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Thermal Property of Multi-Walled-Carbon-Nanotube Reinforced Epoxy Composites

Min Ye Koo, Gyo Woo Lee

***Abstract*—**In this study, epoxy composite specimens reinforced with multi-walled carbon nanotube filler were fabricated using shear mixer and ultra-sonication processor. The mechanical and thermal properties of the fabricated specimens were measured and evaluated. From the electron microscope images and the results from the measurements of tensile strengths, the specimens having 0.6 wt% nanotube content show better dispersion and higher strength than those of the other specimens. The Young's moduli of the specimens increased as the contents of the nanotube filler in the matrix were increased. The specimen having a 0.6 wt% nanotube filler content showed higher thermal conductivity than that of the other specimens. While, in the measurement of thermal expansion, specimens having 0.4 and 0.6 wt% filler contents showed a lower value of thermal expansion than that of the other specimens. On the basis of the measured and evaluated properties of the composites, we believe that the simple and time-saving fabrication process used in this study was sufficient to obtain improved properties of the specimens.

***Keywords*—**Carbon Nanotube Filler, Epoxy Composite, Ultra-Sonication, Shear Mixer, Mechanical Property, Thermal Property.

I. Introduction

EPOXY resins are widely used as matrices of composites for their high adhesiveness to other substrates and good heat and chemical resistances. Epoxy composites reinforced with carbon nanotubes (CNTs) filler have received a great deal of attention [1]. Due to their high strength, stiffness, aspect ratio, and thermal and electrical conductivity, carbon nanotubes are widely used as a filler material. In 2000, Yu et al. [2] measured the outer shell strength of a multi-walled carbon nanotube as ranging from 11 to 63 GPa using an atomic force microscope (AFM) tip. Also, they measured the Young's modulus of the outermost layer as varying from 270 to 950 GPa. In the same year, Xie et al. [3] reported the average tensile strength and Young's modulus of the chemical vapor deposition (CVD) -grown long tubes as ~3.6 GPa and ~450 GPa, respectively. The thermal conductivity and thermoelectric power of a single carbon nanotube were measured using a micro-fabricated suspended device [4]. They reported that the thermal conductivity was more than 3,000 $Wm^{-1}K^{-1}$ at room temperature, and the linear temperature dependence of thermoelectric power was 80 μVK^{-1}.

Attractive forces such as van der Waal's forces among carbon nanotubes render it difficult to disperse the filler in matrices. Well-known effective dispersion methods are divided into three categories: mechanical, physical, and chemical [1], [5]. Ultrasonic dispersing and high-shear mixing are examples of commonly used mechanical dispersion methods. Physical methods involve the absorption and/or wrapping of polymers or surfactants to the surface of the nanotubes, while chemical methods consist of covalent chemical bonding of polymer chains to the CNTs surfaces [1]. Using the chemical method, the higher accomplishment of dispersion and resultant composite properties than that of the other methods are possible, but it is a more time-consuming and expensive process than the other methods.

Lots of works have been carried out related to the improvement of the mechanical properties of CNTs-reinforced epoxy composites. In 2004, Gojny et al. [6] applied a shear mixing technique to disperse double-walled carbon nanotubes in epoxy resin, with results showing poor improvement of tensile strength and stiffness. In the following year, Song and Youn [7] reported the effects of different dispersions of CNTs on the rheological, mechanical, electrical, and thermal properties of epoxy nanocomposites. In this work, the authors used field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM) to characterize the dispersion. The dispersion states were altered depending on whether or not a solvent was employed. Seo and Park [8] studied the effect of the chemical treatment of multi-walled carbon nanotubes (MWNTs) on the glass transition temperature, thermal stability, and dynamic viscoelastic behaviors of the composites. The chemical treatment was carried out using 35 wt% H_3PO_4 and 35 wt% KOH. The acid (H_3PO_4) treated case showed higher thermal stability and viscoelastic properties than the treated and untreated base (KOH) samples. The mechanical dispersion method, using an ultrasonic liquid processor and a high-speed mechanical agitator, was selected to fabricate the composite specimens [9]. The case of 0.3 wt% CNTs-infusion showed the maximum strength enhancement. Untreated and acid-treated MWNTs were used to fabricate epoxy composite samples using the sonication technique [10]. The results of a tensile test showed higher Young's modulus values for the composite samples prepared using acid-treated MWNTs. Gkikas et al. [11] also showed the enhancement of thermo-mechanical and toughness properties of MWNTs-reinforced epoxy composites. An ultrasonic mixer was used to disperse CNTs into the epoxy resin. From the results of dynamic mechanical analysis (DMA) and fracture toughness, they verified the effect of the ultrasonic dispersion of CNTs. In 2014, Lee et al. [12] fabricated MWNT-reinforced

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epoxy composites by using the vacuum assisted resin transfer molding (VARTM) method. The mechanical properties, fracture surface morphologies, and thermal stabilities of the composites were evaluated with respect to the filler concentrations.

The linear coefficient of thermal expansion (CTE) was evaluated for investigation of the thermal stability of the hybrid composites, in which carbon nanofibers and silicon dioxide particles were used as filler materials [13]. Lavorgna et al. [14] reported that both the elastic and rubbery modulus increased with the addition of the MWNTs filler that was silanized and silica-enriched in epoxy composites. In particular, in the rubbery region, the storage modulus of composites with silanized and silica enriched MWNTs were about 240% and 285% higher, respectively, than that of neat epoxy.

The above literature review indicates that the mechanical dispersion of carbon nanotube filler is relatively less effective than chemical dispersion for enhancing the various properties of nanotube-reinforced composite. However, the mechanical dispersion method has a number of advantages, including being a simple, inexpensive, and environmentally sustainable process. In the present work, multi-walled-carbon-nanotube reinforced epoxy composites were fabricated using shear mixing and sonication. The concentrations of nanotube filler in the matrix were varied from 0 to 1.0 wt%. The mechanical and thermal properties of the specimens fabricated with this simple mechanical dispersion process were measured and evaluated.

II. Experimental Details

A. Materials and Composite Fabrication

YDF-161 (Bisphenol-F type) epoxy resin purchased from Kukdo Chemical Co., Ltd. (Seoul, South Korea) was chosen as the matrix. Based on the material data from the manufacturer, the viscosity and density of the epoxy resin were 5 ~7 Pa·s and 1.17 g/cm^3 at 25^{o}C, respectively. Jeffamine D-230 manufactured by Huntsman International LLC was used as a curing agent for the epoxy resin. The viscosity and density of the hardener were about 9·10^{-3} Pa·s and 0.948 g/cm^3 at 25^{o}C, respectively. Commercial grade multi-walled carbon nanotube, M90, from Carbon Nano-material Technology Co., Ltd. (Pohang, South Korea) was selected as a filler material to improve the various properties of the epoxy composite. Carbon nanotubes were used as received without any further purification. These carbon nanotubes had dimensions of 5□20 nm in diameter and about 10 μm in length, with an aspect ratio of more than 500. Composite samples were fabricated using YDF-161 resin along with the hardener at a weight ratio of 3:1. The carbon nanotubes were then added to the resin in appropriate amounts to reach the desired loadings, and were then dispersed in the resin using a shear mixer (PDM-300 Paste mixer, Dae Wha Tech. Co., Ltd., Yongin, South Korea) and an ultrasonic bath sonicator (WUC-A03H, Daihan Scientific Co., 100 W peak out, 40 kHz frequency, Seoul, South Korea). After mixing with the filler, a curing agent was added and mixed with the epoxy resin using a paste mixer. When the mixing of epoxy resin with the filler and hardener was completed, the resin mixture was poured into silicone molds and cured at 400 kPa pressure and room temperature for one day. This was followed by post curing in an oven at 80^{o}C for 6 hours. The detailed fabrication process is shown in Fig. 1.

Specimens having different filler loadings were prepared from baseline (that is, neat epoxy) to 1.0 wt% filler content specimens with respect to the total weight of the resin and the hardener. 115 mm-long and more than 4 mm-thick dog-bone shaped specimens fabricated following the standard test method (ASTM D638-10) were used in the investigation of the tensile strength and stiffness. Rectangular specimens (45 mm (L) x 10 mm (W)) of 3 mm thickness were fabricated and used to determine the coefficient of thermal expansion. The thermal conductivities were measured from the 25 mm-diameter circular specimens of 2 and 3 mm thickness.

B. Measurements

In this study, a field emission scanning electron microscope (FE-SEM, S-4700, Hitachi Ltd., in KBSI (Korea Basic Science Institute) Jeonju Center, Jeonju, South Korea) was used to qualitatively assess the dispersion of the nanotube filler in a matrix, using high and low magnified images. A tensile test, using a universal testing machine (RB 301 Unitech T, R&B Inc., Daejeon, South Korea), was also used to quantitatively assess the filler dispersion from the values and deviations of the tensile strengths and stiffnesses. It is well known that mechanical properties such as the tensile strength of well-dispersed specimens usually have relatively small deviation.

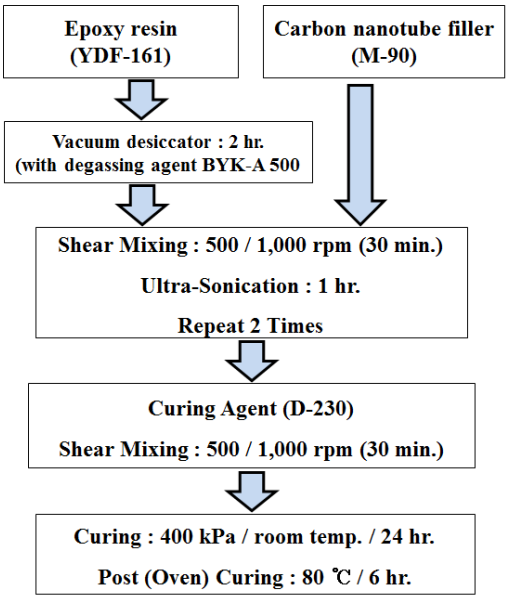

Fig. 1 Fabrication process of specimen

The coefficients of thermal expansion of the specimens were calculated from measured thermal strain differences divided by temperature differences. The thermal strains were measured using strain gages (CEA-13-240UZ-120, Micro-measurements) and a strain indicator (P3, Micro-measurements) using a half bridge connection. Also, the temperatures of the specimens

were measured using T-type thermocouples (TG-T-36-500, Omega Eng. Inc.) and an A/D converter (34970A, Agilent Technologies). Another thermal property, the thermal conductivity, was measured using a thermal conductivity measurement system (ThermoCon M100, Hantech Co., Ltd., Gunpo, South Korea) in accordance with the ASTM D5470 standard.

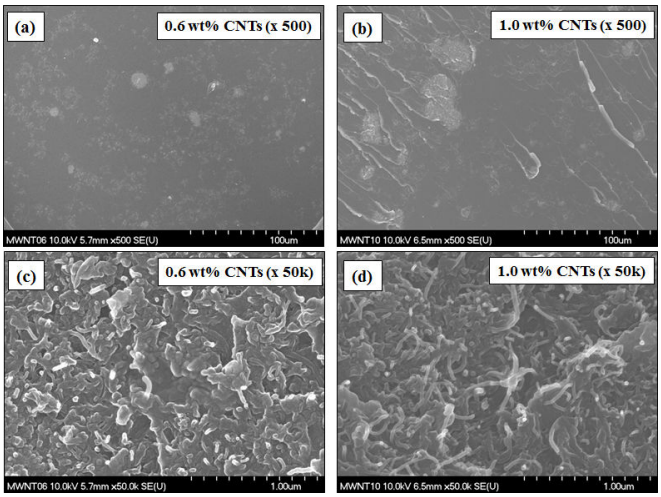

Fig. 2 SEM images of the fracture surfaces of specimens for 0.6 wt% ((a) and (c), images of the left hand side) and 1.0 wt% ((b) and (d), right hand side) silica filler concentrations

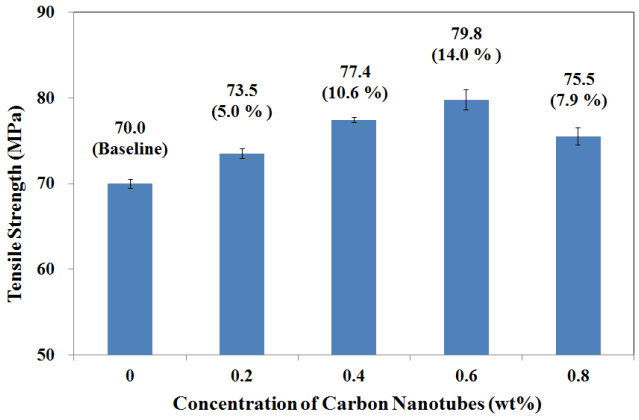

Fig. 3 Averaged tensile strengths and standard deviations with respect to the concentrations of carbon nanotube filler

III. Results and Discussion

The well-dispersion of the nanotube filler in the matrix is essential for the improvement of several properties of the composites. To assess the filler dispersion in the epoxy matrix, the fracture surfaces of the specimens that were cooled by the liquid nitrogen were magnified and are shown in Fig. 2. Figs. 2 (a) and (c) show 500 and 50,000 times magnified fracture surface images, respectively, of the specimen containing 0.6 wt% carbon nanotube filler. Figs. 2 (b) and (d) show the composite specimen having a 1.0 wt% nanotube filler. It is difficult to determine the dispersion status in the two lower, highly magnified, images. However, it is clear that the case of 0.6 wt% nanotube filler in Fig. 2 (a) shows better dispersion than the case of 1.0 wt% filler content shown in Fig. 2 (c). Fig. 2 (c) shows more and larger agglomerates of carbon nanotubes than those in Fig. 2 (a). Although the results are restricted to the fabrication process used in this study, from this qualitative result we believe that the specimen with 1.0 wt% nanotube has an excessive amount of nanotube filler.

Figs. 3 and 4 show the tensile strength and stiffness of the composite specimens, respectively. More than 5 specimens were tested in each case, and the data were averaged. Data labels in both figures are the strengths and moduli. The values in parentheses indicate a percentile increment with respect to those of baseline specimens. In the case of 0.6 wt% CNTs specimens, approximately 14% improvement in tensile strength is obtained with respect to the baseline, showing the highest tensile strength tested. The case of the 0.8 wt% CNTs specimens showed a lower strength than the case of the 0.6 wt% CNTs specimens, but was still higher than the baseline. As shown in Fig. 3, from the relatively small deviations with respect to the significant increments of strength, it is believed that the fabrication process of this study is sufficiently reliable. In contrast to the tensile strengths shown in Fig. 3, the Young's moduli shown in Fig. 4 demonstrates a tendency to increase from the baseline to the 0.8 wt% CNTs samples. The measured Young's modulus of the 0.8 wt% CNTs specimens is 3.11 GPa, which is 13.1% higher than that of the baseline samples.

Thermal strains with temperature increase were measured. The temperature increment was 1 ^{o}C per 3 minutes from room temperature to 67 ^{o}C. The temperature of the specimen surface and the thermal strain were measured and stored at one second increments using a data logger and computer. From these raw data, linear sections were selected from 30 to 50 ^{o}C to calculate the coefficients of thermal expansion. Three groups of thermal strain measurements were performed and the coefficients of thermal expansion (CTEs) were calculated. The CTEs were then averaged and normalized with respect to those of the baseline, as shown in Fig. 5. The specimens containing 0.4 wt% and 0.6 wt% CNTs show lower thermal expansions than those of the other specimens. A thermal stability enhancement of only 2.6% was obtained. While the strengthening of the cross-link of the epoxy composite with carbon nanotube filler may be helpful, the improved heat transfer of the specimen by the filler is detrimental to the thermal stability of the composite specimen. The competition between these two factors of positive and negative contributions to thermal stability might cause the small increase of thermal stability.

Thermal conductivity, another factor related to the thermal property of the composite, was measured and plotted as shown in Fig. 6. The averaged thermal conductivities of the specimens with 0.2, 0.4, 0.6, and 0.8 wt% of CNTs filler were measured to be around 0.27, 0.31, 0.36, and 0.33 $Wm^{-1}K^{-1}$, respectively, while the conductivity of the baseline was measured to be 0.22 $Wm^{-1}K^{-1}$. Similar to the result of tensile strength, the 0.6 wt% CNTs specimens show higher thermal conductivity than that of the other specimens. An improvement of thermal conductivity of about 64% with respect to that of the baseline was achieved with a nanotube filler of only 0.6 wt%.

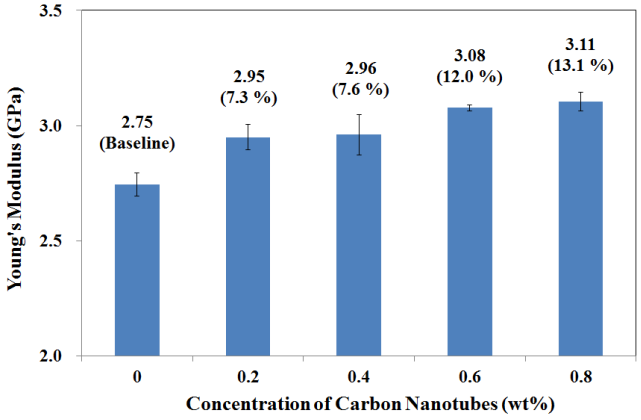

Fig. 4 Averaged Young's moduli and standard deviations with respect to the concentrations of carbon nanotube filler

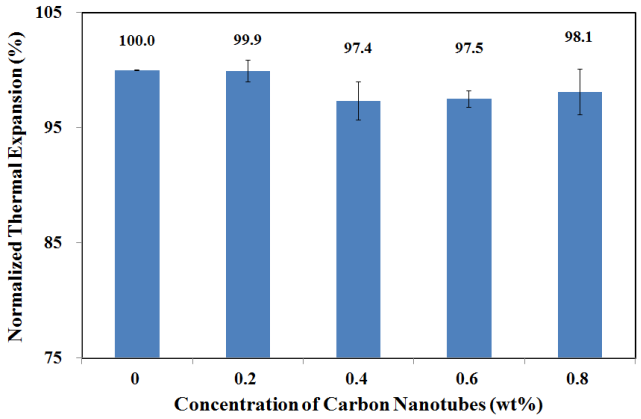

Fig. 5 Normalized coefficients of thermal expansion of specimens with concentrations of carbon nanotubes

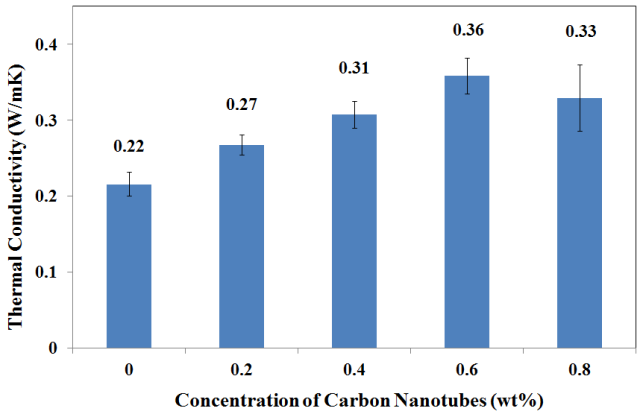

Fig. 6 Coefficients of thermal expansion of specimens with concentrations of carbon nanotubes

IV. Conclusion

In this experiment, epoxy composite specimens reinforced with multi-walled carbon nanotube filler were fabricated using shear mixer and ultra-sonication processor. The concentrations of the nanotube filler in the matrix were varied from 0 to 1.0 wt%. The mechanical and thermal properties of the fabricated specimens were measured and evaluated. On the basis of the images and the measured tensile strengths, the specimens having a nanotube content of 0.6 wt% show better dispersion and higher strength than those of the other specimens. The Young's moduli of the specimens were increased as the contents of nanotube filler in the matrix were increased. A higher thermal conductivity than that of the other specimens was measured for the specimen having 0.6 wt% nanotube filler content. In contrast, for the measurement of thermal expansion, lower values were measured than the other specimens for those having 0.4 and 0.6 wt% filler contents. Based on the measured and evaluated properties of the composites, it is believed that the simple and efficient fabrication process for the nanotube reinforced specimen proposed in this study was sufficient to obtain specimens with improved properties.

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