

# EMI shielding effectiveness and mechanical properties of MWCNTs-reinforced biodegradable epoxy matrix composites

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## Abstract

Biodegradable epoxy (B-epoxy) was prepared from diglycidyl ether of bisphenol A and epoxidized linseed oil. The mechanical properties of B-epoxy composites reinforced with multi-walled carbon nanotubes (MWCNTs/B-epoxy) were examined by employing dynamic mechanical analysis, critical stress intensity factor ( $K_{Ic}$ ) tests, and impact strength tests. The electromagnetic interference shielding effectiveness (EMI-SE) of the composites was evaluated using reflection and absorption methods. Mechanical properties of MWCNTs/B-epoxy were enhanced with an increase in the MWCNT content, whereas they deteriorated when the MWCNT content was >5 parts per hundred resin (phr). This can likely be attributed to the entanglement of MWCNTs with each other in the B-epoxy due to the presence of an excess amount of MWCNTs. The highest EMI-SE obtained was ~16 dB for the MWCNTs/B-epoxy composites with a MWCNT content of 13 phr at 1.4 GHz. The composites (13 phr) exhibited the minimum EMI-SE (90%) when used as shielding materials at 1.4 GHz. The EMI-SE of the MWCNTs/B-epoxy also increased with an increase in the MWCNT content, which is a key factor affecting the EMI-SE.

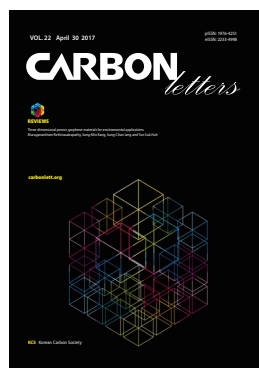
**Key words:** Multi-walled carbon nanotubes, Biodegradable epoxy, EMI shielding effectiveness, mechanical properties

## 1. Introduction

With advances in the development of electronic devices and components, electromagnetic interference (EMI) has emerged as a serious problem [1,2]. EMI not only causes operational malfunction of electronic devices, but also has a negative impact on human health. Therefore, EMI shielding materials have recently been developed by many researchers [3-6]. Metal materials have commonly been used for reducing EMI, even though they exhibit several disadvantages such as heaviness, rapid corrosion, and poor processability [7,8]. Because of these disadvantages, polymer-based composites consisting of carbon fillers embedded in a polymer matrix have recently received much attention as EMI shielding materials. Polymer-based composites are lightweight materials exhibiting corrosion resistance and good processability [9-13]. The EMI shielding effectiveness (EMI-SE) of carbon/polymer composites depends on the intrinsic conductivity and the aspect ratio of the carbon fillers [14,15]. Among various carbon fillers, carbon nanotubes, owing to their high aspect ratio (>1000) and nanoscopic dimensions, impart electrical conductivity and mechanical properties to the polymer matrix [16,17].

Carbon/polymer composites have been used in different fields as well as for EMI shielding. However, the polymer industry faces serious problems owing to environmental pollution and Earth's limited petroleum reserves. Accordingly, the development of biodegradable polymers using green environment materials is important [18-22]. Vegetable oils are valuable resources in the manufacturing of biodegradable polymers. Epoxidized vegetable oil, owing to its low cost and environmental advantages, has been synthesized for use as a new biodegradable polymer by many researchers [23-25].

In this study, we prepare multi-walled carbon nanotube (MWCNT)-reinforced vegeta-



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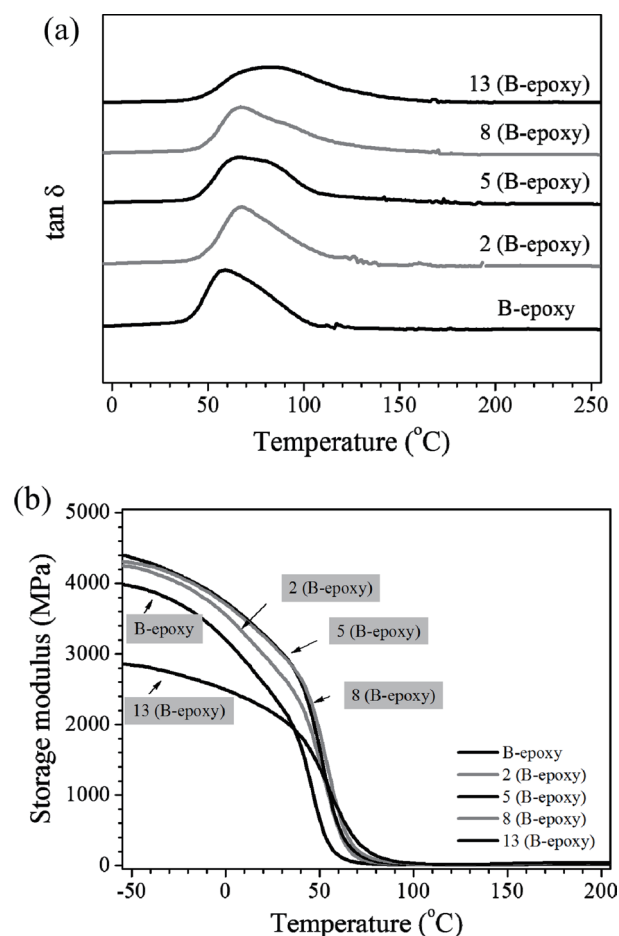
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ASTM D4935-89, the EMI-SE of the composites was measured with an EMI shielding tester (Agilent, USA) in a frequency range of 0.15–1.5 GHz.

### 3. Results and Discussion

Temperature-dependent mechanical properties were examined using DMA with a ramp rate of 5°C/min and a frequency of 1 Hz. Typical DMA curves are shown in Fig. 2. Fig. 2a shows the  $\tan \delta$  values for the MWCNTs/B-epoxy composite as a function of the MWCNT content. The temperature, determined from the peak position of  $\tan \delta$ , corresponds to the glass transition temperature ( $T_g$ ) of the composites. The results indicate that the  $T_g$  values of the composites increased slightly with the MWCNT content. MWCNTs dispersed in the matrix are assumed to lower the fluidity of the composite materials due to the interaction between the MWCNTs and the matrix [26]. Fig. 2b shows the storage modulus of the MWCNTs/B-epoxy composites as a function of the MWCNT content. The addition of MWCNTs resulted in an increase in the storage modulus in both the glassy and rubbery regions, whereas the storage modulus decreased at



**Fig. 2.** Typical dynamic mechanical analyzer curves for MWCNTs/B-epoxy composites as a function of MWCNT content: (a) storage modulus and (b)  $\tan \delta$ . MWCNT, multi-walled carbon nanotube; B-epoxy, biodegradable epoxy.

>13 phr [27]. From the  $\tan \delta$  results, MWCNTs, owing to their reinforcement effects, are assumed to interfere with the movement of the B-epoxy. On the other hand, MWCNTs might be entangled with each other in the B-epoxy due to the presence of an excessive amount of MWCNTs at >13 phr. The average bulk structure of the carbon materials can be readily examined using X-ray diffraction.

As a function of MWCNT content, the mechanical properties of the MWCNTs/B-epoxy composites were determined by evaluating the  $K_{IC}$ . The value of  $K_{IC}$  was calculated using the following equation [28,29].

$$K_{IC} = \frac{P \cdot L}{b \cdot d^{3/2}} \cdot Y \quad (1)$$

and

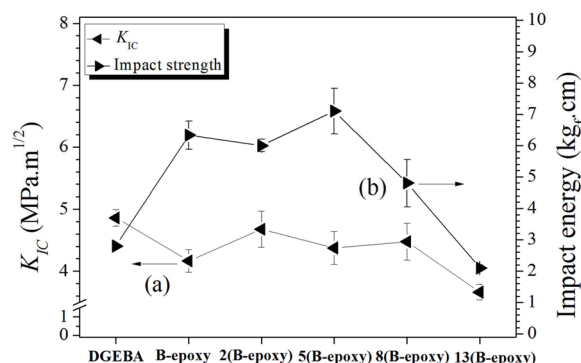
$$Y = \frac{3(a/d)^{1/2} [1.99 - (a/d)(1 - a/d)(2.15 - 3.93a/d + 2.7a^2/d^2)]}{2(1 + 2a/d)(1 - a/d)^{3/2}} \quad (2)$$

, where  $P$  is the rupture force,  $L$  is the span between the supports, and  $Y$  is the geometrical factor, where  $a$ ,  $b$ , and  $d$  are the specimen pre-crack length, width, and thickness, respectively.

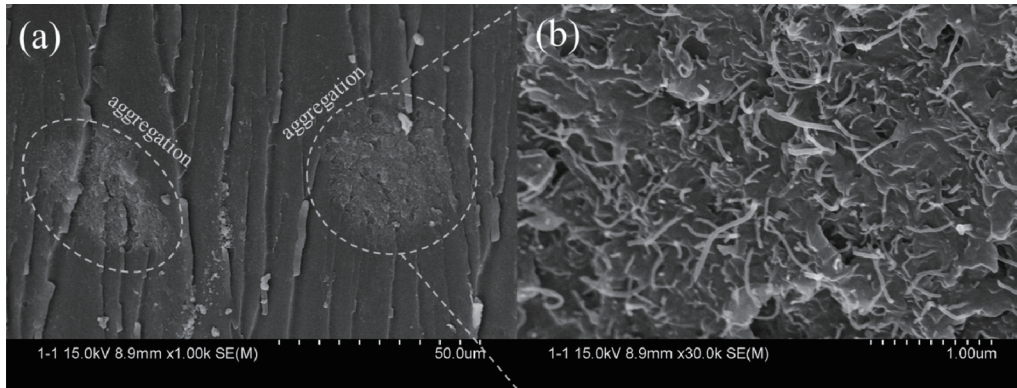
The influence of the MWCNT content on the mechanical properties of the MWCNTs/B-epoxy composites is shown in Fig. 3. Fig. 3a shows the  $K_{IC}$  values of the composites as a function of the MWCNT content. The  $K_{IC}$  values gradually increased with the MWCNT content, as shown by the DMA results. By interfering with the movement of the polymer matrix, MWCNTs are assumed to improve composite resistance to cracks. However, the  $K_{IC}$  values decreased above 8 (B-epoxy). MWCNTs got entangled with each other in the matrix due to the presence of an excess amount of MWCNTs [30].

Fig. 3b shows the impact strength of the MWCNTs/B-epoxy composites as a function of the MWCNT content. The change in the impact strength is similar to that in  $K_{IC}$ . The 5 (B-epoxy) exhibited the maximum impact strength; however, the impact strength decreased owing to the formation of MWCNT aggregates at >5 phr.

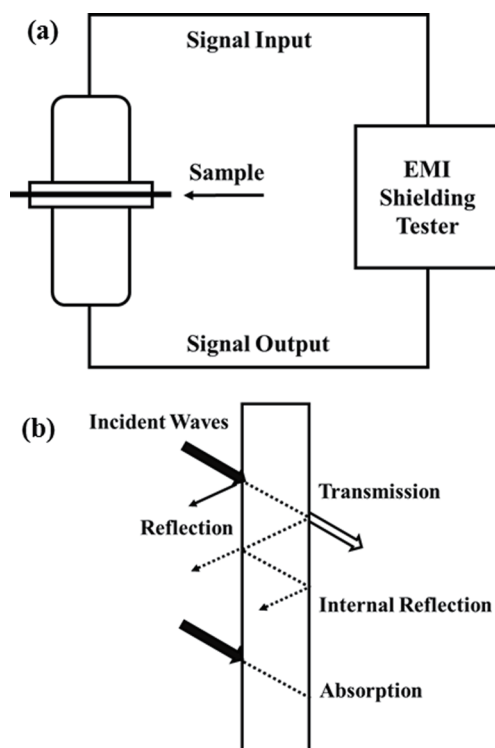
Fig. 4 provides SEM pictures of the fracture surface of the 8 (B-epoxy) composites. The white regions in Fig. 4a represent the aggregated MWCNTs. In order to verify the existence of aggregated MWCNTs, the region indicated with a circle is magnified



**Fig. 3.** Mechanical properties of MWCNTs/B-epoxy composites as a function of MWCNT content: (a) critical stress intensity factor ( $K_{IC}$ ) and (b) impact strength. MWCNT, multi-walled carbon nanotube; B-epoxy, biodegradable epoxy; DGEBA, diglycidyl ether of bisphenol A.



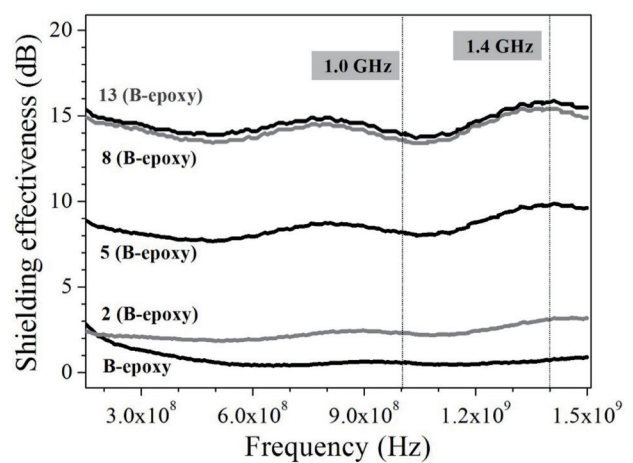
**Fig. 4.** Scanning electron microscope pictures of the fracture surface in 8 (B-epoxy) composites. B-epoxy, biodegradable epoxy.



**Fig. 5.** (a) Apparatus of the electromagnetic interference (EMI) shielding tester and (b) schematic representation of the EMI shielding mechanism.

and shown in Fig. 4b. It can be confirmed that this region is aggregated MWCNTs. Because they act as defects in the MWCNTs/B-epoxy composites, the aggregated MWCNTs reduce the reinforcing effects of the MWCNTs. This is why the presence of an excess amount of MWCNTs lowers the mechanical properties.

Schematic diagrams of the EMI shielding tester and the EMI shielding mechanism are shown in Fig. 5a and b, respectively. The EMI-SE of the materials is defined as the attenuation of the propagating electromagnetic waves produced by the shielding materials. Thus, the total EMI-SE ( $SE_{total}$ ) can be represented as the sum of contributions from absorption loss ( $SE_A$ ), reflection loss ( $SE_R$ ), and multiple reflections ( $SE_M$ ), i.e.,



**Fig. 6.** Electromagnetic interference shielding effectiveness of MWCNTs/B-epoxy composites as a function of MWCNT content. MWCNT, multi-walled carbon nanotube; B-epoxy, biodegradable epoxy.

$SE_{total} = SE_A + SE_R + SE_M$ . The EMI-SE of a material can also be defined as the ratio of the transmitted power to the incident power, which can be represented by the following equation [31,32].

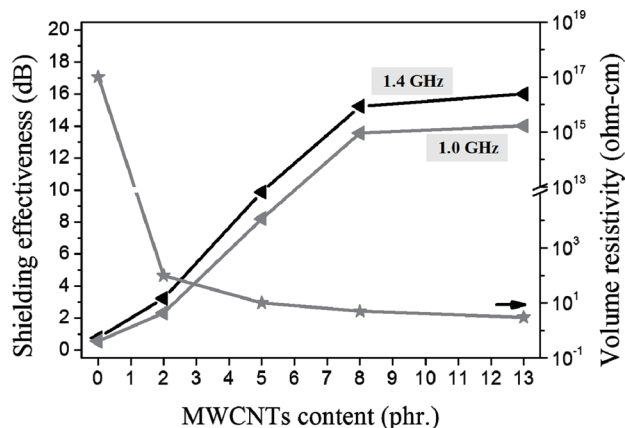
$$SE(dB) = 10 \log \frac{P1}{P2} \quad (3)$$

where  $P1$  is the incident power and  $P2$  is the transmitted power. Eq. 3 was used to experimentally calculate the contribution of the absorption and the reflection loss.

The EMI-SE of the composites was calculated using Eq. 3. Fig. 6 shows the EMI-SE values of the MWCNTs/B-epoxy composites as a function of the MWCNT content in the frequency range of 0.5–1.5 GHz. The high performance obtained for the composites in terms of EMI-SE demonstrated in our work can be mainly attributed to the high conductivity and to the high number density of MWCNTs, which resulted in the formation of good conductive networks in the insulating B-epoxy matrix.

Most EMI shielding materials are electrically conductive. Accordingly, the volume resistivity of the MWCNTs/B-epoxy composites was measured to confirm their electrical conductivity. Fig. 7 shows the effect of the MWCNT content on the volume resistivity of the composites. The volume resistivity gradually decreased with





**Fig. 7.** Electromagnetic interference shielding effectiveness (1.0 & 1.4 GHz) and volume resistivity of MWCNTs/B-epoxy composites as a function of MWCNT content. MWCNT, multi-walled carbon nanotube; B-epoxy, biodegradable epoxy.

an increase in the MWCNT content. This stepwise change in the volume resistivity can be attributed to the formation of an interconnected network structure of MWCNTs. A considerable reduction in the volume resistivity was observed at 2 phr; this value could be regarded as the electrical percolation threshold [33]. A high percentage of electrons were permitted to flow through the specimen between 2 and 5 phr due to the formation of an interconnecting conductive pathway. When the content of MWCNTs was varied between 8 and 13 phr, the volume resistivity marginally decreased with an increase in the MWCNT content.

In particular, 2 (B-epoxy) exhibited a large change in EMI-SE; this is because the MWCNT content was associated with the electrical percolation threshold. It can be thought that, once percolation is achieved, EMI SE values increase dramatically. This simply means that EMI SE values are also enhanced because interconnecting conductive pathways are created at beyond-percolation concentrations of MWCNTs. In addition, similar results have been reported in other studies [34-36].

Among the MWCNTs/B-epoxy composites, the highest EMI-SE of ~16 dB was obtained for 13 (B-epoxy) at 1.4 GHz. The 13 (B-epoxy) exhibited the minimum EMI-SE (90%) as shielding materials at 1.4 GHz. On the other hand, the EMI-SE of B-epoxy was ~1 dB at 1.4 GHz. B-epoxy exhibited no EMI-SE (0%). Hence, the MWCNTs/B-epoxy composites can be used as EMI shielding materials, especially at 1.4 GHz. The EMI-SE of the MWCNTs/B-epoxy composites was enhanced with an increase in the MWCNT content. This experimental trend is similar to the trend observed for the electric conductivity. The increase in the EMI-SE of 8 (B-epoxy) was not significant compared with that of 13 (B-epoxy). This indicates that the optimal EMI-SE can be achieved at 13 phr, suggesting that a further increase in MWCNT content is not necessary.

#### 4. Conclusions

In this study, the effects of the concentration of MWCNTs (ranging from 2 to 13 phr) on the EMI-SE and mechanical properties of MWCNTs/B-epoxy composites were investigated.

Our experimental results suggest that the mechanical properties gradually improved with an increase in the MWCNT content. However, the mechanical properties deteriorated when the MWCNT content was increased above a certain value. The MWCNTs became entangled with each other in the matrix due to the presence of an excess amount of MWCNTs. The electrical conductivity and EMI-SE of the MWCNTs/B-epoxy composites also improved with an increase in the MWCNT content because of the formation of enhanced electric networks. The EMI-SE of 13 (B-epoxy) was found to be similar to that of 8 (B-epoxy), indicating that a further increase in the MWCNT content is unnecessary.

#### Conflict of Interest

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

#### Acknowledgements

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