Design Optimization and Fabrication of Carbon Nanotube and Graphene Nanoplatelet Based Multiscale Composites for EMI Shielding

J. Gnidakouong[1*], H. W. Park[1], Y.B. Park[1], H.S. Jeong[2]

[1] *School of Mechanical and Advanced Materials Engineering, Ulsan National Institute of Science and Technology. UNIST-gil 50, Eonyang-eup, Ulju-gun, Ulsan 689-798, Republic of Korea*
[2] *Young Kwang P.M.S., 206-8 Dalcheon-dong, Buk-gu, Ulsan 683-470, Republic of Korea*
**ngouanom@unist.ac.kr*

Keywords: Multiscale Hybrid Composite, Carbon Nanotube, Graphene Nanosheet, EMI Shielding

Abstract

We investigated the tailored electromagnetic interference (EMI) shielding of polyester-matrix composites consisting of carbon nanotube- and exfoliated graphite nanoplatelet-coated glass fiber reinforcement. The effects of various combinations of material parameters, including carbon nanotube length, exfoliated graphite nanoplatelet size, and amount of carbon nanomaterials coated per unit area, on the EMI shielding effectiveness were studied. Due to their capability to form conductive networks more efficiently, high-aspect-ratio nanomaterials exhibited better EMI shielding, ranging from 35.3 dB to 56.8 dB. For all the composites fabricated and tested, the EMI shielding effectiveness decreased with increasing frequency.

1 Introduction

Over the last thirty years, the volume and number of applications of composite materials have grown steadily, penetrating and conquering new markets relentlessly. Modern composite materials constitute a significant proportion of the engineered materials market ranging from everyday products to sophisticated niche applications. The emergence of composites materials is not, however, unexpected because even the nature itself is made of composites materials, like human body. For instance, in his effort to merge and clarify many composites theory models of human muscle, Peter A. Huijing [1] considered it as a composite consisting of an extracellular matrix with triple reinforcement by fibrous material. The reinforcement is obtained by an active component (myofibers) being able to generate force and bear loads actively. The load bearing capacity is shared, but only passively, by the basal lamina and the passive fascial apparatus of the organ.

Fiber reinforced polymers (FRP) are most commonly made using glass, carbon, or aramid fibers in general. FRPs are about 1/4 the weight of steel. In order to succeed in today's markets, manufacturers must produce end-products and systems that are lighter, stronger, more durable, multifunctional and more reliable but cheap at the same time. In this context, glass fiber is one of the most attractive plastic reinforcement materials mostly because of his unrivalled cost-performance ratio. In order to take greater advantages of the cost-effectiveness of glass-fiber-reinforced plastics (GFRPs), many researchers [2-6] have tried to broaden the application fields of these composites by engineering conductive GFRP with the aid of conductive nanomaterials, such as carbon nanotube (CNT), exfoliated graphite nanoplatelet (xGnP), graphene, etc., resulting in *multiscale composites*. In this regard GFRP can be considered as a multifunctional materials used variously and simultaneously for structural, electromagnetic interference (EMI) shielding, self-sensing applications [7], etc. Evidently, the majority of research on multiscale hybrid composites, including GFRPs, has been focused on reducing the bulk resistivity of the matrix by "pre-dispersing" the conductive nanoscale materials in the resin and subsequently incorporating them with the microscale fiber reinforcement for composite fabrication.

Lee et al. [2] impregnated a glass fabric with pre-disperded MWNTs in epoxy to fabricate a radar absorbing structure with load-bearing ability in the X-band, and the evaluation of the composites reflection loss allowed to confirm the absorbing properties. Park et al. [3] designed and fabricated an absorbed sandwich structure where glass fabric/epoxy composites containing conductive carbon black and carbon fabric/epoxy composites were used as the face sheets, Multiwalled carbon nanotubes (MWCNTs) were added to polyurethane foam to fabricate the core, and high reflection losses were predicted, such as 10-dB absorbing bandwidth.

We investigated the EMI shielding capability of multiscale hybrid composites consisting of unsaturated polyester (UPE), glass fiber textile, and carbon nanomaterials. Two types of nanomaterials were used, including (MWCNTs) – two types with low and high aspect ratios – and xGnPs with small and large lateral dimensions. Thin coatings of atomized nanomaterials were deposited on 150 X 150 mm^2 woven glass fiber fabrics using compressed-air-assisted spraying, followed by stacking an optimal predesigned combination, and infusion of UPE via vacuum-assisted resin transfer molding (VARTM). The spray deposition technique was chosen because it is a simple and cost-effective method for coating a fabric surface with carbon nanomaterials with reasonable uniformity, which can be scaled up for potential large-volume, wide-area applications.

2 Experimental

2.1 Materials

MWCNTs with purity of > 95% and average diameter range of 25-30 nm were purchased from Hanwha Nanotech (Incheon, Korea) The lengths of MWNTs (100 μm and 250 μm) are indicated in their product names, CM-100 and CM-250. Exfoliated graphite nanoplatelets with an average size of 5 μm (xGnP M-5) and 15 μm (xGnP M-15) were purchased from XG Sciences (East Lansing, MI). DBLT 850-E glass fiber (Cymax) with ply thickness of ~0.6 mm was supplied by Jet Korea (Changwon, Korea). Unsaturated polyester resin, curing agent, and catalyst were supplied by Cray Valley Korea, Arkema, and Jet Korea, respectively.

2.2 Composites manufacturing

MWCNTs and MWCNTs/xGnP in equal proportions were horn-sonicated in methanol at a concentration of 1 g/L for 30 min to obtain a homogeneous MWCNT suspension. During the sonication process, the beaker containing the mixture was submerged in an ice bath to prevent it from heating up. A 150 mm X 150 mm fiber textile was coated by spraying the MWCNT suspension using an air brush (Creamy(K) 3A, Kinki, Japan) with a nozzle diameter of 0.5 mm at a regulated pressure of ~2 kgf/cm^2. A single coat consisted of 0.1 g of MWCNT sprayed over the 150 mm X 150 mm area. The solvent was removed from the MWCNT-spray-coated fiber textile by drying it in a vacuum oven
overnight at 60°C.

Multiscale hybrid composites were fabricated using VARTM, in which vacuum was used to pull the neat resin into the stacked woven glass fiber preforms, and the resin was subsequently allowed to cure at room temperature. Eight composites with various configurations as shown in Figure 1 were fabricated and their EMI shielding was measured using the EMI shielding effectiveness (SE) test system manufactured by Rhode and Schwartz (Munich, Germany). The measurements were made using the coaxial cable (transmission line) method with type-N connectors in accordance with ASTM-D4935, and the measuring frequency range was up to 1.5 GHz. The attenuations of electromagnetic waves were recorded as functions of frequency.

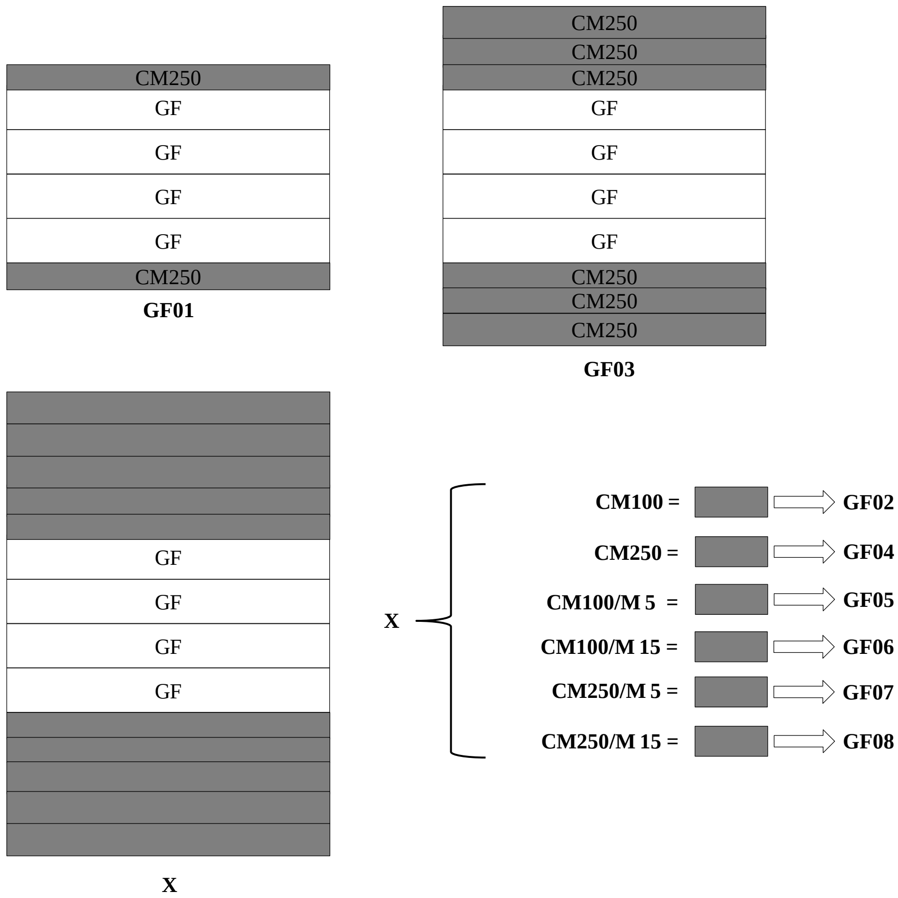

Figure 1. Composite configurations. Short (CM100) and long (CM250)CNTs are used. The effect of mixing them with small (M-5) and large (M-15) xGnPs were also investigated.

3 Results and discussionss

3.1 EMI shielding of composites

Clearly, in the above configurations, the integrity of the glass fibers composites was preserved, while the sprayed nanomaterials only affected the conductive properties of the composites. It was shown that coating the outermost, instead of intermediate with glass fiber plies with MWCNTs was found to maximize the SE of the composite. GF01 is a typical example of such a structure. It yielded after measurement values of SE ranging from 41.1dB to 14.7dB corresponding, respectively to the frequency range of 30 MHz to 1.5 GHz.

The results are shown in Figure 2 along with the case where three and five layers were coated, Respecti vely, on each face. It can be seen that GF02 to 4 exhibit the same behavior as GF01,

their EMI shielding decrease when the frequency increases which is similar to a typical reflection contribution leading to the suggestion that the reflection is the dominant shielding mechanism. This makes sense because the absorption and multiple reflections contributions are not expected to significantly and positively impact the overall EMI SE owing to the very small thickness of deposited conductive layers.
On the other hand, for the fabrication of each composite from GF01 to 4 as shown on figure1, nanomaterials are not mixed up, only one type is used alone (CM100 or CM250) depending on the case, consequently, the wave reflections at the surface of each composite account for the overall reflection contribution. Moreover, the negative contribution of the multiple reflections is minimized at the lowest frequency and maximized at the highest frequency. The reflection also tends to decrease with higher frequency due to the loss tangent. As a result, recognizing that the absorption is constant, we end up with a SE decreasing with increasing frequency. The highest EMI SE was obtained with the largest amount of nanomaterials deposited, that is, 5 layers on each side, and it ranged from 56.8 dB at 30MHz to 35.3 dB at 1.5GHz, confirming that conductive nanomaterial-coated glass fibers can be effectively used as an EMI shielding materials.

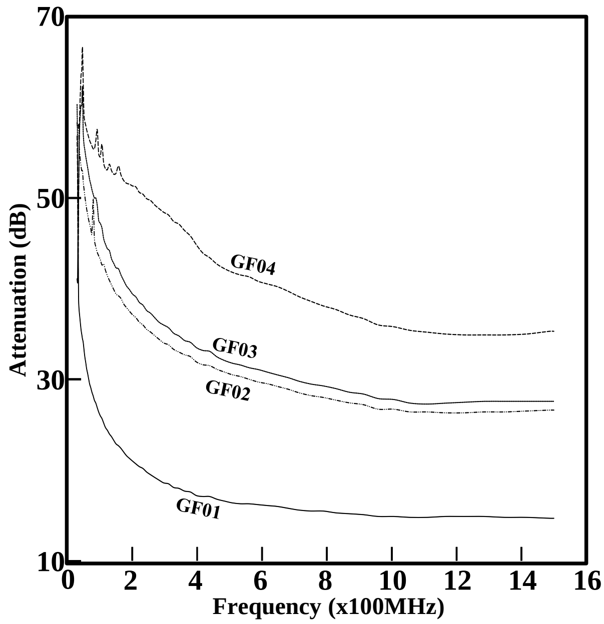

Figure2. EMI shielding results of GF01-GF04.

3.2 Effects of CNT length

In Figure 1, GF02 is obtained with short MWCNTs (CM100), five layers on each side. It turned out that the EMI SE of the composite having five layers of CM100 is comparable with that having three layers of long MWCNTs (CM250). This suggests that long MWCNTs yield better EMI SE, as they are more efficient in terms of conductive network formation. A normal consequence of this is that the composites made solely with CM250 will show a higher conductivity as compared to those made solely with CM100. The more efficiently conductive networks are formed, the higher EMI shielding. Of all the composites tested, those containing CM250 always showed highest EMI SE even when they were mixed with xGnP, as shown in Figure 3, where GF05 and GF06, comprised of CM100, gave smaller EMI SE.

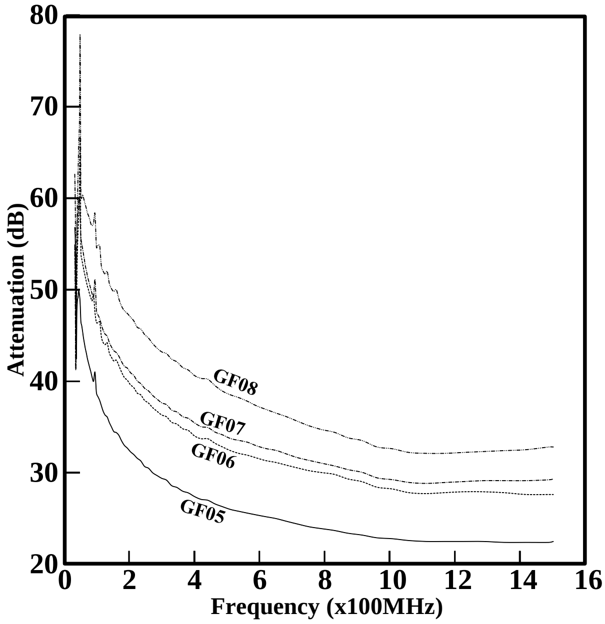

Figure3. EMI shielding of blended CNT/xGnP coated glass fibers composites.

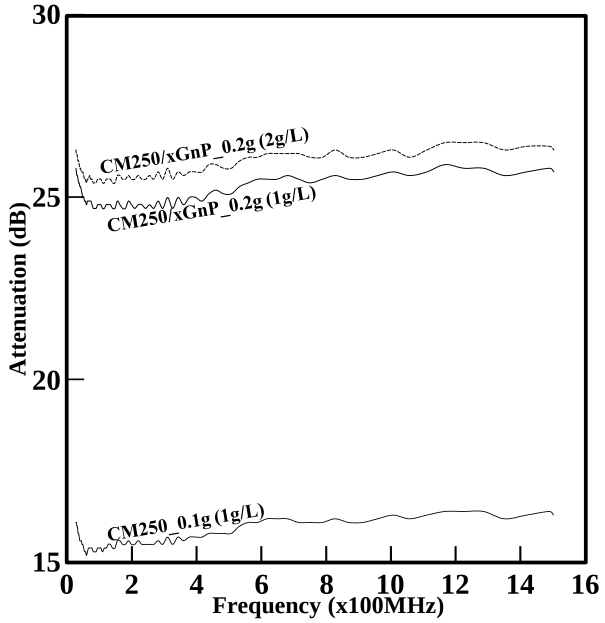

Figure4. EMI shielding of blended CNT/xGnP and CNT coated PET.

3.3 Effects of CNT-xGnP interactions

In Figure 3, it is observed that CNT length is a dominant factor that governs the EMI SE – whether CNTs are used alone or combined with xGnPs – and this is related to the surface area of the carbon nanomaterial. The greater the surface area, the greater the EMI shielding. For example GF06 and GF08 gave higher EMI SE as compared to GF05 and GF07, respectively. Again, it is easier to form a conductivities network using nanoparticles with a higher surface area so, high-aspect-ratio nanomaterials are favorable in term of EMI shielding. In addition, given the intricate surface of glass fiber textile, the positive interaction of xGnP surface with the undulated fibers is likely to be hindered. However, when mixed with high-aspect-ratio CNTs, CNT are expected to allow flat and stable placement of xGnPs on fiber surfaces by bridging between them, acting as a mesh or a net.

3.4 Effects of nanomaterial concentration

In order to speed up the coating process, the effects of CNT-xGnP concentration in methanol solution were investigated. The sonicated CNT-xGnP solutions at two different concentrations – 1 g/L and 2 g/L – were sprayed on PET substrates, results from which are shown in Figure 4. The average EMI SEs for 1 and 2 g/L were 25.8 and 26.3 dB, respectively, which indicates no significant difference. (One should not be misled by the scales in Figure 4.) It is worth mentioning that the PET substrate coated with 0.2 g of CNT-xGnP showed higher EMI SE than that coated with 0.1g of CM250, which can be attributed to the thickness effect and nanomaterial structure.

4 Conclusions

MWCNT-coated glass fiber composites were fabricated, and their EMI shielding properties were characterized. It was found that EMI shielding effectiveness decreases with increasing frequency. At the highest measured frequency, we obtained the attenuation value of 35.3 dB, while 63.8 dB was observed for the lowest frequency. Experiments revealed the surface area and geometry (e.g. fiber vs. platelet) both affect the EMI SE of the composite. Blending CNT and xGnP can lead to a much more cost-effectiveness EMI shielding coating; however, the way the uneven surface of glass fiber textile interacts with carbon nanomaterials with varying geometries and configurations warrants further studies.

References

[1] Huijing P.A. Muscle as a collagen fiber reinforced composite: a review of force transmission in muscle and whole limb. Journal of Biomechanics, 32, pp. 329-345 (1999).

[2] Lee S., Kang J., Kim C. Fabrication and design of multi-layered radar absorbing structures of MWCNT-filled glass/epoxy plain-weave composites. Compos Struct, 76, pp.397-405 (2006).

[3] Park K., Sang EL., Kim CG., Han JH. Fabrication and electromagnetic characteristics of electromagnetic wave absorbing sandwich structures. Compos Sci Technol, 66, pp. 576–84 (2006).

[4] Park K., Lee S., Kim C., Han J. Application of MWCNT-added glass fabric/epoxy composites to electromagnetic wave shielding enclosures. Compos Struct, 81, pp. 401-6 (2007).

[5] Jung W., Kim B., Won M., Ahn S. Fabrication of radar absorbing structure (RAS) using GFR-nano composite and spring-back compensation of hybrid composite RAS shells. Composite Structures,75, pp. 571–576 (2006).

[6] Kupke M.,Wentzel H.,Schulte. Electrically conductive glass fibre reinforced epoxy resin. Mat Res Innovat, 2, pp. 164–169 (1998).

[7] Böger. L.,Wichmann M., Meyer L., Schulte K. Load and health monitoring in glass fibre reinforced composites with an electrically conductive nanocomposite epoxy matrix. Composites Science and Technology, 68, pp. 1886–1894 (2008).