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Flexural, electrical, thermal and electromagnetic interference shielding properties of xGnP and carbon nanotube filled epoxy hybrid nanocomposites

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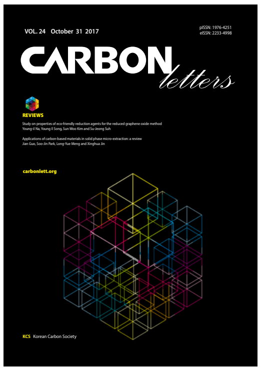

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Abstract

The microstructure, flexural properties, electrical conductivity, thermal conductivity and electromagnetic interference (EMI) shielding effectiveness (SE) of epoxy composites filled with multi-walled carbon nanotubes (CNTs), exfoliated graphite nanoplatelets (xGnPs) and CNT-xGnP hybrid filler were investigated. The EMI SE of the CNT-xGnP hybrid composite was higher than 25 dB at 100 MHz while that of the xGnP based composite was almost zero. The flexural modulus of the CNT-xGnP based epoxy composite continuously increased to 3.32 GPa with combined filler content up to 10 wt% while that of the CNT based epoxy composites slightly decreased to 1.96 GPa at 4 wt% CNT, and dropped to 1.57 GPa at 5 wt% loading, which is lower than that of epoxy. The CNT and CNT-xGnP samples had the same EMI SE at the same surface resistivity, because samples with the same surface conductivity have the same amount of the charge carriers.

Key words: multi-walled carbon nanotube, exfoliated graphite nanoplatelet, epoxy, nanocomposite, electromagnetic interference shielding

1. Introduction

The interference shielding of electromagnetic waves using a barrier made of conductive materials is important for commercial and military purposes [1-3]. The importance of electromagnetic interference (EMI) shielding has also increased in electronics and communication industries, due to the widespread use of densely packed highly sensitive electronic devices. EMI shielding is necessary to protect human health as well as electrical equipment [3,4].

In the past, a variety of metallic materials have been used as EMI shielding. Although these traditional shielding materials are capable of effectively shield EMI, they are not easily applied to real structures. Their heavy weight, poor processability, and corrosion problems are the main hindrances [5]. As alternatives, polymer composites and fiber-reinforced composites containing conductive fillers such as carbon particles, carbon fibers, carbon nanotubes (CNTs), and magnetic loss materials have been extensively used for EMI shielding. Recently, several studies have reported on the use of CNTs reinforced thermoplastic polymer composites as effective and lightweight X-band (8.2–12.4 GHz) EMI shielding materials. The polymer materials include poly(methyl methacrylate) [6-9], polystyrene [7,10], polypropylene [11], polyurethane [12], polyvinylidene fluoride [13], poly(trimethylene terephthalate) [14], polyacrylate [15], ethylene vinyl acetate [16], and polycarbonate [17].

Epoxy resins are well established as thermosetting matrices for advanced structural composites, and have a number of promising characteristics for a wide range of applications, including excellent mechanical properties, low cost, and ease of processing. However, to date, few studies have reported on CNT-epoxy and graphene-epoxy composites as EMI shielding material.

Huang et al. [18] reported on the EMI shielding effectiveness (SE) of 18 dB observed for a composite with 15 wt% small single-walled carbon nanotubes (SWCNTs), and 23–28 dB for composites with 15 wt% long SWCNTs in the frequency band of 8–12.4 GHz. Li et al. [19] observed a SE of 49.2 dB at 10 MHz for composites with 15 wt% long SWCNTs and reported that the composites with 10 and 15 wt% loadings exhibited a SE of 20 dB at 1 GHz. Singh et al. [20] prepared epoxy composites with 20 wt% multi-walled carbon nanotube (MWCNT) and reported an EMI SE of -19 dB for 0.35 mm thick film and -60 dB for 1.75 mm thick composites in the X-band. Liang et al. [21] reported an EMI SE of 21 dB for composite with 15 wt% graphene in the X-band.

In our previous study [22], epoxy hybrid nanocomposites containing MWCNT and exfoliated graphite nanoplatelets (xGnP) were prepared, and their mechanical properties were investigated. The synergistic effect of epoxy/MWCNT/xGnP hybrid nanocomposites on mechanical properties was observed, in comparison to epoxy/MWCNT and epoxy/xGnP composites. In the present study, we investigated whether a synergistic effect on EMI shielding can be observed using the epoxy hybrid nanocomposites containing MWCNT and xGnP.

2. Experimental

2.1. Materials

CVD-grown MWCNTs were supplied by Applied Carbon Nano Technology (Pohang, Korea). The diameters of the CNTs were 10–20 nm, and their average length was 10–50 μm. The xGnPs (M-5) used in this research were provided by Hanwha Nanotech (Incheon, Korea). The lateral dimensions and thickness of the xGnP were ~5 μm and 6–8 nm, respectively. The bisphenol-F epoxy resin (YDF-170) and curing agent (SH-101A) were supplied by Kukdo Chemical (Korea) and Sejin E&C (Korea), respectively. To reduce the viscosity of the carbon nanomaterial-epoxy resin mixture, an aliphatic-glycidyl-ether-based reactive diluent (BGE) supplied by Kukdo Chemical was used. The manufacturer-recommended composition of 100:25 ratio between resin and curing agent by weight was used, and the amount of reactive diluents was 10% by weight with respect to the resin.

2.2. Preparation of epoxy composites

In the first set of experiments, 1, 3, 5, 7, and 10 wt% xGnP-epoxy composites were fabricated. Weighed amounts of the xGnP and epoxy were premixed using a paste mixer (PDM-300) manufactured by Dae Wha Tech (Korea) and were subsequently calendered using a three-roll mill (80S, silicon carbide rolls) manufactured by EXAKT (Germany). The rotational speed of roller 3 was 256 rpm. After being passed through the three-roll mill five times, a curing agent was added, and the mixture was stirred and degassed under vacuum for 30 min. The mixture was poured into an aluminum mold, which was placed in a heated press. The nanocomposite mixture was cured at 120°C for 2 h and post cured at 150°C for 2 h, resulting in a 12 mm by 150 mm nanocomposite sheet with a thickness of 3 mm, for mechanical properties testing, and a circular sheet with a diameter of 135 mm and thickness of 1.5 mm for investigating the EMI shielding effect.

In the second set of experiments, 1, 2, 3, 4, and 5 wt% CNT-epoxy composites were fabricated. The samples used for mechanical properties and EMI shielding tests were prepared according to the same procedure as above.

In the third set of experiments, a CNT to xGnP ratio of 50:50 was fixed, and 3, 5, 7, 10, and 13 wt% of the combined filler-epoxy composites were fabricated. The same nanofiller dispersion and nanocomposite sheet fabrication methods were employed as in the first set of experiments.

2.3. Characterization

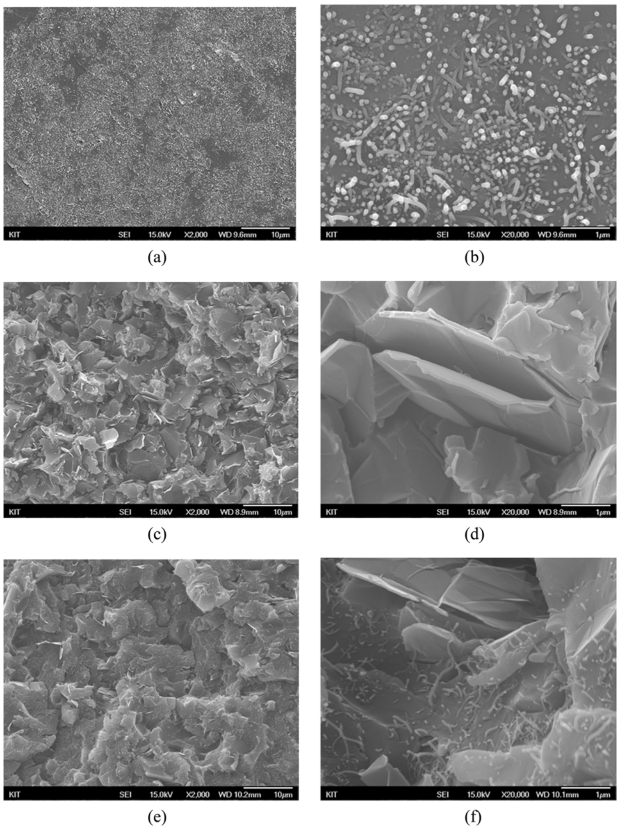
The flexural properties were measured using a universal material testing system (Shimadzu, Japan) equipped with a 50-kN load cell. Flexural test specimens were rectangular-shaped specimens measuring 150 mm (L) and 12 mm (W) by with a thickness (T) of 3 mm. A span of 40 mm and a crosshead speed of 6.8 mm/min were employed. The surface resistivity of high resistivity nanocomposite samples was measured using a two-point probe surface resistance measurement system (ACL 800 Megohmmeter, USA). Low resistivity samples were measured using a four-point probe surface resistance measurement system (CMT-SR1000N) manufactured by Advanced Instrument Technology (Korea). EMI SE was measured by placing the composite films (diameter of 135 mm and thickness of 1.5 mm) on the specimen holder using a vector network analyzer (Agilent Technology, E5071C) in the frequency range of 30 MHz–1 GHz. The microstructure of the fracture surfaces of selected nanocomposites was observed and analyzed using a scanning electron microscope (SEM; JSM-6500F, JEOL, Japan).

3. Results and Discussion

3.1. Microstructures of carbon nanofiller/epoxy composites

The SEM images of epoxy composites containing 5 wt% of CNT, xGnP, and CNT-xGnP, respectively, are shown in Fig. 1. The CNTs are well dispersed in the epoxy matrix, but free CNT regions are also observed due to the agglomeration of CNTs, as shown in Fig. 1a and b. For the composites containing only CNT, the existence of the agglomeration suggests poor compatibility between the CNTs and the matrix epoxy, resulting in reductions in mechanical properties such as flexural strength and modulus with higher loading of CNT. This is discussed in detail in the next sections.

The xGnPs were well embedded in the epoxy matrix, as shown in Fig. 1c and d. For the CNT-xGnP combined filler, it was observed that the CNTs are well dispersed on the surface of the xGnP as well as in the epoxy matrix, as shown in Fig. 1e and f. For the composites containing xGnP and CNT-xGnP, the observed microstructures show better dispersions, resulting in continuous increases in the mechanical properties with higher loading of nanofillers. Also, it was observed that the addition



(a) (b)

(c) (d)

(e) (f)

Fig. 1. Scanning electron microscope images of the fractured surfaces of epoxy composites with 5 wt% CNT (a, b), 5 wt% xGnP (c, d), and 5 wt% CNT-xGnP (e, f). CNT, carbon nanotubes; xGnP, exfoliated graphite nanoplatelets.

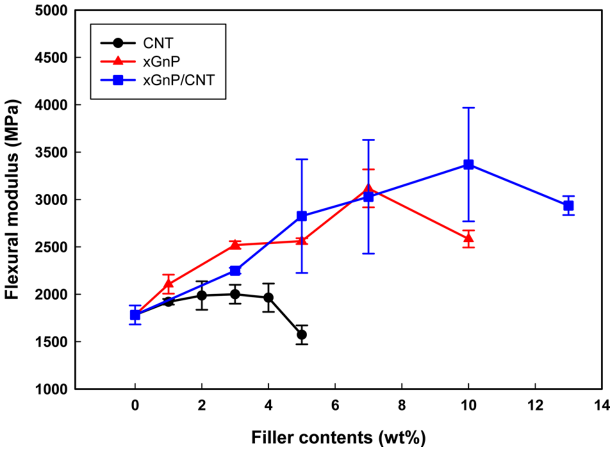


Fig. 2. Flexural moduli of epoxy composites with carbon nanotube (CNT), exfoliated graphite nanoplatelets (xGnP), and CNT-xGnP as a function of filler contents.

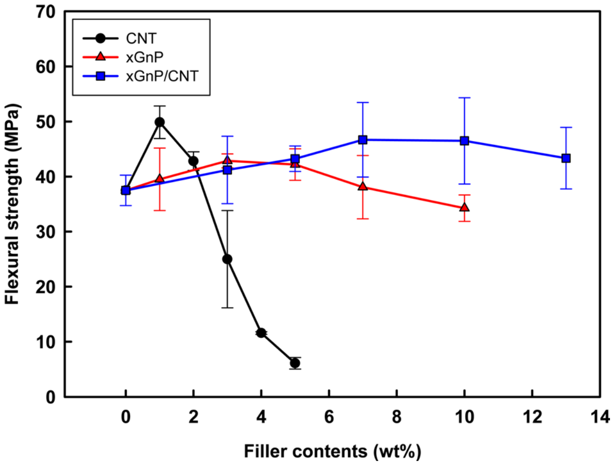


Fig. 3. Flexural strengths of epoxy composites with carbon nanotube (CNT), exfoliated graphite nanoplatelets (xGnP), and CNT-xGnP as a function of filler contents.

of CNTs influences the quality of the dispersion of the xGnP. Reductions in the number and the size of agglomerates can enhance the contact between the nanofiller and the matrix epoxy, resulting in an improvement in the mechanical properties of the composites.

3.2. Flexural properties

Flexural tests were performed with rectangular-shaped specimens under a three-point bend configuration. The flexural modulus and strength of the composites are shown in Figs. 2 and 3, respectively. The flexural modulus of the CNT based epoxy composites continuously increased from 1.78 GPa for the epoxy, to 2.0 GPa for the CNT based epoxy composite containing 3 wt% CNT. At 4 wt% loading, it slightly decreased to 1.96 GPa, and dropped to 1.57 GPa at 5 wt% loading, which is lower than that of epoxy.

It is thought that the low flexural modulus at 5 wt% loading stems from the limited mixing efficiency of the three-roll mill, as discussed in the previous section, which is related to the microstructure of the composites. It was difficult to mix more than 5 wt% CNT with the three-roll mill. The flexural modulus of the xGnP based epoxy composites continuously increased with xGnP content up to 7 wt% loading, which exhibited 3.12 GPa, and decreased to 2.58 GPa at 10 wt% loading. Higher loading of xGnP may be difficult to mix with the three-roll mill, as was the case with the 5 wt% CNT.

In comparison with the 3 wt% loading of CNT and xGnP, the flexural modulus increased from 2.0 GPa for the CNT based epoxy composite, to 2.52 GPa for the xGnP based epoxy composite. This indicates that the xGnP is more effective than CNT in affecting the flexural modulus of the epoxy composite, likely because of the plate-like shape of the xGnP.

For the CNT-xGnP based epoxy composite, the flexural modulus continuously increased to 3.32 GPa with combined filler content up to 10 wt%, and decreased at 13 wt% loading, which shows the limit of mixing with the three-roll mill. The combined filler of 10 wt% consisted of 5 wt% CNT and xGnP, respectively.

The results of the flexural strength for pure epoxy and carbon nanofiller filled epoxy nanocomposites are shown in Fig. 3. The flexural strength of the CNT based epoxy composite was up to about 50 MPa at the low loading of 1 wt% CNT, and shows about a 40% increase compared to that of the pristine epoxy.

However, the flexural strength of the CNT based composite shows a rapid decrease with further increases in concentration (up to 5 wt%). Agglomeration of the CNT at higher concentration can reduce the reinforcing effect of the nanofiller, leading to a reduction in the flexural strength of the composites.

The uniform dispersion of the xGnP following the incorporation of CNT results in good load transfer from the epoxy matrix to the xGnP, resulting in a continuous improvement in flexural strength at high concentration of nanofiller for the xGnP-CNT based epoxy composite. The dispersion quality of the xGnPs in the matrix epoxy has been enhanced by the incorporation of CNTs, as shown in the Fig, 1, resulting in better interaction between the xGnP and the matrix. As a result, the flexural properties of the composites could be enhanced by the CNT-xGnP.

3.3. Electrical, thermal, and EMI shielding properties

Fig. 4 shows the percolation curves for the epoxy composites with CNT, xGnP, CNT-xGnP as a function of the filler content. Compared to the composites with CNT and CNT-xGnP, the epoxy composite with xGnP shows a higher percolation threshold and saturated surface resistivity, which indicate poor network formation and the low intrinsic electrical conductivity of the xGnP. The rigid two-dimensional xGnPs have some difficulty creating a network structure, in contrast to flexible one-dimensional CNTs. At higher concentrations of xGnP, the substantial improvement in electrical conductivity can be explained as resulting from the additional formation of a network structure, while the CNT and CNT-xGnP composites show saturation at higher concentration.

The percolation threshold of the xGnP composite for electrical conductivity is around 1.9 wt% in epoxy [23], which is consistent with the results of this study. The observed percolation threshold was found to be 0.5 wt% for the CNT, 1.0 wt% for the CNT-xGnP and 2.0 wt% for the xGnP composites, respectively. It can be observed that the percolation thresholds of the CNT, xGnP, and CNT-xGnP composites in this study are in good agreement with the model predictions [23].

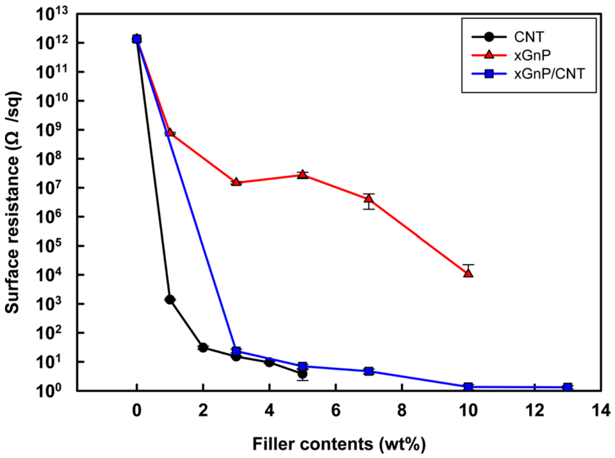


Fig. 4. Surface resistivity of epoxy composites with carbon nanotube (CNT), exfoliated graphite nanoplatelets (xGnP), and CNT-xGnP as a function of filler contents.

The thermal conductivities of the epoxy composites with CNT, xGnP, and CNT-xGnP as a function of filler contents are depicted in Fig. 5. As shown in this figure, the CNT composite attains minimal thermal conductivity at low concentration compared to the other two composites. For identical filler weight %, the xGnPs exhibit the best thermal conductivity because of their higher surface area, compared to the CNTs, and CNT-xGnPs. But at 5 wt% of filler, the thermal conductivity of the CNT has the highest value, compared to the others. This result is related to the formation of CNT agglomeration at higher loading, which enhances the local density of the conducting paths.

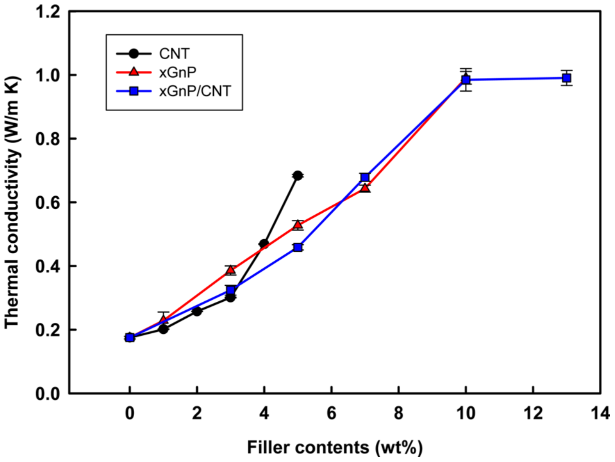


Fig. 5. Thermal conductivity of epoxy composites with carbon nanotube (CNT), exfoliated graphite nanoplatelets (xGnP), and CNT-xGnP as a function of filler contents.

Fig. 6 depicts the EMI SE of the epoxy composites with CNT, xGnP, CNT-xGnP as a function of the filler content at 100 MHz. It should be noted that the variation in EMI SE with frequency was very small. As mentioned before, the enhancement of the electrical conductivity of the xGnP composite with increasing

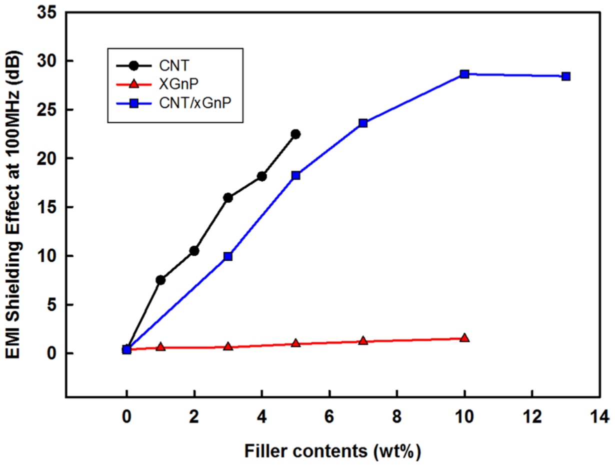


Fig. 6. Electromagnetic interference (EMI) shielding effectiveness of epoxy composites with carbon nanotube (CNT), exfoliated graphite nanoplatelets (xGnP), and CNT-xGnP at 100 MHz as a function of filler contents.

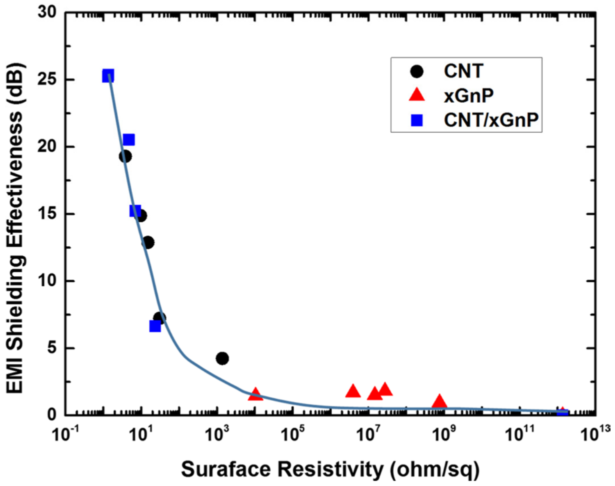


Fig. 7. Electromagnetic interference (EMI) shielding effectiveness of epoxy composites with carbon nanotube (CNT), exfoliated graphite nanoplatelets (xGnP), and CNT-xGnP as a function of the surface resistivity of the composite.

xGnP concentration is relatively low, so their EMI SE is negligible for all ranges of concentration.

The increase in EMI SE with increasing concentration of CNT is due to the formation of more cages in the conductive network, and the increased possibility of free electrons in the composite, which can interact with the electromagnetic waves. The EMI SE of the CNT composite increased more than 20 dB with increasing CNT concentration. At same carbon nanofiller concentration, the EMI SE of the CNT based nanocomposite was higher than that of the xGnP and CNT-GnP based nanocomposites. Above 10 wt% of CNT-xGnP concentration, the EMI SE of the CNT-xGnP composite was saturated at 27 dB.

Fig. 7 shows the EMI SE for the different carbon nanofillers, versus their surface resistivity, to obtain better insight into the correlation between EMI SE and electrical conductivity. The EMI SE of the xGnP composite was almost zero, since the surface resistivity of the composite was higher than 10^4 ohm/sq. By decreasing the surface resistivity, the electrical conductivity made a greater contribution to the SE, below a surface resistivity of 10^3 ohm/sq, which can be the threshold of the EMI SE. It should be noted that the CNT and CNT-xGnP composites samples had the same EMI SE at the same surface resistivity, because samples with same surface conductivity have the same amount of charge carriers.

4. Conclusions

The flexural, electrical, thermal, and EMI SE properties of CNT, xGnP, and CNT-xGnP based epoxy composites were studied to reveal the effect of carbon nanofiller type on the aforementioned properties, to characterize the mechanical enhancement and EMI shielding mechanisms, and to determine the relationship between electrical conductivity and EMI SE. The CNT-xGnP hybrid based epoxy composite showed outstanding properties compared to the CNT and xGnP based composites. The CNT-xGnP hybrid based epoxy nanocomposite exhibited the highest flexural modulus at high concentration, and relatively good EMI SE performance, owing to the plate-like shape of the xGnP, and the enhancement of network structure, due to the presence of CNTs between the xGnPs. By decreasing surface resistivity, electrical conductivity made a greater contribution to EMI SE when the surface resistivity was less than 10^3 ohm/sq, which can be considered the threshold of the EMI SE.

Conflict of Interest

No potential conflict of interest relevant to this article was reported.

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