

Influence of Functionalization on Physicochemical Properties of Multi-walled Carbon Nanotubes/Epoxy Matrix Nanocomposites

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In this study, the effect of multi-step purification or functionalization on physicochemical properties of multi-walled carbon nanotubes (MWNTs)/epoxy (EP) nanocomposites was investigated. The nanocomposites containing multi-step purified MWNTs showed a stronger influence on T_g and increased in mechanical properties in comparison to nanocomposites containing the same amount of only purified MWNTs. Consequently, the multi-step purification of MWNTs led to an improvement of thermomechanical properties of nanocomposites, resulting from improving the intermolecular interaction of MWNTs in epoxy matrix resins.

Key Words: Multi-walled carbon nanotubes, Nanocomposites, Multi-step purification, Physicochemical properties

Introduction

Since Iijima's 1991¹ discovery of carbon nanotubes (multi-walled carbon nanotubes: MWNTs), research activity has focused mostly on the evaluation of MWNT properties themselves, MWNTs' high potential as nano-structured polymer composite filler, and their expected novel material properties. The unique mechanical properties of MWNTs, namely their high strength and stiffness and enormous aspect ratio make them a potential structural element for the improvement of (fracture-) mechanical properties.²⁻⁶ Further potential advantages of the use of MWNTs as ultimate polymer filler are their electrical and thermal conductivity together with their low density.⁷

Mechanical reinforcement of polymers by MWNTs can be realized only by solving two main problems: (i) dispersion of MWNTs and (ii) interfacial adhesion between the nanotubes and the matrix. The first experimental work focusing on the interfacial interaction in MWNT/epoxy nanocomposites was Cooper *et al.*'s.⁸ They investigated the detachment of MWNTs from an epoxy matrix. In a special pull-out test of individual MWNTs, the interfacial shear strength values were found to be in the 35-376 MPa range. Wagner⁹ also reported an interfacial shear strength value of 50 MPa. Further investigations on the nanotube/polymer interfacial interactions had been performed by Barber *et al.*¹⁰

The realization of MWNTs-reinforced epoxy requires, besides homogenous dispersion, strong interfacial interaction between the MWNTs and the polymer. We believe that MWNTs' effectiveness as reinforcing elements in tough epoxy matrices is hindered by weak interfacial interactions. As such, stress-induced deformation of composites would lead to failure of the MWNTs/epoxy interface, and finally to pull-out. Further enhancement of MWNTs' with composite materials possibly is achieved by chemical functionalization of their surfaces, through physical bonds to the polymeric matrix. These bonds will enable stress transfer between the polymer and the MWNTs, leading to improved

interfacial interactions, as qualitatively determined previously.

The nature of the interfacial zone accords with the microstructural characteristics of the reinforcing MWNTs, in which any of the three mechanisms, physical interaction, physical-chemical interaction or mechanical interlock, may be dominant, and in which the van der Waals forces of attraction are the primary binding forces at the interface.¹¹ Also having a significant influence on the fracture toughness of the interface is the surface roughness of the reinforcement.

This paper proposes a new method by which MWNTs can be homogeneously disperse in an epoxy matrix. In the present study, the influence of MWNT properties, especially the functionalization (or multi-step purification) effect, on the thermo-mechanical properties of MWNTs/epoxy matrix composites are investigated.

Experimental

Materials. Reinforcing MWNTs manufactured by the CVD process (degree of purity: < 90%, length: 10-50 μm , diameter: 10-20 nm) were supplied by Iljin Nanotech Co. of Korea. The matrix was an epoxy resin based on diglycidyl ether of bisphenol A (DGEBA, YD-128, Kukdo Chem. Co.), which had an epoxide equivalent weight of $187\text{g} \cdot \text{eq}^{-1}$ and a viscosity of about 5000 cps at 25°C. Diaminodiphenylmethane (DDM) was used as a hardener.

Sample preparation. The raw materials, in the course of a multi-step purification process, initially were first ultrasonicated and acidic-treated to disperse the MWNTs, after which they were immersed in 90°C bromine water for 3 h. Then, the residue was heated in air at 520°C for 45 min, followed by soaking in 5 mol/l hydrochloric acid at room temperature in order to remove the iron particles, finally, the sample was washed with de-ionized water, A 50 wt% yield being obtained after 12 h drying in an oven at 150°C.

The epoxy resin was mixed with 0.5 wt% of the purified

MWNTs. In order to achieve a homogeneous mixture, high-energy ultrasonication was performed at 60°C for 3 h. Then, a curing agent was added to the MWNTs/epoxy (MWNTs/EP) mixtures and stirred thoroughly. The mixtures were degassed to remove the bubbles, before being cast in a mold. The samples were cured for 2 h at 120°C, 2 h at 150°C, and 1 h at 200°C.

Characterization and measurements. The materials obtained before and after the bromination were characterized by high-resolution transmission electron microscopy (HRTEM) using a JEOL model 2010 TEM with 100 keV beam energy. The samples were prepared by adding methanol and dispersing the suspended tubes in an ultrasonic bath. After the ultrasonication, a drop of the suspension was placed on a microgrid and dried in air before the HRTEM observation. Post-fracture-test changes in the morphology of the MWNTs/EP composites were examined with reference to scanning electron micrographs (SEM), taken with a JEOL JSM-840A (5 keV beam energy).

The thermo-mechanical behavior was investigated by dynamic-mechanical thermal analysis (DMTA) using a TA Instruments SDT 2960. Preparatory to the investigation, rectangular specimens of 50 mm length, 5 mm width and 2 mm thickness were prepared. The tests analysis was performed in the tensile mode for a frequency of 10 Hz, a static strain of 0.6%, a dynamic strain of $\pm 0.1\%$, a 30-300°C temperature range, and a heating rate of 2°C/min.

In preparing sandwich-type specimens for Mode II, a thin layer of MWNTs with different surface properties was embedded at the required position in the epoxy matrix resins. The MWNTs/EP composites were then, according to conventional composite processing, 7.4 MPa hot-pressed at 150°C for 3 h with a vacuum bagging method. By selecting differently sized the composite specimens, the interface size was varied. The length-to-depth ratio was 2.0. The thickness of each specimen was 80 mm. Double-edge notches were made in the compact-tension specimens by diamond saw cut. The failure surface area of the interface was used to calculate the strength of interface in both tension and shear. The bond strength was calculated as the failure load divided by the interfacial area. Direct shear loading was applied in two-way shear in Mode II failure, which was conducted on a united test machine (Instron Model 1125 mechanical test-

er). All of the bond-strength-in-shear values were obtained by averaging five experimental values.

Results and Discussion

Morphology. Figure 1 presents HRTEM images of the raw materials, the purified samples without bromination and those with bromination, respectively. The diameters of the MWNTs in the images range from 5 to 20 nm. The raw material contains numerous MWNTs, but also significant amounts of iron particles, amorphous carbon and multishell carbon nanocapsules. As a result of purification without bromination, the purity of the MWNTs, as is apparent in Figure 1(b), is improved, though some metal particles, amorphous carbon, and multishell carbon nanocapsules remained in the sample. There is almost no trace of those metal particles, amorphous carbon-, or multishell carbon nanocapsules, however, after purification with bromination, which indicates, as in Figure 1 (c), the high efficiency of the process.

The material properties of polymers are known to be improved by the addition of MWNTs.¹¹ This focus on mechanical properties' improvement has led to two common, key issues for investigation: (a) dispersion and (b) interfacial adhesion. In the present study, suspending the MWNTs directly in the hardener by sonication produced an advanced

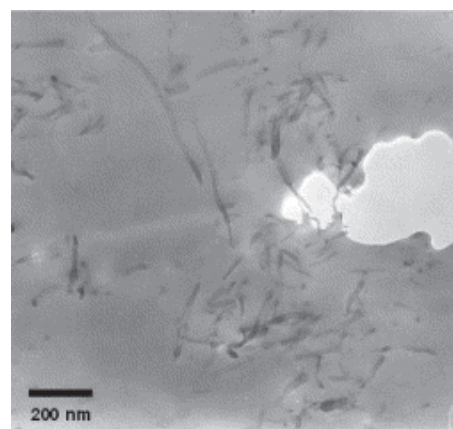


Figure 2. HRTEM image of dispersion of bromo-functionalized MWNTs in epoxy matrix resins.

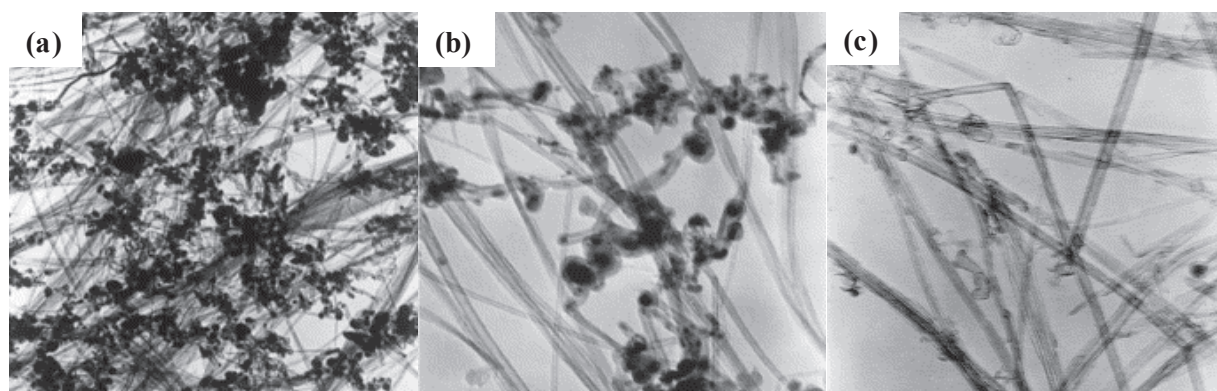


Figure 1. HRTEM images of (a) as-received MWNTs, (b) purified MWNTs without bromination, and (c) purified MWNTs with bromination.

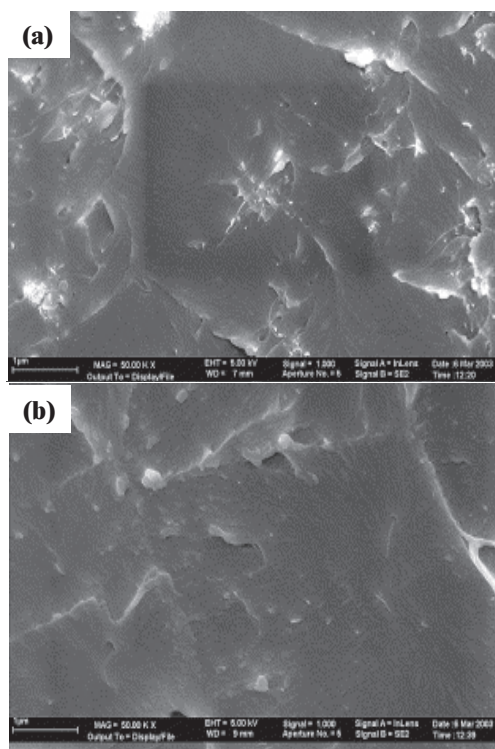


Figure 3. SEM-images of fracture surfaces of MWNTs/EP composites with (a) and without (b) 0.5 wt% bromo-functionalized MWNTs.

dispersion. Long-chained polar solvents seemed to have interacted strongly with the MWNTs, especially once functionalized, and to have stabilized the suspension. A qualitative TEM investigation revealed, in the case of functionalized MWNTs, the absence of agglomerates, and for the non-functionalized ones, a reduction in the agglomerates' dimensions.

Figure 2 shows the observed dispersion in a representative section of a sample containing functionalized MWNTs. The importance of a homogeneous dispersion can be deduced from the pattern of the fracture surfaces of the two samples each containing 0.5 wt% functionalized MWNTs (Figures 3(a) and (b)). The dispersion of the MWNTs in sample (3(a)) is achieved by sonication in acetone, mixing the suspension with the epoxy resin and evaporating the solvent, whereas sample (3(b)) is prepared as described in the "Experimental" section. The MWNTs in sample (3(b)) are randomly distributed. As apparent in Figure 3(a), the fracture surface has a hexagonal pattern and still contains small agglomerates. Agglomerates are always located in hexagons' center, from which cracks begin to propagate and, finally initiate failure. The observed fracture pattern reveals the agglomerates' initiation of the failure. The samples manufactured by our method neither show agglomerates nor the kind of fracture pattern that evidences an initiation of failure.

Thermo-mechanical properties. The tensile elastic (storage) modulus and the damping properties of the nanocomposites were investigated by DMTA. The tests were performed in order to evaluate the influence of MWNTs on the mechanical properties of nanocomposites in general and especially, to confirm the relevance of MWNT functional-

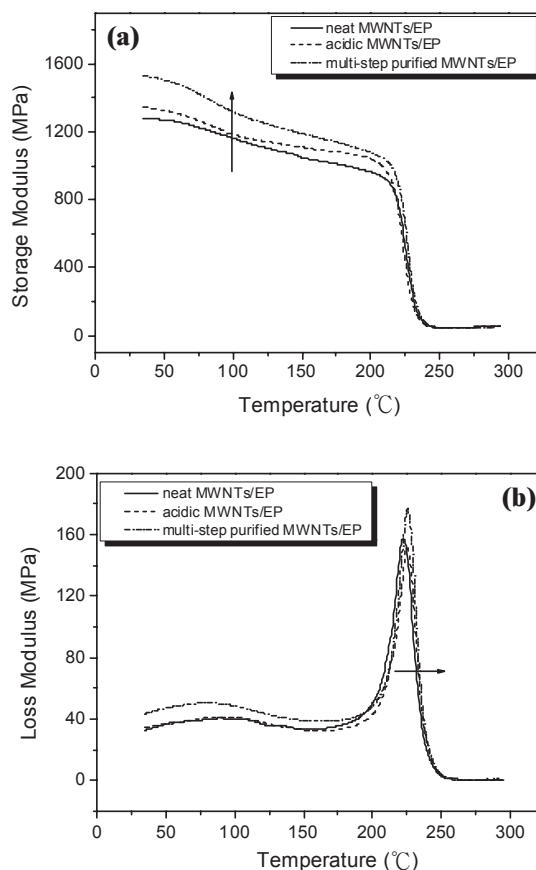


Figure 4. Storage (a) and loss modulus (b) of multi-step purified 0.5 wt% MWNTs/EP composites.

ization. Figures 4(a) and (b) show the dynamic measurements of the storage modulus and loss factor as a function of temperature. The addition of both MWNT types (bromo-functionalized and non-functionalized) to the epoxy resin does show any influence of the MWNT content on the storage modulus in the glassy region as well as in the rubbery region. The addition of the MWNTs improves the elastic properties of the epoxy system at elevated temperatures. Particularly, at temperature close to or higher than the glass transition temperature (T_g) of the nanocomposites, indicated by a peak in the loss modulus, the presence of more MWNTs is able to impart greater stiffness to the polymer matrix.¹² This behavior can be explained by reference to the interaction between the MWNTs and the epoxy resins as a result of the enormous surface area.^{13,14} This interfacial interaction reduces the mobility of the epoxy matrix around MWNTs and leads to the observed increase in thermal stability. This effect will appear basically around and above T_g , due to the limited potential movement of the polymeric matrix below. A strong increase of the storage modulus, especially below T_g cannot have been expected for the MWNT contents used in this study. The load transfer only is performed between the outermost layers of MWNTs and the epoxy matrix, resulting in a much lower effective content of reinforcing MWNTs.

Increasing numbers of MWNTs result in glass transition temperature shift. In the present study, the T_g is shifted from

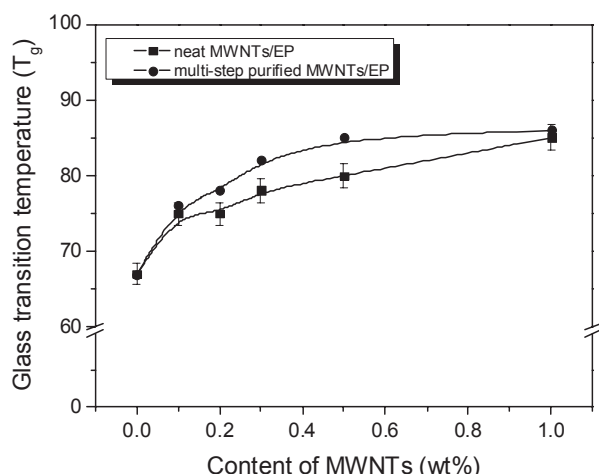


Figure 5. Glass transition temperature of multi-step purified MWNTs/EP composites as a function of MWNT content.

64°C for the neat resin, to 80°C for samples containing 0.5 wt% MWNTs, and to 83°C for samples containing 0.5 wt% bromo-functionalized MWNTs. This gain in thermostability can again be interpreted as a reduction of the mobility of the epoxy matrix around the MWNTs, resulting from the interfacial interactions. Improved interaction between MWNTs and the epoxy matrix should lead to a stronger shift of the glass transition temperature. Bromo-functionalized MWNTs are supposed to react with the epoxy resin, forming physical bonds. For samples containing the functionalized MWNTs, a stronger increase of the T_g , along with an almost linear dependence on the MWNT content, can be observed. The data shown in Figure 5 represent the maxima of the loss modulus acquired from the dynamic measurements. We estimate the physical bonds between the bromo-functions on the surface of the MWNTs and the epoxy matrix will reduce the matrix mobility, which expresses itself in a strong shift of T_g .

Mechanical interfacial properties. Composites are three-phase heterogeneous materials with matrix resins, reinforcement or filler, and an interface between them.¹⁵ The effectiveness of composites' load transfer mechanisms depends on the degree of interaction of the various phases, the strength of matrix resins, and the characteristics of the reinforcing and cohesive forces at the interface. The contribution of coarse reinforcement in transferring stresses in high-performance composites is very important. Microcrack

formation and crack growth at the interface are significantly influenced by the bond strength and fracture toughness.¹⁶ Since the matrix resins-reinforcement interface in high-performance composites is stronger, cracks transmit into the reinforcement. Moreover, the properties of the interfacial regions, that is, the fiber-matrix or filler-matrix, are central to the performance of those high-performance composites. The development of bond strength is intimately related to the nature of these interfacial zones.

Table 1 lists the bond-strength-in-shear (Mode II) results for the MWNTs/EP composites with purified MWNTs. The bond shear strengths of the interface with neat MWNTs/EP composites against the 0° and 10° inclinations are 0.8 and 1.7 MPa, respectively. These values are 2.1 and 2.8, respectively, with the multi-step purified MWNTs/EP composites. Further, it has been observed that the shear strength also increases as the inclination of the interface increases, leading to a higher shielding effect of the MWNTs. That is, higher values of shear strength have been observed for the combination of rougher surfaces and higher phase angles.¹⁷ The results clearly indicate that surface properties of MWNTs significantly influence the type of bond formed in the interface, and that the bond-strength-in-shear values in multi-step purified MWNTs/EP composites are higher than in composites with only purified MWNTs/EP and pure epoxy resins.¹⁸⁻²⁰ Therefore, it is to be noted that the interfacial fracture energy markedly increases as the loading phase, that is, the shear effect, increases. This increase has been attributed to the shielding effects at the interfaces with increased shear loading. In the present study, consequently, the maximum value of the bond strength in shear is obtained by addition of multi-step purified MWNTs. Therefore, we suggest that the additional energy needed to extend the interfacial crack under this condition can be attributed to increased interfacial adhesion between the reinforcement and the matrix resins.

Conclusions

In the present study, nanocomposites consisting of MWNTs (functionalized and non-functionalized MWNTs) and epoxy matrices were produced by a multi-step purification technique. The experimental results revealed the possibility of achieving homogeneous dispersion by MWNT suspension in a curing agent, which seems to stabilize the

Table 1. Experimental observation of bond strength of interface under Mode II loading conditions in sandwich-type multi-step purified 0.5 wt% MWNTs/EP composites

| Specimens | Inclination of surface (°) | Contact area (mm ²) | Shear force at failure (kN) | Bond strength in shear (MPa) |
|---------------------|----------------------------|---------------------------------|-----------------------------|------------------------------|
| Neat MWNTs/EP | 0 | 10,560 | 8.30 | 0.8 |
| | 10 | 9,392 | 12.10 | 1.7 |
| Acidic MWNTs/EP | 0 | 9,520 | 14.00 | 1.5 |
| | 10 | 10,024 | 22.00 | 2.0 |
| Multi-step MWNTs/EP | 0 | 10,348 | 20.00 | 2.1 |
| | 10 | 11,312 | 40.00 | 2.8 |

MWNT suspension. Functionalized MWNTs seem to strongly interact with an amine curing agent, which expressed itself in the absence of agglomerates in final composites. The addition of MWNTs to nanocomposites resulted in a general increase in thermal stability. This effect arose from MWNTs' reduction of the mobility of the matrix by means of interfacial interactions. The distinctive increase of the glass transition temperature of nanocomposites containing functionalized MWNTs was linearly accords with the MWNT content. The different behaviors of the two series of samples, bromo-functionalized and non-functionalized, were further evidence of the influence of chemical functionalization of MWNT surfaces on interfacial adhesion between MWNTs and epoxy resins.

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