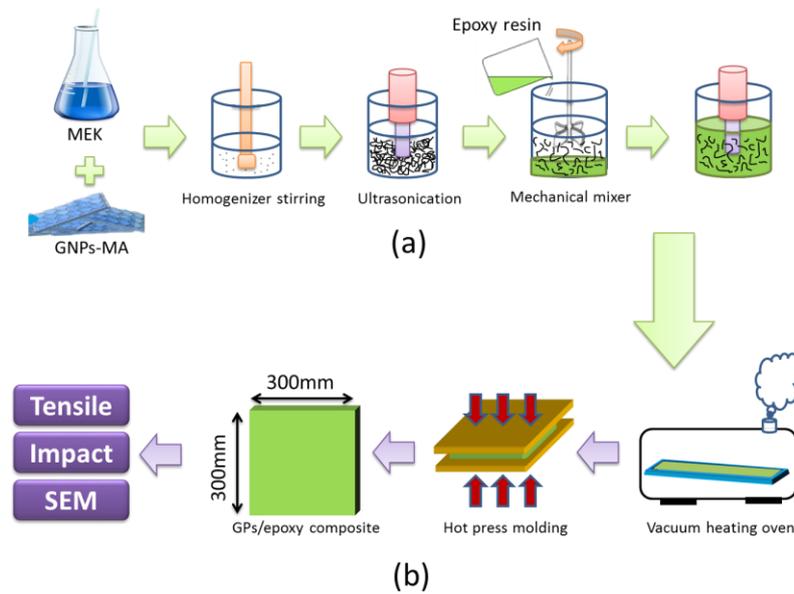


Figure 1. A schematic illustration of the fabrication of composites: (a) GNPs/epoxy resin solution; (b) GNPs/epoxy nanocomposites;

3. Results and discussion

3.1. Characterization of GNPs-MA

Figure 2 shows the reaction of maleic anhydride (MA) and the epoxide group. This confirmed that MA can react with epoxy resin and reinforcing the interfacial strength between carbon nanomaterials and the resin. The fourier transform infrared (FT-IR) spectra images were shown in Figures 3. FT-IR was utilized to characterize the modification of GNPs powders. The figures showed that the key absorption peak near 1,600–1,850 cm^{-1} was the $-\text{C}=\text{O}$ functional group, a standard absorption peak of acid anhydrides; these results indicated the successful MA modification of GNPs.

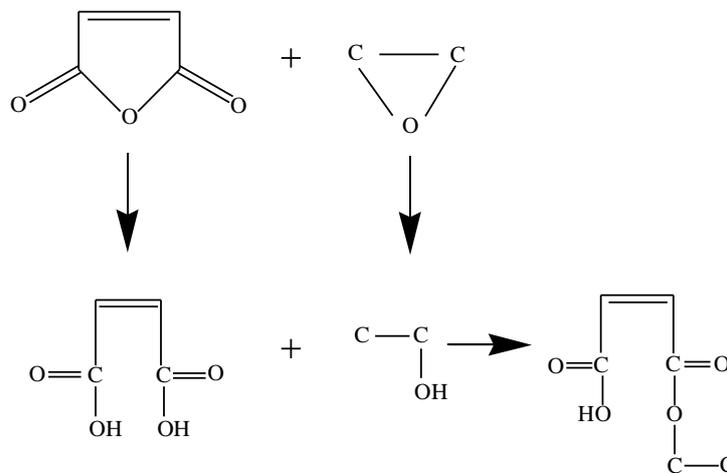


Figure 2. Reaction of maleic anhydride and epoxide group.

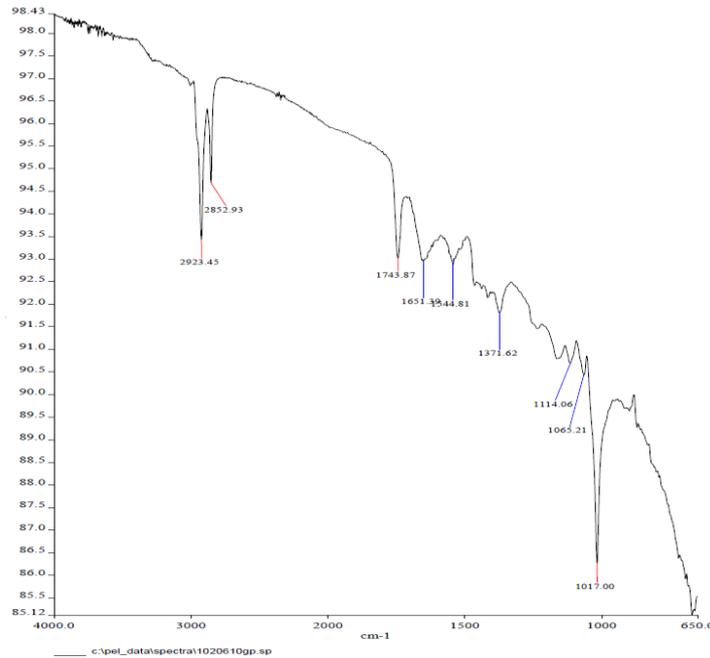


Figure 3. FT-IR spectra of GNPs-MA.

3.2. Tensile properties of GNPs/epoxy nanocomposites.

Figure 4 and Table 1 show the ultimate tensile strength and young's modulus of the nanocomposites without and with the four proportions of GNPs contents. The tensile strength and young's modulus of the nanocomposite with GNPs added at 0.25 wt% shows the best enhancement compared to the composite without any GNPs added. The strength begins to degrade at the 0.5 wt% GNPs loading.

The mobility of polymer chains was restricted because of the dispersion of nanofillers under low content. The high aspect ratio, high modulus, strength of nanofillers, and robust interfacial adhesion between the nanofillers and matrix also contributed to the reinforcement. However, the decrease in strength with high nanofiller content can be attributed to the following two effects: 1) non-uniform dispersion of the nanofillers in higher loading systems. Acoustic cavitation is one parameter for nanoparticle dispersion under low content. 2) Voids might also have decreased the strength. Choi et al. reported that few voids were produced during the fabrication process and that voids increased with higher nanoparticle content [14-16].

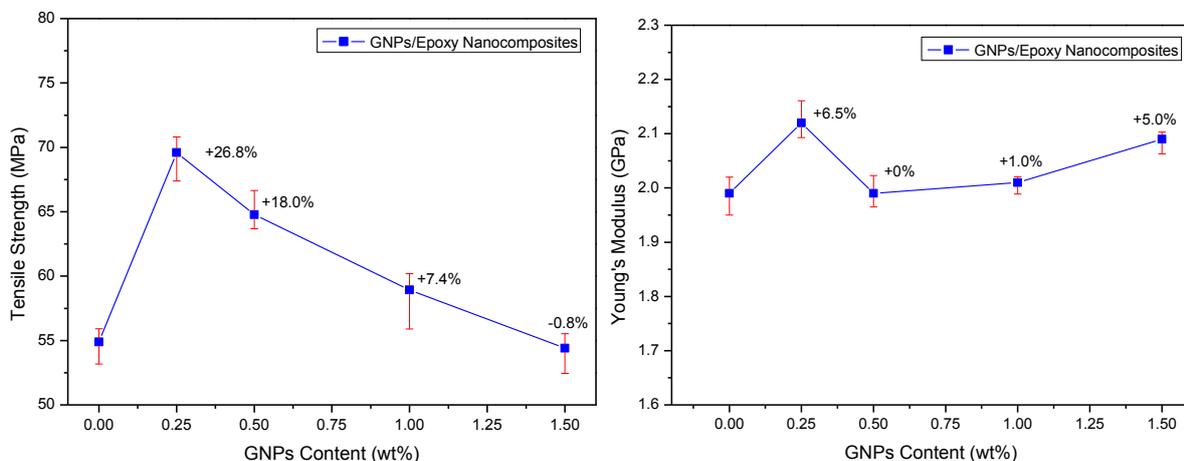


Figure 4. Tensile properties of GNPs/epoxy nanocomposites. (a) Tensile strength; (b) Young's modulus.

3.3. Impact Strength of GNPs/epoxy nanocomposites.

The results shown in Fig. 5 indicate that the impact test results for the GNPs/epoxy nanocomposites and indicate that the impact strength of neat epoxy resin cured without adding GNPs is approximately 61.8 J/m. When the GNPs added in an amount of 0.5 and 1.0 wt%, The impact strength of the GNPs/epoxy nanocomposites compared to neat epoxy resin were increased by 152.5 % and 121.1 %, respectively.

A comprehensive knowledge about the influence of nanoparticles on the micromechanics is required in order to explain the observed toughening effect of nanoparticles. The mechanisms of increasing the fracture toughness of polymers via the incorporation of particles have been extensively studied within the last three decades [17-20]. The application of microparticles (spherical or fibrous) exhibits the highest effect in brittle (e.g., thermosetting) matrix systems. Several theories have been developed to explain and understand the effects of particle-toughening and they are often in good agreement with experimental results. The most important micromechanical mechanisms leading to an increase in fracture toughness are (i) localized inelastic matrix deformation and void nucleation, (ii) particle/fibre debonding, (iii) crack deflection, (iv) crack pinning, (v) fibre pull-out, (vi) crack tip blunting (or crack tip deformation), and (vii) particle/fibre deformation or breaking at the crack tip.

In this study, GNPs reinforce epoxy resin and investigate their impact properties. Based on the aforementioned literature and experimental results, the crack growth suppression behavior in nanocomposite was primarily caused by the crack pinning and crack deflection of GNPs. When cracks begin to grow, the cracks in the nanocomposite deflect due to the interactions of GNPs, consequently suppressing crack growth effectively. This is the reason that the reinforcement effect of impact strength became increasingly noticeable as the carbon nanomaterial content increased.

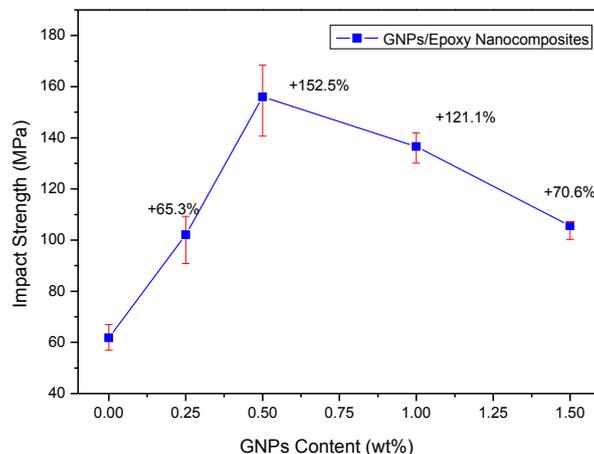


Figure 5. Impact strength of GNPs/epoxy nanocomposites.

3.4. Fracture surface of GNPs/epoxy nanocomposites.

The fracture surfaces of the neat epoxy composites (without adding GNPs) and the GNP/epoxy nanocomposites were comparatively examined using SEM. Neat epoxy resin composites exhibited a relatively smooth fracture surface, and the higher magnification SEM image in Figure 6 (a) and 6(b) indicates a smooth, mirror-like fracture surface representing the brittle failure of the unfilled epoxy.

As GNPs content increased to 0.25 wt%, considerable corrugation was found in the crevices among the matrix, as shown in Fig.7(a) and 7(b). GNPs cross-linked in the crevices in the corrugation area restrain creviced growth. The static mechanical properties can be enhanced because both the corrugation and GNPs increase the interfacial fraction between the GNPs and matrix.

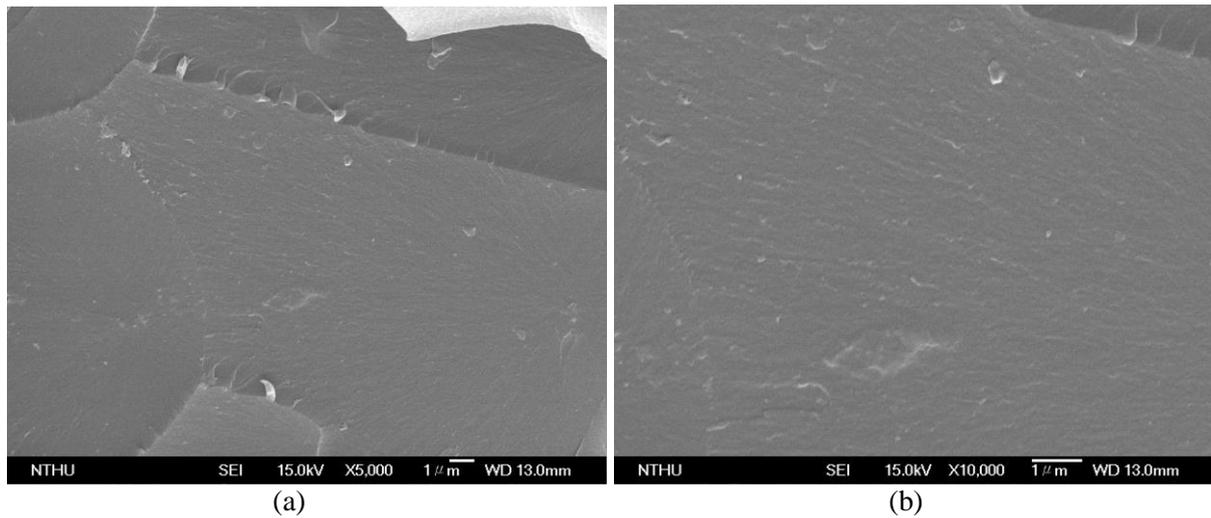


Figure 6. Fracture surface of neat epoxy composites. (a) $\times 5,000$, (b) $\times 10,000$.

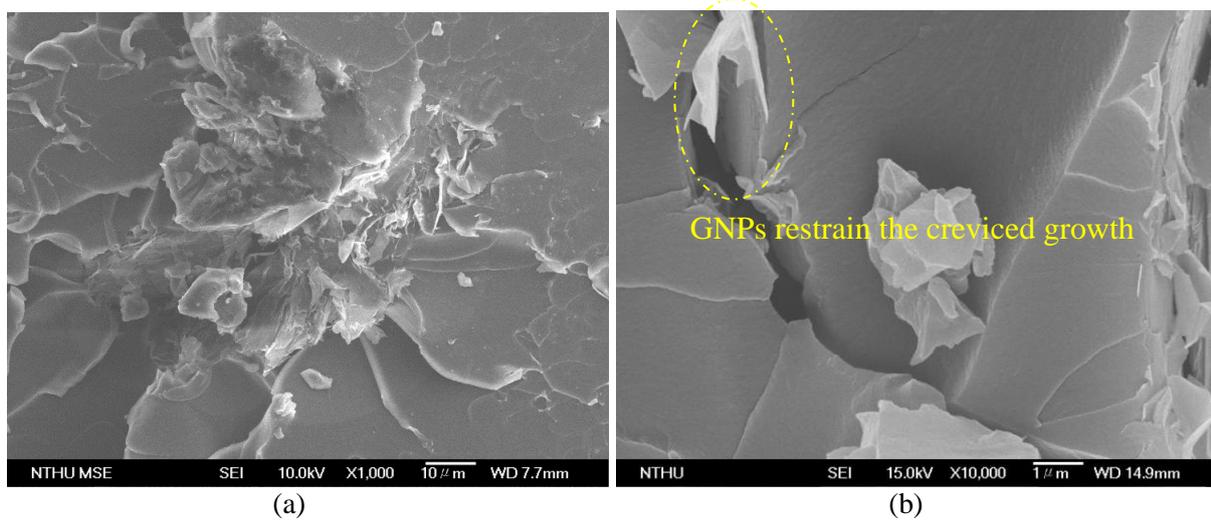


Figure 7. Fracture surface of the 0.25 wt% GNPs/epoxy nanocomposite. (a) $\times 1,000$, (b) $\times 10,000$.

Table 1. Mechanical properties of GNPs/epoxy nanocomposites

Test item (unit)	GNPs content (wt%)				
	0	0.25	0.5	1	1.5
TS (MPa)	54.89	69.63	64.77	58.93	54.41
%Enhancement		(+26.8%)	(+18.0%)	(+7.4%)	(-0.8%)
YM (GPa)	1.99	2.12	1.99	2.01	2.09
%Enhancement		(+6.5%)	(+0%)	(+1%)	(+5%)
IS (J/m)	61.78	102.12	156.03	136.59	105.59
%Enhancement		(+65.3%)	(+152.5%)	(+121.1%)	(+70.6%)

※GNPs/epoxy nanocomposites, TS: Tensile Strength, YM: Young's Modulus, IS: Impact Strength.

3. Conclusions

The experimental results showed that the mechanical properties of GNPs/epoxy composites have optimal characteristics with reinforcement through GNPs addition; furthermore, the ultimate tensile strength, young's modulus and impact strength were all improved. Based on the experimental results, adding the present GNPs to the epoxy resin provides a considerable reinforcement effect.

When the concentration of GNPs was 0.25 wt%, the tensile properties provided the superior reinforcing effect compared with neat epoxy resin. A noticeable improvement was observed in the impact strength of the GNPs/epoxy nanocomposites. Based on the aforementioned literature and experimental results, the crack growth suppression behavior in nanocomposite was primarily caused by the crack pinning and crack deflection of GNPs.

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