Nondestructive Damage Sensitivity for Functionalized Carbon Nanotube and Nanofiber/Epoxy Composites Using Electrical Resistance Measurement and Acoustic Emission

Dae-Sik Kim*, Joung-Man Park*,†, and Tae-Wook Kim**

전기저항 측정과 음향방출을 이용한 표면 처리된 탄소 나노튜브와 나노 섬유 강화 에폭시 복합재료의 비파괴적 손상 감지능

김대식*·박종만*,†·김태욱**

KEY WORDS: carbon nanocomposites, electrical sensitivity, damage sensing, functionalization, percolation threshold, apparent modulus

ABSTRACT

Nondestructive damage sensing and mechanical properties for acid-treated carbon nanotube (CNT) and nanofiber (CNF)/epoxy composites were investigated using electro-micromechanical technique and acoustic emission (AE). Carbon black (CB) was used to compare to CNT and CNF. The results were compared to the untreated case. The fracture of carbon fiber was detected by nondestructive acoustic emission (AE) relating to electrical resistivity under double-matrix composites test. Sensing for fiber tension was performed by electro-pullout test under uniform cyclic strain. The sensitivity for fiber damage such as fiber fracture and fiber tension was the highest for CNT/epoxy composites. Reinforcing effect of CNT obtained from apparent modulus measurement was the highest in the same content. For surface treatment case, the damage sensitivity and reinforcing effect were higher than those of the untreated case. The results obtained from sensing fiber damage were correlated with the morphological observation of nano-scale structure using FE-SEM. The information on fiber damage and matrix deformation and reinforcing effect of carbon nanocomposites could be obtained from electrical resistivity measurement as a new concept of nondestructive evaluation.

Nomenclature

ER	: Electrical resistance
$\Delta\rho$	: Change in electrical resistivity
ρ_v	: Electrical volume resistivity
ρ_c	: Electrical contact resistivity
L_{ec}	: Voltage contact length
A	: Area

*Department of Polymer Science and Engineering
Engineering Research Institute
Gyeongsang National University
** Composite Materials Group
Korea Institute of Machinery and Materials
†To whom correspondence should be addressed.
E-mail: jmpark@nongae.gsnu.ac.kr

1. INTRODUCTION

Carbon nanocomposites have high stiffness, strength and good electrical conductivity at relatively low concentrations of reinforcing materials [1]. Electrical and mechanical properties of carbon nanomaterial (CNM) reinforced polymer composites depend on many factors such as inherent properties of CNM, the degree of dispersion, orientation, interfacial adhesion, aspect ratio, fiber shape and content, etc [2]. Especially, the degree of dispersion is well known as one of the most important factors in electrical properties [3]. To provide a conductive path throughout CNM, three-dimensional network of conductive reinforcements is needed, which is known as percolation structure [4]. The percolation threshold, the critical concentration for percolation structure of CNT and CNF is much lower than that of particulate conductive filler such as CB and metal power, etc. The experimentally observed percolation threshold values strongly depend on the aspect ratio of the reinforcement. CNT and CNF have high electrical conductivity and large aspect ratio. CNT and CNF reinforced polymer composites are expected that low percolation threshold can be obtained compared with CB.

The electro-micromechanical technique had been studied as an economical and new nondestructive evaluation (NDE) method for damage sensing, characterization of interfacial properties, and nondestructive behavior because conductive fiber can act as a sensor in itself as well as a reinforcing fiber [4]. The nondestructive damage sensitivity and reinforcing effect was studied for functionalized CNT and CNF/epoxy composites with their content using electrical resistance measurement and AE.

2. EXPERIMENTAL

2. 1. Materials

CNT (Iljin Nanotech Co., Korea) and CNF (SDK Co., Japan) as reinforcing and sensing materials were used and their average diameters were 20 nm and 150 nm. CB (Korea Carbon Black Co, Korea) was used to compare to CNT and CNF. Carbon fiber (Taekwang Co., TZ-307, Korea) with average diameter of 8 μm was used as a reinforcement and epoxy resin (YD-128, Kukdo Chemical Co., Korea) based on diglycidyl ether of bisphenol-A was used as a matrix. Flexibility of the epoxy matrix was controlled by changing the ratio of Jeffamine (polyoxypropylene diamine, Huntsman Petrochem. Co.) D400 *versus* D2000 in the curing mixture.

2.2. Methodologies

2.2.1. Specimen Preparation: Surface of CNM was treated to improve interfacial adhesion and the degree of dispersion by hydrochloric-nitric acid for 20 minutes. Double-matrix composite (DMC) test was performed to sense fiber fracture through conductive inner matrix embedded carbon fiber. Figure 1 shows the dispersion process for preparation carbon nanocomposites. CNF, CNT and CB were mixed into epoxy matrix to make homogenous conductive inner matrix using ultrasonic (Crest Co, Germany). The intersecting point between copper wire and carbon fiber was connected electrically with a silver paste. In DMC test, conductive inner matrix embedded carbon fiber was fixed in the silicone mold. After epoxy mixture was poured into the mold, epoxy was procured at 80°C for 2 hours and then postcured at 120°C for 2 hours. DMC specimens were tested tensilely by universal testing machine (UTM, LR-10K, Lloyd Instrument Ltd., U.K.) with 10 kN load cell and the crosshead speed of 0.25 mm/minute. The fracture surface of carbon nanocomposites was observed using field emission-scanning electron microscope (FE-SEM, XL-30SF, Philips Co.) and their morphological observations were correlated with results of the electrical properties.

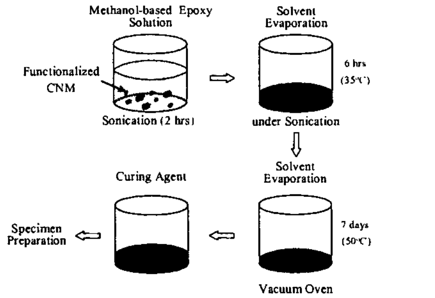

Fig. 1 Dispersion process for carbon nanocomposites.

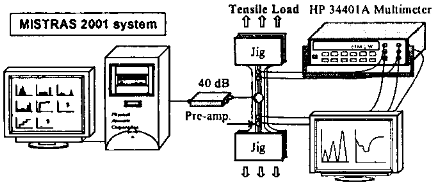

Fig. 2 Schematic illustration for measuring electrical resistivity and AE system.

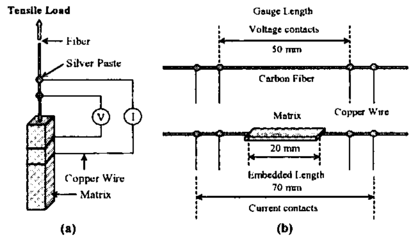

Fig. 3 Schematic figures for (a) electro-pullout and (b) cyclic loading test.

2.2.2. Measurement of Electrical Resistivity: Figure 2 shows the scheme for the electrical resistance measurement in DMC test. Under tensile loading, the electrical resistance was measured using a digital multimeter (HP34401A). The change in electrical resistance (ΔR) for fiber fracture was measured relating to acoustic emission (AE, MISTRAS 2001 System, Physical Acoustics Co.) parameters. Figure 3 shows experimental schemes for (a) electro-pullout and (b) cyclic loading tests. ΔR for fiber tension was measured through conductive matrix during electro-pullout test. The reinforcing effect was measured indirectly by apparent modulus using cyclic loading test. For electro-pullout and cyclic loading tests, strain-stress curve was measured by mini-UTM (Hounsfield Test Equipment

Ltd., U.K.). Testing speed and load cell were 0.5 mm/minute and 100 N, respectively. After a testing specimen was fixed into the UTM grip, the composite and the multimeter were connected electrically using a very thin copper wire. While 5 cyclic loads were applied, the electrical resistance of the microcomposites was measured simultaneously with stress/strain changes. Electrical resistivity was obtained from the measured electrical resistance, cross-sectional area of the conductive fiber, A, and electrical contact length, L_{ec} of the testing fiber connecting to copper wire. The relationship between electrical volume resistivity, ρ_v and resistance, R_v is as follow:

$$\rho_v = \left(\frac{A_v}{L_{ec}}\right) \times R_v \quad (\Omega \cdot cm) \qquad (1)$$

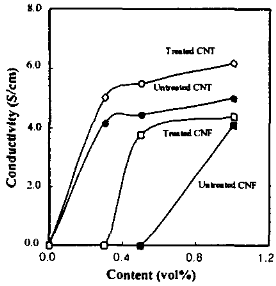

Fig. 4 Electrical conductivity for carbon nanocomposites with treatment condition

3. RESULTS AND DISCUSSION

3.1. Nondestructive Fiber Damage Sensing: Figure 4 shows electrical conductivity of matrix with CNM content and treatment conditions. Electrical conductivity and percolation threshold of surface treated CNT/epoxy composites were lowest in the same volume content. In the surface treatment case electrical conductivity decreased compared to the untreated case. It might be because the degree of dispersion was improved. Figure 5 shows sensitivity of fiber fracture for the untreated (a) 0.1 vol% CNT, (b) 2 vol% CNT, (c) 2 vol% CNF and (d) 7 vol% CB in DMC test. When the first fiber fracture occurred, electrical resistance (ER) increased infinitely because matrix was electrically insulator shown in Figure 4(a). In case of CNT composite, the sensitivity for carbon fiber fracture relating to AE signals was higher than that of CNF and CB cases, and ER was lower. It could be because electrical contact point of CNT with high aspect ratio was much more than that of CNF and CB. ER increased like stepwise with progressing fiber fracture due to maintaining electrical contact by CNT. And then they increased gradually because of occurring matrix deformation. Figure 6 shows FE-SEM photographs for fracture surface of the untreated CNM/epoxy composites. The electrical contact point of CNT was more than CNF and CB cases. The morphological trends were consistent with the results of ER.

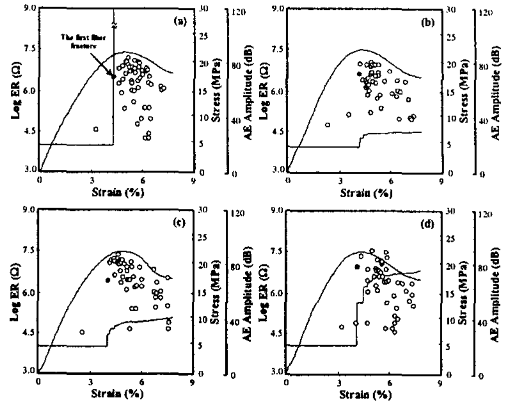

Fig. 5 Sensitivity for fiber fracture of the untreated (a) 0.1 vol% CNT, (b) 2 vol% CNT, (c) 2 vol% CNF and (d) 7 vol% CB under DMC test.

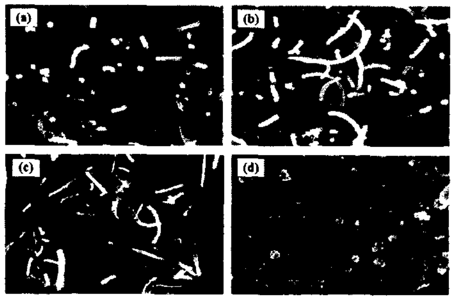

Fig. 6 FE-SEM photographs for the untreated (a) 0.5 vol% CNT, (b) 2 vol% CNT, (c) 2 vol% CNF and (d) 7 vol% CB in epoxy matrix.

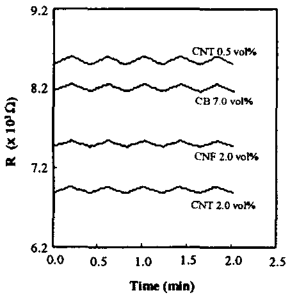

Fig. 7 The scale of ER for fiber tension with CNM type and the content under electro-pullout test.

Figure 7 shows the scale of ΔR for fiber tension with CNM type and the content under electro-pullout test. The change in stress and strain was corresponded with ΔR in high CNM content. The result may indicate that fiber damage and matrix deformation can be detected by epoxy matrix added conductive CNM. In case of the low CNM content, stress and strain was not reversible for ΔR

because they were electrically insulator. Electrical resistance of 2 vol% CNT was lowest due to lower electrical volume resistivity, whereas 0.5 vol% CNT case was highest in the electrically conductive nanocomposites. In the same volume fraction, damage sensitivity of carbon fiber tension for CNT composite was highest and the result was consistent with trend under DMC test.

3.2. Reinforcing Effect: Figure 8 shows (a) tensile strength and (b) modulus of carbon nanocomposites with CNM type and content. For 2.0 vol% CNT composite, tensile strength improved about 50 percents and modulus increased about two times compared with neat epoxy. In case of CNF they were rather lower than those of CNT, whereas they were much lower in CB case. Mechanical properties of carbon nanocomposites obtained from tensile test were highest in CNT adding case. CNT in epoxy matrix may be entangled easily because the aspect ratio and specific surface area of CNT are largest among three CNMs.

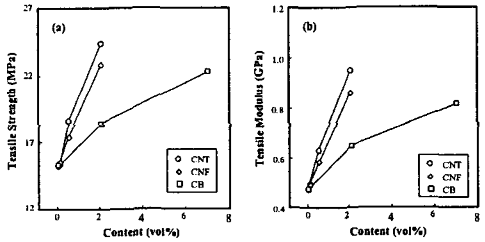

Fig. 8 (a) tensile strength and (b) modulus of carbon nanocomposites with CNM type and content.

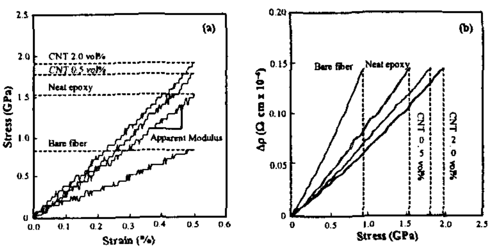

Fig. 9 (a) Stress-strain and (b) $\Delta\rho$-stress curves for carbon nanocomposites by uniform cyclic strain test.

Reinforcing effect of carbon nanocomposites with their types and contents could be measured indirectly by the electrical resistance measurement of carbon fiber embedded in carbon nanocomposites. Apparent modulus means the fiber modulus embedded in the matrix from stress-strain curve comparing with the modulus of carbon bare fiber in itself [5,6]. Figure 9 shows (a) stress-strain and (b) $\Delta\rho$-stress curve of CNT/epoxy composite with CNT content. The slope of curve was apparent modulus that increased with improving matrix modulus. Apparent modulus of 2.0 vol% CNT composite with high modulus was higher than that of neat epoxy. The apparent modulus was consistent with the change in electrical resistivity ($\Delta\rho$) value.

4. CONCLUSIONS

Electro-micromechanical techniques were applied to obtain the fiber damage and reinforcing effect of carbon nanocomposites with their content. Electrical conductivity and percolation threshold of surface treated CNT/epoxy composites was lowest in the same volume content. The sensitivity for fiber damage such as fiber fracture, matrix deformation and fiber tension was highest for CNT composite, and for CB case they were lowest compared to CNT and CNF. For CNT added case mechanical properties and apparent modulus indicating the reinforcing effect were highest among three CNMs. Morphological trends were consistent well with the result of damage sensitivity based on electrical properties. The new information on fiber damage and matrix deformation and reinforcing effect of carbon nanocomposites could be obtained from the electrical resistance measurement as a feasibly new concept of the nondestructive evaluation.

ACKNOWLEDGMENT: This work was financially supported from CNMT of the 21st C Frontier R&D program (NM02-1201-001-1-0-2) by Ministry of Science and Technology (MST), through Engineering Research Institute (ERI), Gyeongsang National University (GNU), Korea.

REFERENCES

(1) R. B. Pipes and P. Hubert, *Compos. Sci. & Technol.*, 62, 2002, pp. 419-428.

(2) H. Bubert, S. Haiber, W. Brandl, G. Marginean, M. Heintze, and V. Brüser. *Diamond Related Mater.*, 2003 (in press).

(3) C. Park, Z. Ounaies, K. A. Watson, R. E. Crooks, Jr J. Smith, S. E. Lowther, J. W. Connell, E. J. Siochi, J. S. Harrison, and T. L. St. Clair. *Chem. Phys. Lett.*, 364, 2002, pp. 303-308.

(4) J. F. Feller, I. Linossier, Y. Grohens. *Mater. Lett.*, 57, 2002, pp. 64-71.

(5) S. Wang, S. I. Lee, D. D. L. Chung and J. M. Park, *Compos. Interf.*, 8(6), 2001, pp. 435-441.

(6) J. M. Park, S. I. Lee and J. R. Lee, *47th Int. SAMPE Sym.*, Long Beach, CA, U.S.A., 47, 2002, pp. 12-16.