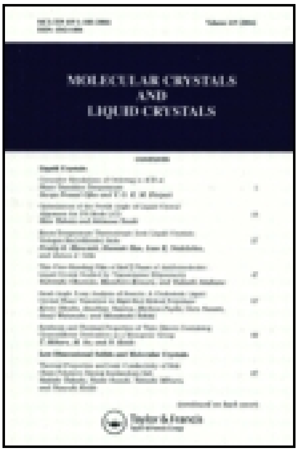

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Chemical Surface Pre-treatment of Carbon Nanotube for Improving the Thermal Conductivity of Carbon Nanotube-Epoxy Composite

Dong Cheul Han [a] [b] , Sunyoung Son [a] , Young Cheol Choi [a] , Han Jae Shin [a] , Man Tae Kim [a] , Giseop Kwak [b] & Do Kyung Lee [a]

[a] R&D Affairs Department, Gumi Electronics and Information Technology Research Institute, Gumi, Gyeongsangbuk-do, 730-853, Republic of Korea

[b] Department of Polymer Science, Kyungpook National University, Daegu, 702-701, Republic of Korea

To cite this article: Dong Cheul Han, Sunyoung Son, Young Cheol Choi, Han Jae Shin, Man Tae Kim, Giseop Kwak & Do Kyung Lee (2011): Chemical Surface Pre-treatment of Carbon Nanotube for Improving the Thermal Conductivity of Carbon Nanotube-Epoxy Composite, Molecular Crystals and Liquid Crystals, 551:1, 228-234

To link to this article: http://dx.doi.org/10.1080/15421406.2011.601134

Mol. Cryst. Liq. Cryst., Vol. 551: pp. 228–234, 2011

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2011.601134

Chemical Surface Pre-treatment of Carbon Nanotube for Improving the Thermal Conductivity of Carbon Nanotube-Epoxy Composite

DONG CHEUL HAN,[1,2] SUNYOUNG SON,[1] YOUNG CHEOL CHOI,[1] HAN JAE SHIN,[1] MAN TAE KIM,[1] GISEOP KWAK,[2] AND DO KYUNG LEE[1,*]

[1]R&D Affairs Department, Gumi Electronics and Information Technology Research Institute, Gumi, Gyeongsangbuk-do 730-853, Republic of Korea
[2]Department of Polymer Science, Kyungpook National University, Daegu 702-701, Republic of Korea

For improving the thermal conductivity of carbon nanotube-epoxy composite, we have performed the chemical surface pre-treatment of multi-walled carbon nanotube (MWCNT) and investigated its effects. In the experiments, the mixtures of nitric and sulfuric acid have been used as the surface modifier for MWCNT. The chemical surface pre-treatments by acid mixtures lead to the production of oxygen-containing functional groups on the surfaces of MWCNT. Also, the surface area and pore volume of acid-treated MWCNT (AT-MWCNT) become larger than those of pristine MWCNT. By actions of the chemical pre-treatment, AT-MWCNT is well dispersed and forms the heat flow network in epoxy matrix, resulting in higher thermal conductivity of carbon nanotube-epoxy composite.

Keywords Multi-walled carbon nanotube; chemical surface pre-treatment; nitric and sulfuric acid mixture; thermal conductivity; CNT-epoxy composite

Introduction

Carbon nanotubes (CNTs) have attracted attention due to their extraordinary electrical, mechanical and thermal properties. Several studies have reported that CNTs are considered to be very promising materials for applications as fillers in polymer composite to enhance thermal transport [1–3]. Thermal conductivity of the CNT-polymer composites has been significantly enhanced even by adding a little amount of CNTs [4]. However, the insolubility and poor dispersion of CNTs in polymeric matrices have limited their practical applications, resulting from the weak interfacial interactions between CNTs and polymer matrix. Hence, CNT-reinforced polymer composites have often led to inefficient thermal conductivity than as expected. To solve these problems, researchers have proposed several surface pre-treatment methods, such as oxidation in acid solution [5], amino functionalization [6], and plasma treatment [7]. Nevertheless, polymer-based CNT composites have still a lower thermal conductivity, and information on the effects of surface pre-treatment of CNT for improving the thermal properties of the composite has been somewhat deficient.

---

*Corresponding author. E-mail: dklee@geri.re.kr

In this work, the surface properties of multi-wall carbon nanotube (MWCNT) modified by chemical treatment using the mixture of nitric and sulfuric acid and their dispersion in epoxy polymer matrix have been studied. In addition, by the chemical surface pre-treatment of MWCNT, the chemical functionalization and morphology change of MWCNT for the enhancement of thermal conductivity in epoxy polymer matrix have been investigated.

Experimental

The MWCNTs used in this work were supplied from Iljin Nanotech Co. in Korea (Purity >95%, length: 10–50 μm, diameter: 10–20 nm). Epoxy resin was selected as the polymer matrix because it is known that CNTs are dispersed well in the epoxy resin compared with other polymer matrices [8]. The used epoxy resin was diglycidyl ether of Bisphenol A (DGEBA). Triethlyenetetramine(TETA) (Kuk-do chemicals Co) was used as curing agents.

Pristine MWCNT powders were slowly added into the mixture solution of nitric and sulfuric acids and then ultrasonicated for 1 hr. The solution was refluxed for 2 hr at 100°C for the acid treatment. After the acid treatment, the solution was washed using distilled water, filtered, and then dried in a vacuum oven at 60°C. The pristine MWCNT and acid-treated MWCNT (AT-MWCNT) were mixed with N-methyl-pyrrolidone (NMP), respectively. Epoxy resin was added into these suspensions with further ultrasonication. The suspension mixtures were stirred for 2 hr in a vacuum oven at 80°C to remove the entrapped air. The curing agent was added to the mixtures and then the mixtures were formed in a 10 cm × 10 cm × 0.5 cm molder. Finally, the composite was pre-cured at 80°C for 1 hr, cured at 120°C for 2 hr and post-cured at 130°C for 2 hr.

Fourier transform infrared (FT-IR) spectra of MWCNT were obtained between 500 and 4000 cm^{-1} on a spectrophotometer (VERTEX-70, Bruker Optics). The morphological observations were executed using a field emission scanning electron microscope (FE-SEM,

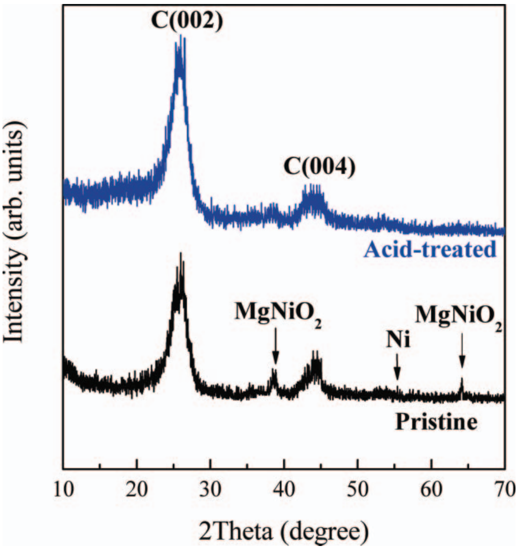

Figure 1. XRD patterns of MWCNTs.

Table 1. Textural properties of pristine and acid-treated MWCNT.

Sample	Specific surface area (m^2/g)	Total pore volume (cm^3/g)
Pristine MWCNT	194	0.51
Acid-treated MWCNT	228	0.79

JSM-7000F, Jeol). In order to estimate the crystallity of the MWCNTs, X-ray diffraction (XRD, D/MAX-2500, Rigaku) analysis was used. The specific area and pore volume of the MWCNTs were measured by the BET method (BELSORP-max, BEL INC.) using nitrogen adsorption at 77 K. The thermal conductivities of the MWCNT-epoxy composites were measured by thermal conductivity meter (LFA 457, Netzsch).

Results and Discussion

Figure 1 shows the XRD patterns of MWCNTs before and after acid treatment. It can be seen that the MWCNTs have the diffraction peaks of graphite corresponding to (002) and (004) reflections. For pristine MWCNT, the diffraction peaks appear corresponding to nickel and magnesium oxide compound phases in the XRD pattern. The diffraction peaks due to nickel and magnesium oxide compound are also observed. This means that pristine MWCNT contain the impurities with metal and metal oxide. After acid treatment, the intense (002) peak of graphite is relatively enlarged and any diffraction peak of impurities was not seen. The enlargement of the (002) peak may be due to the removal of amorphous impurities, such as soot and ash [9].

Table 1 indicates the textural properties of pristine and acid-treated MWCNT. A pristine MWCNT exhibits a specific surface area of 194 m^2/g and a total pore volume of 0.51 cm^3/g,

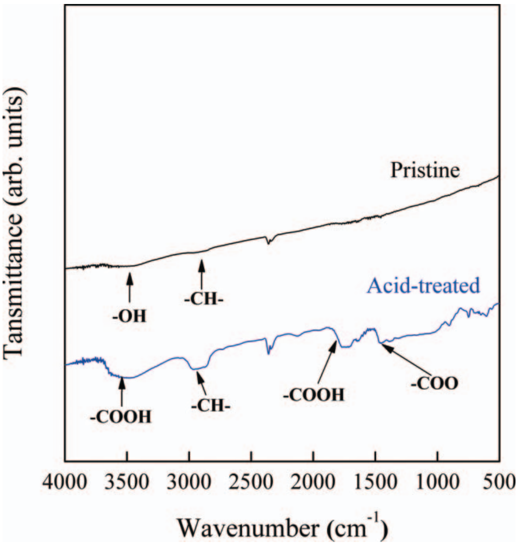

Figure 2. FT-IR spectra of MWCNTs.

whereas the AT-MWCNT shows the specific surface area of 228 m^2/g and the total pore volume of 0.79 cm^3/g. It is found that the surface area and pore volume of MWCNT are increased by acid treatment. These results can be considered that the impurities such as non-porous carbon, metal, and metal oxide are removed by acid treatment, which is also accordant with typical XRD result, as shown in Fig. 1. Therefore, it is expected to increase the interfacial interaction between MWCNT and epoxy matrix in composite [10].

Figure 2 shows the FT-IR spectra of MWCNTs. In pristine MWCNT spectrum, the absorption peaks due to C-H and O-H stretching motions are barely seen around 2,800 and 3,400 cm^{-1}, respectively. This reconfirms that the pristine MWCNT contains a little amount of non-porous carbon and metal oxide [11]. The spectrum of AT-MWCNT clearly shows that the absorption peaks around 1450 and 2,800 cm^{-1} are due to –COO and C-H stretching, respectively. Also, characteristic peaks due to carboxylic groups at 1720 and 3,500 cm^{-1} are observed. This indicates that the functional group as carboxylic acid is newly formed on the surface of MWCNT after acid treatment.

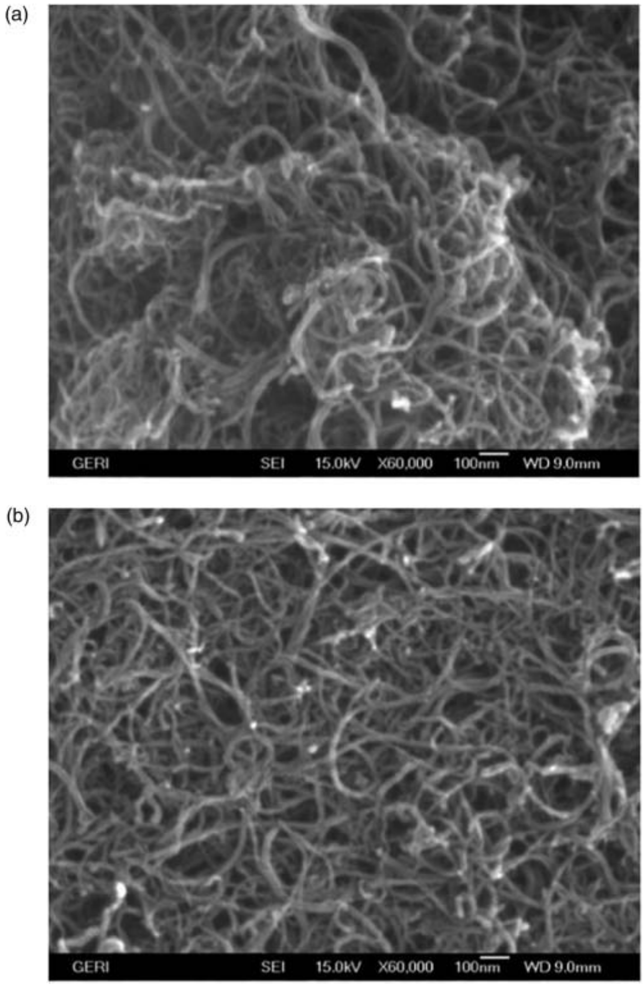

Figure 3. FE-SEM images of MWCNTs: (a) pristine MWCNT (b) acid-treated MWCNT.

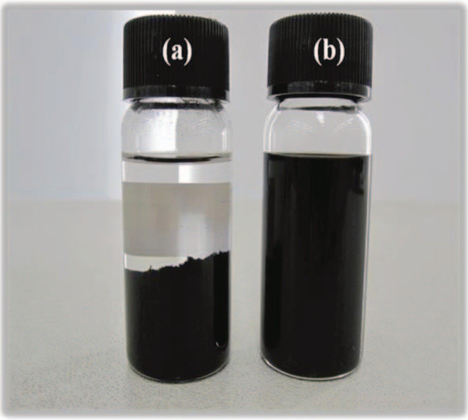

Figure 4. Photographs of MWCNTs in NMP: (a) pristine MWCNT (b) acid-treated MWCNT. The photographs were taken after three month of storage at room temperature.

Figure 3 illustrates the FE-SEM images of MWCNTs. The pristine MWCNT shows high degree of aggregation due to van der Waals interactions. However, the AT-MWCNT shows relatively lower degree of aggregation. This low degree of aggregation in AT-MWCNT may be originated in the reduced intermolecular interaction, which is attributed by the functional carboxylic acid group.

The dispersion of MWCNTs in NMP solvent is represented in Fig. 4. The pristine MWCNT is settled down to the bottom of the vial, while the AT-MWCNT shows a good dispersion. Furthermore, the dispersion stability of AT-MWCNT in NMP was retained for more than three months. Accordingly, the functionalization on MWCNT can give rise to the

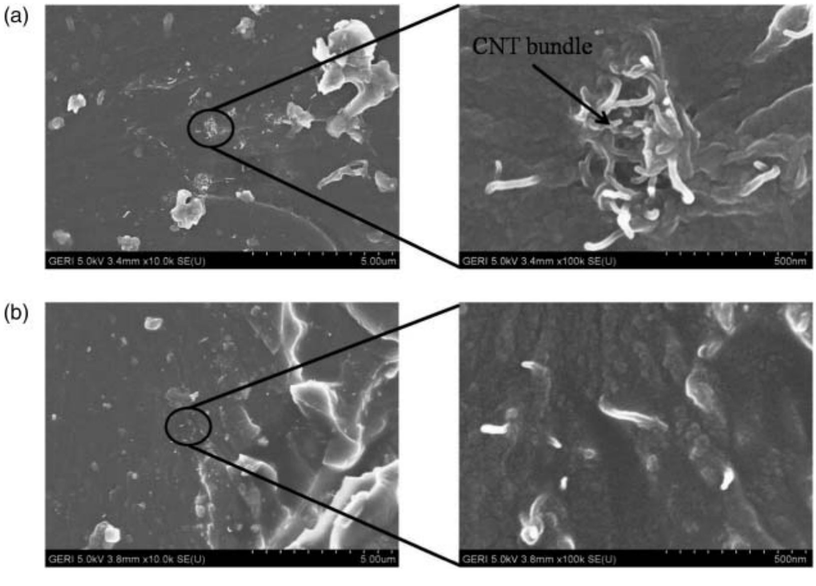

Figure 5. FE-SEM images of 0.5 wt% MWCNT-epoxy composite: (a) pristine MWCNT (b) acid-treated MWCNT.

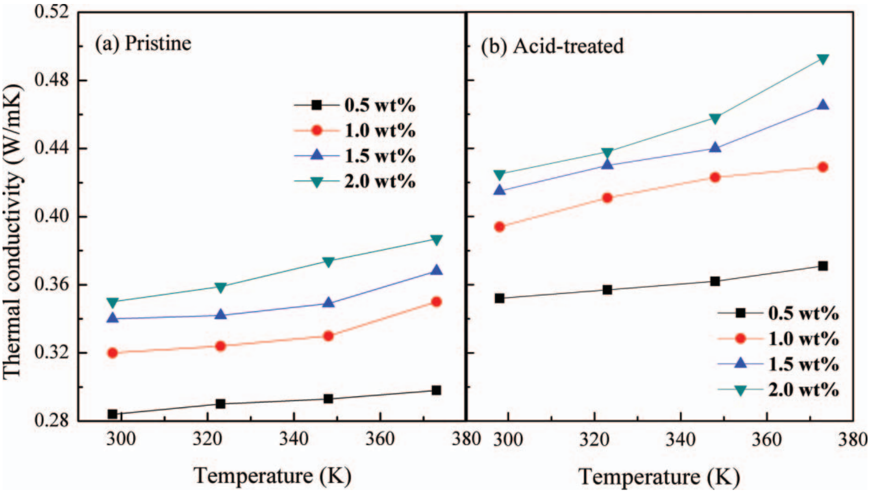

Figure 6. Thermal conductivity of the MWCNT-epoxy composites.

increase in the degree of dispersion with improvement of the interactions between CNTs and solvent [12].

Figure 5 shows that the FE-SEM images of MWCNT-epoxy resin composite containing 0.5 wt% MWCNT. The pristine MWCNT shows the fracture surface of the composite as bundle-like agglomerate. On the other hand, the AT-MWCNT is well dispersed in epoxy matrix. It is reported that the dispersion of MWCNT in a polymer matrix is significantly dependent on the presence of functional groups [12]. Hence, the well dispersion of AT-MWCNT in the epoxy is attributed to the functional carboxylic acid groups on the surface of AT-MWCNT, as mentioned previously.

Figure 6 indicates the thermal conductivities of MWCNT-epoxy composites. As the temperature increases, the thermal conductivities of both composites increase. This is a common trend for most polymer matrices because the dominant thermal carrier in polymer is a phonon [10]. Also, the enhancement of the thermal conductivity depends on the MWCNT filler concentration in the composites. This result is in good agreement with the study by A. Lazarenko et al. [4]. It should be noted that the composite of AT-MWCNT and epoxy shows a greater enhancement in thermal conductivity than pristine MWCNT-epoxy. The thermal conductivity for composite of 2.0 wt% AT-MWCNT and epoxy at 300K shows 0.43 W/m·k, which is greater than that of 2.0 wt% pristine MWCNT-epoxy composite (0.35 /m·k at 300 K). This is due to the fact that the AT-MWCNT is well dispersed in the epoxy matrix, resulting from the increased specific surface area and pore volume. Thus, owing to the better dispersion of AT-MWCNT in epoxy matrix, superior heat flow network is formed and thereby higher thermal conductivity is occurred.

Conclusions

Effects of chemical surface pre-treatment on the thermal properties of MWCNT-epoxy composites have been investigated. The acid treatment of MWCNT significantly results in the increases of the specific surface area and pore volume in MWCNT. The composite of AT-MWCNT and epoxy shows greater enhancement in thermal conductivity than the pristine MWNCT-epoxy composite, due to the increasing interfacial interaction between

MWCNT and polymer matrix. This study suggests that the acid pre-treatment of MWCNT can enhance the thermal conductivity of MWCNT-polymer composite for the application of heat sink in electronic devices.

References

[1] Yang, S. Y., Ma, C. C, Teng, C. C., Liao, S. H., & Chiou, K. C. (2010). *Carbon*, **48**, 592.

[2] Jin, S. H., Park, Y. B., & Yoon, K. H. (2007). *Compos. Sci. Technol.*, **76**, 3434.

[3] Kim, S. D., Kim, J. W., Im, J. S., Kim, Y. H., & Young Seak Lee, Y. S., (2007). *J. Fluoro. Chem.*, **128**, 60.

[4] Lazarenko, A., Vovchenko, L., Matsui D., Prylutsky, Y., Matzuy, L., & Scharff, P. (2008). *Mol. Cryst. Liq. Cryst.*, **497**, 65.

[5] Hu, C. C., Su, J. H., & Wen, T. C. (2007). *J. phys. Chem. Sol.*, **68**, 2353.

[6] Gojny, F. H., & Schulte, K. (2004). *Compos. Sci. Technol.*, **64**, 2303.

[7] Kalita, G., Adhikari, S., Aryal, H. R, Sharon, M., & Umeno, M. (2009). *Curr. Appl. Phys.*, **9**, 346.

[8] Yang, K., Guo, Y., Pan, X., & Mu, G. (2009). *Carbon*, **47**, 1723.

[9] Chen, X. H., Chen, C. S., Chen, Q., Cheng, F. Q., Zhang, G., & Chen, Z. Z. (2002). *Materials Letters*, **57**, 734.

[10] Li, S. Q., Wang, F., Wang, Y., Wang, J. W., & Xiao, J. (2008). *J. Mater. Sci.*, **43**, 2635.

[11] Upadhyay, D. J., Cui, N. Y., Anderson, C. A., & Brown, N. M. D. (2004). *Appl. Surf. Sci.*, **229**, 352.

[12] Chen, J., Hamon, M. A., Chen, Y., Rao, A. M., Eklund, P. C., & Haddon, R. C. (1998). *Science*, **282**, 95.