Nondestructive Damage Sensitivity of Carbon Nanotube and Nanofiber/Epoxy Composites Using Electro-Micromechanical Technique and Acoustic Emission

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

Electro-Micromechanical 시험법과 음향방출을 이용한 탄소 나노튜브와 나노섬유 강화 에폭시 복합재료의 비파괴적 손상 감지능

김대식* · 박종만*,† · 이재락** · 김태욱***

KEY WORDS: carbon nanocomposites, electrical sensitivity, damage sensing, uniform cyclic strain test electrical contact resistivity, apparent modulus

ABSTRACT

Electro-micromechanical techniques were applied using four-probe method for carbon nanotube (CNT) or nanofiber (CNF)/epoxy composites with their content. Carbon black (CB) was used to compare with CNT and CNF. The fracture of carbon fiber was detected by nondestructive acoustic emission (AE) relating to electrical resistivity for 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, and in CB case they were the lowest compared with CNT and CNF. Reinforcing effect of CNT obtained from apparent modulus measurement was the highest in the same content. 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
**Advanced Material Davison
Korea Research Institute of Chemical Technology
*** Composite Materials Group
Korea Institute of Machinery and Materials
† To whom correspondence should be addressed.

1. INTRODUCTION

Recently, carbon nanomaterials (CNM) such as carbon nanotube (CNT) and nanofiber (CNF) reinforced polymeric matrix composites have attracted with considerable attention in the research and industrial field due to their unique mechanical and electrical properties [1-5]. Carbon nanocomposites have high stiffness, strength and good electrical conductivity at relatively low concentrations of reinforcing materials [6,7]. 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 [8,9]. Nondestructive damage sensitivity and reinforcing effect was studied for carbon nanocomposites with their content using electrical resistance measurement and acoustic emission (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. Carbon black (CB, Korea Carbon Black Co, Korea) was used to compare with 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.

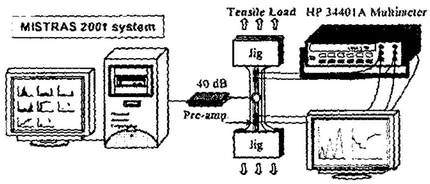

Fig. 1 Schematic illustration for measuring electrical resistivity and AE system.

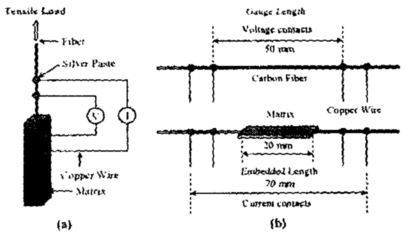

Fig. 2 Schematic figures for (a) electro-pullout and (b) cyclic loading test.

2.2. Methodologies

2.2.1. Specimen Preparation: Double-matrix composite (DMC) test was performed to sense fiber fracture through conductive inner matrix embedded carbon fiber. CNF, CNT and CB were mixed into epoxy matrix to make homogenous conductive inner matrix using ultrasonic. Selected three CNM contents were 0.1, 0.5, 2 and 7 vol% for the comparison. 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-30 SF, Philiphs Co.,) and their morphological observations were correlated with results of the electrical sensitivity.

2.2.2. Measurement of Electrical Resistivity: Figure 1 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 of electrical resistivity (Δρ) for fiber fracture was measured relating to acoustic emission (AE, MISTRAS 2001 System, Physical Acoustics Co.) parameters. Figure 2 shows experimental schemes for (a) electro-pullout and (b) cyclic loading tests. Δρ 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:

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

The electrical contact resistivity, ρ_c is as follow:

$$\rho_c = A_c \times R_c \quad (\Omega \cdot cm^2) \qquad (2)$$

where, A_c and R_c are electrical contact area and resistance, respectively.

3. RESULTS AND DISCUSSION

3.1. Nondestructive Fiber Damage Sensing: Figure 3 shows ρ_v of matrix with CNM content. ρ_v of CNT/epoxy composites was the lowest in the same volume content. Figure 4 shows sensitivity of fiber fracture for (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 5 shows FE-SEM photographs for fracture surface of carbon nanocomposites. The electrical contact point of CNT was more than CNF and CB cases. The morphological trends were consistent well with the results of ER.

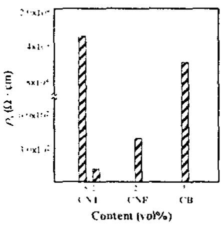

Fig. 3 Electrical volume resistivity for CNM/epoxy composites.

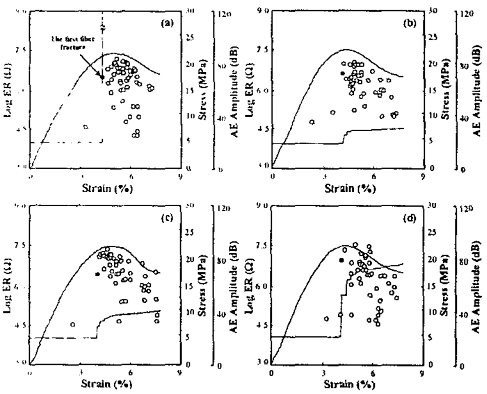

Fig. 4 Sensitivity for fiber fracture of carbon nanocomposites for (a) 0.1 vol% CNT, (b) 2 vol% CNT, (c) 2 vol% CNF and (d) 7 vol% CB in DMC test.

Figure 6 shows $\Delta\rho_c$ for fiber tension of carbon nanocomposites using electro-pullout test. The stress and strain was corresponded well with $\Delta\rho_c$ in high CNM content. The results 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 $\Delta\rho_c$ because they were electrically insulator. Figure 7 shows scale of $\Delta\rho_c$ for fiber tension in electro-pullout test. ρ_c of 2 vol% CNT was the lowest due to low ρ_v and 0.5 vol% CNT case was the highest in the electrically conductive nanocomposites.

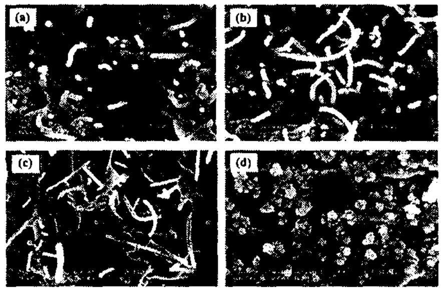

Fig. 5 FE-SEM photographs for (a) 0.5 vol% CNT, (b) 2 vol% CNT, (c) 2 vol% CNF and (d) 7 vol% CB in epoxy matrix.

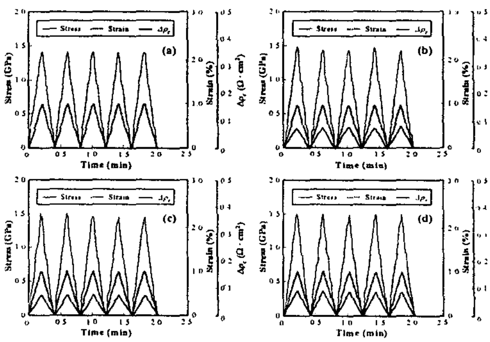

Fig. 6 Sensitivity of fiber tension for (a) 0.1 vol% CNT, (b) 2 vol% CNT, (c) 2 vol% CNF and (d) 7 vol% CB.

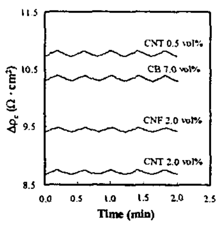

Fig. 7 $\Delta\rho_c$ for fiber tension in electro-pullout test.

3.2. Reinforcing Effect: Figure 8 shows the change in stress for (a) carbon bare fiber, (b) neat epoxy, (c) 0.5 vol% CNT, and (d) 2 vol% CNT under uniform cyclic strain test. The maximum stress of carbon bare fiber was the lowest. As CNT content increased, the maximum stress increased gradually. Figure 9 shows stress-strain and Δρ-stress curves for carbon bare fiber, neat epoxy and CNT/epoxy composites. The slope in curves was apparent modulus that increased with improving matrix modulus. The apparent modulus means the fiber modulus embedded in the matrix in stress-strain curve comparing to the carbon bare fiber modulus in itself [10]. Reinforcing effect of CNT obtained from apparent modulus measurement was the highest compared with CNF and CB in the same volume content. It may be because specific gravity of CNT was the lowest. In the same volume percentage, weight percentage of material with low specific gravity was higher. Figure 10 shows apparent modulus for carbon nanocomposites with their content. For both CNT and CNF cases, apparent modulus increased rapidly with increasing their content, whereas in CB case apparent modulus increased slowly. Apparent modulus of 7 vol% CB was similar to 2 vol% CNF case. For CNT reinforced composites, the reinforcing effect might be the highest among three CNMs.

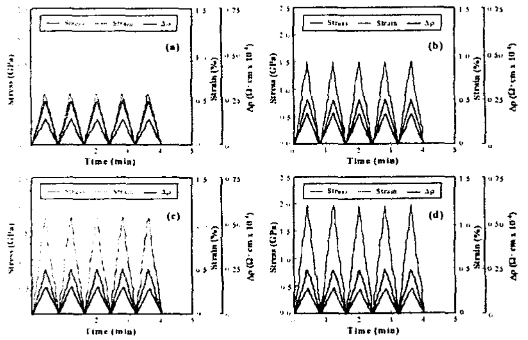

Fig. 8 The change in stress for (a) carbon bare fiber, (b) 2 vol% CNT, (c) 2 vol% CNF and (d) 7 vol% CB under uniform cyclic strain test.

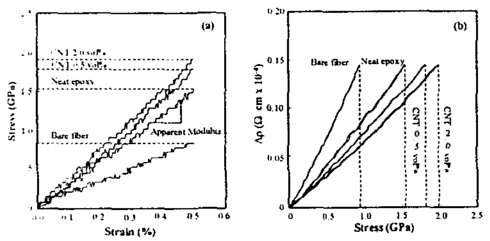

Fig. 9 (a) Stress-strain and (b) Δρ-stress curves for carbon nanocomposites by uniform cyclic strain test.

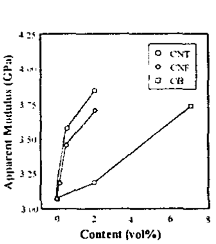

Fig. 10 Apparent modulus for carbon nanocomposites.

4. CONCLUSIONS

Electro-micromechanical techniques were applied to obtain the fiber damage and reinforcing effect of carbon nanocomposites with their content. The sensitivity for fiber damage such as fiber fracture and fiber tension was the highest for CNT composites, and for CB case they were the lowest compared to CNT and CNF. Sensitivity for fiber damage in CNT or CNF composites was almost same in high content, whereas in low content that of CNT composite was higher because of their high aspect ratio and low specific gravity. Apparent modulus indicating the reinforcing effect of CNT composites was the highest among three CNMs. In this work, new information on fiber damage and matrix deformation and reinforcing effect of carbon nanocomposites could be obtained from the electrical resistivity measurement as a feasibly new concept of the nondestructive evaluation.

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

REFERENCES

(1) A. Allaoui, S. Bai, H. M. Cheng and J. B. Bai, *Compos. Sci. & Technol.*, 62, 2002, pp. 1993-1998.

(2) H. Dai, *Surf. Sci.*, 500, 2002, pp. 218-241.

(3) E. Kymakis, I. Alexandou and G. A. J. Amaratunga, *Syn. Met.*, 127, 2002, pp. 59-62.

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

(5) Y. J. Liu and X. L. Chen, *Mech. Mater.*, 35, 2003, pp. 69-81.

(6) K. T. Lau and D. Hui, *Compos. Part B*, 33, 2002, pp. 263-277.

(7) P. Tsotra and K. Friedrich, *Compos. Part A*, 34, 2003, pp. 75-82.

(8) 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.

(9) J. M. Park, S. I. Lee, K. W. Kim and D. J. Yoon, J. *Colloid Interf. Sci.*, 237, 2001, pp. 80-90.

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