

실리카 코팅된 다중벽 탄소 나노튜브/에폭시 복합체의 기계적 물성

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Mechanical Properties of Silica-coated Multi-walled Carbon Nanotube/Epoxy Composites

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초록: 다중벽 탄소 나노튜브(MWCNTs)/에폭시 복합체의 기계적 강도와 전기 절연성을 증가시키기 위하여, tetraethyl orthosilicate(TEOS)를 전구체로 사용한 1 단계 졸-겔 반응을 통하여 다중벽 탄소 나노튜브(MWCNTs)를 실리카 층으로 코팅하였다. MWCNTs 표면을 화학적으로 개질하지 않고 폴리에틸렌이민을 커플링제로 사용하여 실리카로 균일하게 코팅하였다. 실리카 코팅된 MWCNTs 및 순수한 MWCNTs를 충전제로 사용하여 제조된 복합체의 기계적 특성, 열적 특성, 전기적 성질을 관찰하였다. 에폭시 사슬들은 MWCNTs 표면의 실리카 층에 강하게 속박되어, 실리카 층은 MWCNTs에 전기 절연막을 형성하였다. 결과적으로, 실리카 코팅된 MWCNTs가 충전된 에폭시 복합체의 기계적 물성 및 전기저항이 증가하였다.

Abstract: Multi-walled carbon nanotubes (MWCNTs) were coated with silica layers via a one-step sol-gel process with tetraethyl orthosilicate (TEOS) as a silica precursor to enhance the mechanical strength and electrical resistivity of MWCNTs-filled epoxy composites. The MWCNTs were coated uniformly with silica using polyethyleneimine as a coupling agent without chemical modification of the surface of the MWCNTs. The silica-coated MWCNTs were used as a filler in the epoxy. The epoxy composites filled with the raw and silica-coated MWCNTs were prepared and their properties were examined in terms of mechanical, thermal and electrical properties. The epoxy chains were bound strongly to the silica layer on the surface of the MWCNTs, and the silica layer provided the MWCNTs with electrically insulating barriers. As a result, the silica-coated MWCNTs-filled epoxy composites showed improved mechanical strength and electrical resistivity.

Keywords: MWCNTs, silica, coating, epoxy composites, mechanical property.

Introduction

Carbon nanotubes (CNTs) have attracted considerable attention as the reinforcements for polymer composites because of their outstanding structural properties and potential usefulness in a range of applications.¹⁻⁴ CNTs have many unique properties, including high mechanical strength, electrical and thermal conductivity along with low density.³⁻⁸ On the other hand, CNTs for reinforcing polymers have poor dispersion in poly-

mer matrices because of the poor interfacial interactions between the CNTs and polymers, and the strong intermolecular interactions called van der Waals forces among CNTs, which can cause aggregation.^{2,9} To maximize the advantages of CNTs as a reinforcing filler for polymer composites, CNTs should have the appropriate dispersion in a polymer matrix.^{9,10} To enhance a distribution of CNTs and increase the interfacial adhesion within a polymer matrix, a surface treatment is necessary for CNTs, which increases the active sites on the surface and then improves the bonding strength between the CNTs and polymer matrix.^{11,12} Considerable research has been carried out on the surface covalent functionalization of CNTs, such as chemical oxidation with acid, different plasma or air.¹³⁻¹⁸ These

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approaches, however, have many disadvantages, including a decrease in the aspect ratio of CNTs and the formation of structural defects on the CNTs walls.^{19,20} Furthermore, structural destruction of CNTs would decrease the mechanical, electrical, and thermal properties.²¹

In our previous study, multi-walled carbon nanotubes (MWCNTs) were successfully coated with silica without prior chemical treatment of MWCNTs.²¹ Therefore, the CNTs could avoid the generation of serious structural defects.^{22,23} In this process, polyethyleneimine (PEI) was used as a coupling agent to modify the surfaces of MWCNTs and enhance the dispersion of MWCNTs in the silica sol. The silica-coated MWCNTs were synthesized using a sol-gel reaction with a basic catalyst. The silica layer was coated uniformly onto the MWCNTs because of the strong interactions between the basically-modified MWCNTs and the acidic tetraethyl orthosilicate (TEOS). The silica-coated MWCNTs synthesized under the optimal conditions were incorporated into epoxy to examine the mechanical strength, thermal conductivity, and surface resistivity of the silica-coated MWCNTs/epoxy composites. When the filler to epoxy ratio was 2 wt%, the mechanical strength of the silica-coated MWCNTs/epoxy composites increased with increasing amount of TEOS, and the value of the samples prepared with different amounts of TEOS was higher than those of the raw MWCNTs/epoxy composites. Electrically insulating epoxy composites with enhanced mechanical strength were prepared and evaluated.

Experimental

Materials. The MWCNTs were purchased from Nanocyl (Belgium). The MWCNTs had a diameter of 9.5 nm, a length of 1.5 μm and a purity of 95%. Polyethyleneimine (PEI, M_w : 800 g mol⁻¹) was supplied by Sigma-Aldrich (USA). Tetraethyl orthosilicate (TEOS, $\geq 95\%$) was obtained from Junsei Chemical Co., Ltd. (Japan), ammonium hydroxide (25-30 wt% NH₃ in water) from OCI Co., Ltd. (S. Korea) and ethanol from Duksan Chemicals Co., Ltd. (S. Korea). Epoxy resin (YD-128, bisphenol-A type) and methylhexahydrophthalic anhydride (HN-2200, hardener) were obtained from Kukdo Chemical (S. Korea). 2-Ethyl-4-methyl-imidazole as a catalyst was purchased from Sigma-Aldrich (USA).

Sample Preparation. Synthesis of Silica-coated MWCNTs with PEI: The procedure for the preparation of silica-coated MWCNTs is reported elsewhere.²¹ 2 g of MWCNTs were poured into 100 mL of ethanol and dispersed by sonication for

1 h. PEI, 200 wt% to MWCNTs, was then added and stirred vigorously for 6 h at room temperature. After the dissolution of PEI, ammonium hydroxide was injected to serve as a catalyst for the sol-gel reaction of TEOS. The sol-gel reaction proceeded with vigorous stirring at ambient temperature for 24 h after injecting TEOS in the above solution. The mixture was filtered and washed with ethanol, and the product was dried at 60 °C in a vacuum oven.

Fabrication of Silica-coated MWCNTs/Epoxy Composites: Raw MWCNTs and silica-coated MWCNTs synthesized using PEI, 200 wt% to MWCNTs, were dispersed in acetone by ultrasonication for 30 min. 3 g of epoxy resin was then added into the suspension and the mixture was stirred for 10 h to completely remove the acetone and then degassed in a vacuum oven. 1.50 g of hardener and 0.16 g of the curing agent were then mixed in the blend. The composites were hot-pressed to obtain the desired dimensions in stainless steel molds at 130 and 160 °C for 1 h and 2 h, respectively. The epoxy composites containing 0, 1, 2, 3, and 5 wt% of the raw MWCNTs and silica-coated MWCNTs were prepared.

Characterization. The surface morphology of the silica-coated MWCNTs was characterized by field-emission transmission electron microscopy (FE-TEM, JEOL JEM-2100F) and scanning electron microscopy (SEM, Hitachi S-4300). Thermogravimetric analysis (TGA, Mettler Toledo TGA/SDTA 851) was used to determine if the silica was well coated, and to evaluate how much silica was coated on the MWCNTs. A three-point bending test was performed at a cross-head speed of 2 mm/min to measure the critical stress intensity factor (K_{IC}), as a representative indicator of the mechanical strength of the epoxy composites. The K_{IC} value of every epoxy composite was calculated using the following eq. (1):

$$K_{IC} = \frac{PS}{BW^{3/2}} f(\alpha/W) \quad (1)$$

$$f(\alpha/W) = \frac{6(\alpha/W)^{1/2} [1.99 - (\alpha/W)(1 - \alpha/W)(2.15 - 3.93\alpha/W + 2.7\alpha^2/W^2)]}{(1 + 2\alpha/W)(1 - \alpha/W)^{3/2}}$$

where P (KN) is the rupture force, S (cm) is the distance between the supports, α (cm) is the crack length, W (cm) is the sample width, and B (cm) is the sample thickness. The interlaminar shear stress (ILSS) of the epoxy composite was calculated using the following eq. (2):

$$ILSS = \frac{3F}{4bd} \quad (2)$$

where $F(N)$ is the rupture force, $b(m)$ is the width of the specimen, and $d(m)$ is the thickness of the specimen. A quick thermal conductivity meter (QTM-500, Kyoto Electronics) was employed to measure the thermal conductivity of the composites. The surface resistivity of the raw MWCNTs/epoxy composites and the silica-coated MWCNTs/epoxy composites were measured using a high-resistivity meter (Hiresta-UP, Mitsubishi Chemical Co.) and a low-resistivity meter (Loresta-GP, Mitsubishi Chemical Co.). A high resistivity meter is based on constant-voltage processing with a concentric ring probe and a measurement range of 10^4 to $10^{13} \Omega$. A low resistivity meter is based on constant-current processing with a linear four-point probe and a measurement range of 10^{-3} to $10^7 \Omega$.

Results and Discussion

The FE-TEM and SEM images in Figure 1 show the morphologies of the resulting product prepared via one-step coating process conducted without and with PEI as a coupling agent. Figure 1(a-1) and (a-2) show that silica particles did not grow on the surface of the MWCNTs in the absence of PEI and appeared to be mixed with the MWCNTs because of the shortage of functional groups on MWCNTs. This morphological study indicates that the silica coating reactions without a coupling agent was not effective. On the other hand, the sil-

ica sol-gel coating process took place effectually when PEI, 200 wt% to MWCNTs, was used as a coupling agent, as shown in Figure 1(b) and (c). The amount of PEI was selected to find the optimal conditions for the uniform silica coating on the MWCNTs as a one-step coating process. According to the morphological study of the SEM and TEM images, the growth of silica particles on the PEI-adsorbed MWCNTs occurred and the silica layer coverage on the PEI-assisted MWCNTs varied with the amount of silica precursor, TEOS, used. The more silica precursor, TEOS, participates in the sol-gel reaction, the more silica is formed on the PEI-adsorbed MWCNTs. This was not enough to fully cover the surface of the MWCNTs with silica until the amount of TEOS was 1500 wt% with respect to the weight of the MWCNTs that the silica was coated uniformly onto the MWCNTs.

Figure 2 presents the TGA curves of the MWCNTs, PEI-adsorbed MWCNTs and the silica-coated MWCNTs prepared with different amounts of TEOS and PEI in air. The process was initiated at ambient temperature, and the temperature was increased to 750 °C at a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ in air. Significant loss in weight did not occur until 200 °C. The slight loss between room temperature and 200 °C may be due to the evaporation of moisture. The weight loss curves for the silica-coated MWCNTs imply a two-step degradation mechanism. The silica-coated MWCNTs first undergo weight loss between

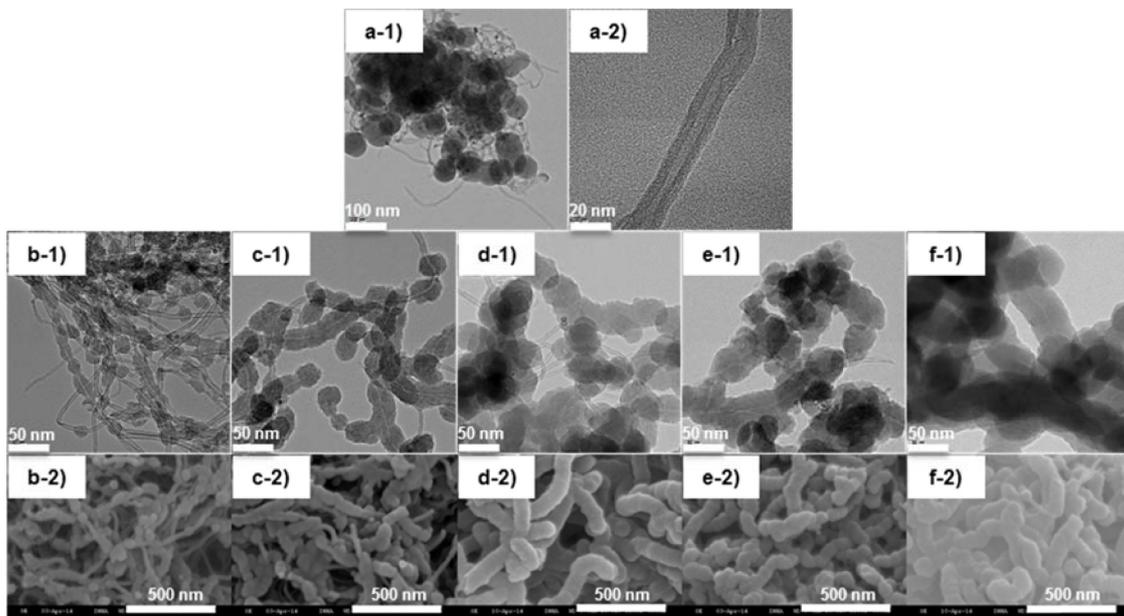


Figure 1. (a-1, a-2) FE-TEM images of the product of the sol-gel reaction of MWCNTs in the absence of PEI; FE-TEM and SEM images of the silica coated MWCNTs prepared with 200 wt% PEI and different amounts of TEOS (b-1, b-2) 500; (c-1, c-2) 1000; (d-1, d-2) 1500; (e-1, e-2) 2000; (f-1, f-2) 2500 wt%.

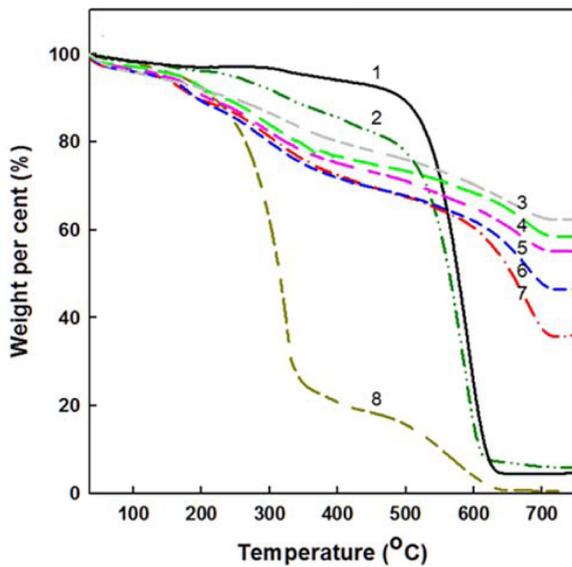


Figure 2. TGA weight loss curves of (1) raw MWCNTs; (2) PEI-absorbed MWCNTs; (3-7) silica-coated MWCNTs prepared with different amounts of TEOS (2500, 2000, 1500, 1000, 500 wt%, respectively); (8) PEI.

200 and 350 °C, which can be attributed to the decomposition behavior of PEI. The second degradation takes place at 350–700 °C because the range of degradation temperatures of the disordered and amorphous carbon is 350–500 °C, and that of the perfect MWCNT structure is 500–700 °C. The significant decrease in weight of the silica-coated MWCNTs begins at temperatures higher than that of the raw MWCNTs because of the improvement of the thermal stability via the silica coating

onto the MWCNTs. From the TGA weight loss curves, the amount of residues of the silica-coated MWCNTs increased with increasing amount of TEOS, which was used for the coating. This tendency is in agreement with the extent of the silica coverage observed in the TEM and SEM images (Figure 1).

Figure 3 presents the variation of the critical stress intensity factor (K_{IC}) and interlaminar shear strength (ILSS) of the raw MWCNTs/epoxy composites and silica-coated MWCNTs/epoxy composites as a function of filler loading ratio. K_{IC} is a general engineering parameter used in fracture mechanics, and suggests that the fracture toughness of a material should exceed a certain critical distance in order for a crack opening displacement to emerge. As shown in Figure 3(a), K_{IC} of the raw MWCNTs/epoxy and silica-coated MWCNTs/epoxy composites had an identical tendency and did not show differences until the filler content was 1 wt%. With the addition of silica-coated MWCNTs over 1 wt%, it began to show approximately 5–35% differences among the raw MWCNTs/epoxy composites and silica-coated MWCNTs/epoxy composites. When the epoxy composites were made with 2 wt% filler, both the K_{IC} value of the silica-coated MWCNTs/epoxy composites and the difference with the K_{IC} value of the raw MWCNTs/epoxy composites were approximately 35% of the maximum value. Similarly, in ILSS, as presented in Figure 3(b), the maximum strength of the silica-coated MWCNTs/epoxy composites with a 2 wt% filler content was approximately 27 MPa, which was an approximately 30% difference with the raw MWCNTs/epoxy composites. As the filler content increased to more than

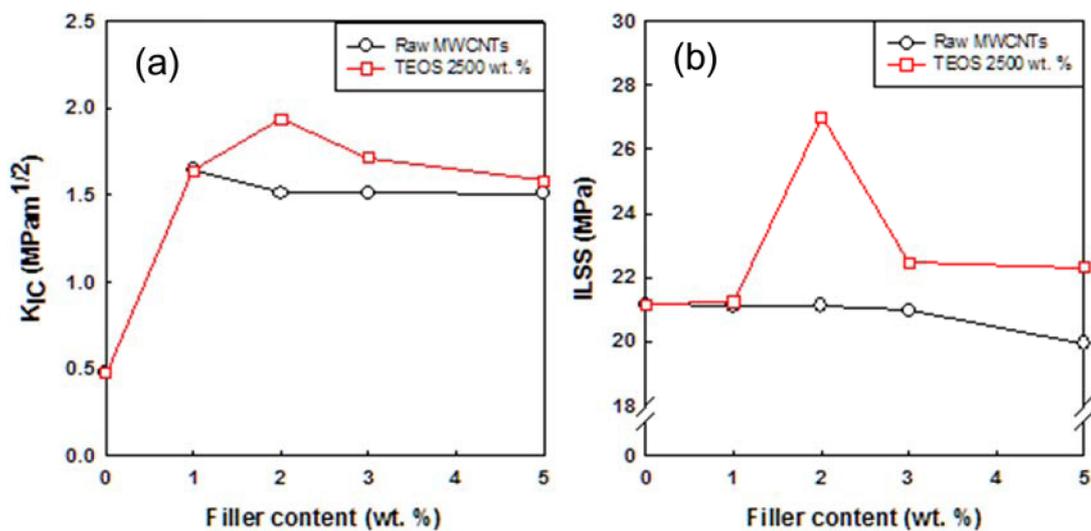


Figure 3. (a) K_{IC} ; (b) ILSS of the raw MWCNTs/epoxy and silica-coated MWCNTs/epoxy composites (prepared at 2500 wt% TEOS to the MWCNTs) with various filler loadings.

3 wt%, the ILSS values of the raw MWCNTs/epoxy composites steadily decreased. The ILSS is the most extensively used indicator, reflecting the degree of adhesion at the interface between the fillers and polymeric matrices. Both K_{IC} and ILSS values of the silica-coated MWCNTs/epoxy composites, which were fabricated with 2500 wt% TEOS, were always higher than those of the raw MWCNTs/epoxy composites with a filler content more than 1 wt%. The improved K_{IC} and ILSS values of the silica-coated MWCNT/epoxy composite are related to the better dispersion, where epoxy chains are bound strongly to the silica layer on the surface of the MWCNTs via hydrogen bonding. By adding the silica coated MWCNTs, the contact areas between the filler and the epoxy matrix increased significantly. For this reason, the mechanical properties of their composites are reinforced with a filler content below 2 wt%.

As silica-coated MWCNTs with a high aspect ratio and a large surface area exceed the optimal content of 2 wt%, their contributions to the mechanical strength of the composites decrease gradually and the composites become brittle and stiff with a decrease in the elastic property of the epoxy polymer. Above the higher content than the optimal value, the silica-coated MWCNTs within the epoxy matrix easily form an agglomerated bulk. The fillers in the agglomerated bulk have poor contact with the polymer chains than the well dispersed silica-coated MWCNTs at the optimal content. A non-uniform interaction, lack of binding ability of the polymer, formation of cracks and voids in the composite matrix occurred. As a result, the mechanical properties of the composites were reduced

gradually over the optimal content.

Figure 4 presents the K_{IC} and ILSS of the raw MWCNTs/epoxy and silica-coated MWCNTs/epoxy composites at various TEOS ratios at constant filler content of 2 wt%. The K_{IC} values of the silica-coated MWCNTs/epoxy composites showed an increase with increasing amount of TEOS used, as shown in Figure 4(a). The K_{IC} values of the silica-coated MWCNTs/epoxy composites prepared with a 500 wt% and 2500 wt% TEOS were 1.660 $\text{MPa}\cdot\text{m}^{1/2}$ (an enhancement of 249.5%) and 1.938 $\text{MPa}\cdot\text{m}^{1/2}$ (an enhancement of 308%), respectively, compared to 0.475 $\text{MPa}\cdot\text{m}^{1/2}$ for the neat epoxy. The fracture toughness of the epoxy composites with the raw MWCNTs was 1.511 $\text{MPa}\cdot\text{m}^{1/2}$. Therefore, the silica-coated MWCNTs/epoxy composite synthesized with a 2500 wt% TEOS showed a 28.3% higher mechanical strength than the raw MWCNTs/epoxy composite. The increase in K_{IC} values with the addition of silica on the MWCNTs may be related to the lower fraction of agglomerates. The ILSS of the composites, shown in Figure 4(b), showed the same tendency as the K_{IC} of the composites. The ILSS values of the neat epoxy and raw MWCNTs/epoxy composites were 21.147 and 21.113 MPa, respectively. Compared to the neat epoxy and raw MWCNTs/epoxy composites, the silica-coated MWCNTs/epoxy composites prepared with 2500 wt% TEOS showed a reinforcement of 27.7% and 27.9%, respectively. The enhancement of the mechanical strength of the epoxy composites depends primarily on the interactions between MWCNTs and the epoxy matrix through hydrogen bonding.

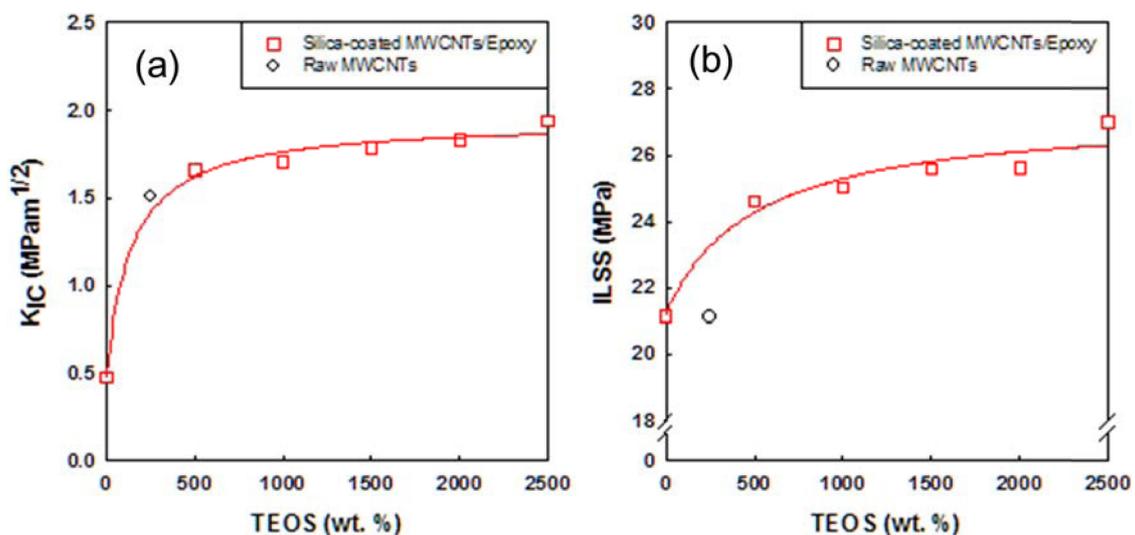


Figure 4. (a) K_{IC} ; (b) ILSS of the raw MWCNTs/epoxy and silica-coated MWCNTs/epoxy composites (prepared at 2 wt% filler content) with various TEOS amounts.

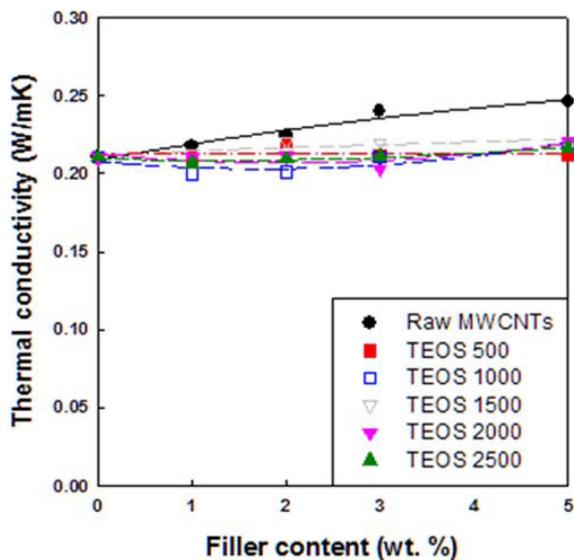


Figure 5. Thermal conductivity of the raw MWCNTs/epoxy and silica-coated MWCNTs/epoxy composites as a function of the filler content.

Figure 5 presents the thermal conductivity of the raw MWCNTs/epoxy and silica-coated MWCNTs/epoxy composites with varying filler contents. The silica-coated MWCNTs/epoxy composites showed lower thermal conductivity at all filler contents than the raw MWCNTs/epoxy composites. At a 5 wt% filler content, the thermal conductivity value of raw MWCNTs/epoxy composites was 0.247 W/mK and that of the silica-coated MWCNTs/epoxy composites prepared with 500 wt% TEOS, which has the lowest thermal conductivity, was 0.212 W/mK. This decrease in thermal conductivity can be explained by the following two reasons. First, because the silica-coated MWCNTs consisted of 65 wt% of crystalline MWCNTs and 35 wt% of amorphous silica according to Figure 2, the silica-coated MWCNTs/epoxy composites include fewer MWCNTs than the raw MWCNTs/epoxy composites. In this system, the MWCNTs are the major component that improves the thermal conductivity. Consequently, the composites containing lower amounts of MWCNTs have lower thermal conductivity. Second, conductive heat transfer is retarded in the interface between the surface of the MWCNTs and the silica layer on the MWCNTs because silica has very low thermal conductivity, 1.4 W/mK, compared to MWCNTs, so interfacial thermal resistance exists between the MWCNTs and silica layer.

Figure 6 presents the changes in the surface resistivity of the raw MWCNTs/epoxy and silica-coated MWCNTs/epoxy composites with varying filler contents. The surface resistivity of

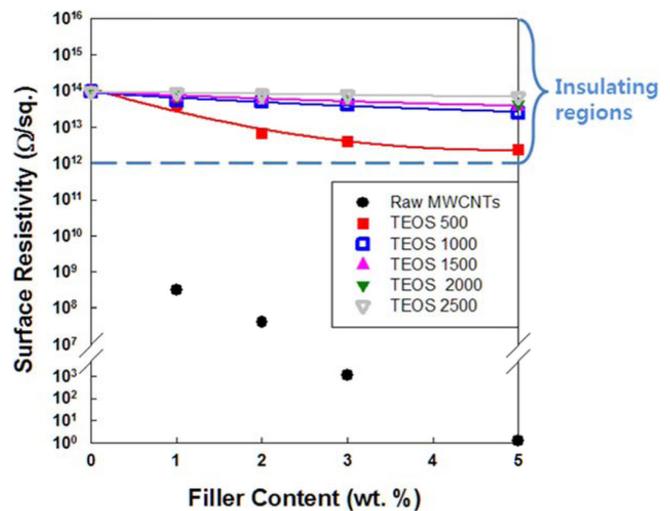


Figure 6. Surface resistivity of the raw MWCNTs/epoxy and silica-coated MWCNTs/epoxy composites with various filler contents.

the raw MWCNTs/epoxy composites decreased drastically with increasing MWCNTs content, whereas the silica-coated MWCNTs/epoxy composites showed constant surface resistivity of over $10^{13} \Omega \text{ sq}^{-1}$ regardless of the filler content, which means that the surface resistivity of these composites belongs to the electrically insulating region, over $10^{12} \Omega \text{ sq}^{-1}$. Although the raw MWCNTs are electrically conductive materials and have low surface resistivity ($2.065 \times 10^2 \Omega \text{ sq}^{-1}$),²¹ the electrically insulating properties of composites with epoxy resin can be improved by coating the surface of MWCNTs. This is because the silica layer coated on the MWCNTs has an electrically insulating property, which suggests that this coating blocks electron flow between the adjacent MWCNTs. In the case of the silica-coated MWCNTs/epoxy composites prepared with 500 wt% TEOS, although the surface resistivity decreased slightly with increasing filler content, it is still in the electrically insulating region. These slight reductions were because the silica particles were not coated uniformly over the surface of the MWCNTs and thus the degree of silica coverage on the MWCNTs was low, as shown in Figure 1. In other words, this suggests that when a uniform silica coating is formed on the PEI-adsorbed MWCNTs and that materials are used as a filler in epoxy resin, the electrical insulating properties of the MWCNTs could be improved and those of the silica-coated MWCNTs/epoxy composites were reinforced.

Conclusions

This work examined the fabrication of silica-coated

MWCNTs and application as a filler in an epoxy matrix. A uniform silica coating was formed on the PEI-adsorbed MWCNTs after the MWCNTs had been modified through non-covalent functionalization under basic conditions. The thickness of the silica layer formed on the MWCNTs depended on the amount of TEOS used, and the amount of silica on the MWCNTs increased with increasing quantity of TEOS added. The silica-coated MWCNTs/epoxy composites had better mechanical properties and electrical resistivity than the raw MWCNTs/epoxy composite. The highest mechanical strength and electrical resistivity were obtained when 2 wt% of the silica-coated MWCNTs, prepared with 2500 wt% TEOS to MWCNTs, were used to fabricate the composites with epoxy resin.

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