Nondestructive Sensing Evaluation of Thermal Treated Carbon Nanotube and Nanofiber/Epoxy Composites Using Electrical Resistance Measurement

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

전기저항 측정 방법을 이용한 표면 처리된 탄소 나노튜브와 나노 섬유 강화된 에폭시 복합재료의 비파괴적 감지능 평가

정진규*·박종만*,†·김대식**·김태욱***

KEY WORDS: nondestructive sensing evaluation, thermal treated carbon nanocomposites, electrical sensitivity, uniform cyclic strain test, electrical contact resistivity, apparent modulus

ABSTRACT

Nondestructive damage sensing and mechanical properties for thermal treated carbon nanotube (CNT) and nanofiber (CNF)/epoxy composites were investigated using electro-micromechanical technique. Carbon black (CB) was used only for the comparison. Electro-micromechanical techniques were applied to obtain the fiber damage and stress transferring effect of carbon nanocomposites with their contents. Thermal treatment and temperature affected on apparent modulus and electrical properties on nanocomposites due to enhanced inherent properties of each CNMs. Coefficient of variation (COV) of volumetric electrical resistance can be used to obtain the dispersion degree indirectly for various CNMs. Dispersion and surface modification are very important parameters to obtain improved mechanical and electrical properties of CNMs for multifunctional applications. Further optimized functionalization and dispersion conditions will be investigated for the following work continuously.

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
**Department of Textile and Apparel
Cornell University, U. S. A.
*** 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 been attracted with considerable attention in the research and industrial field due to their unique and multifunctional properties such as 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]. Some research works on functionalization and surface modification of carbon nanotube have been studied recently to improve dispersion and interfacial adhesion [10,11].

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, respectively. Carbon black (CB, Korea Carbon Black Co, Korea) was used to compare with CNT and CNF. Conventional 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.

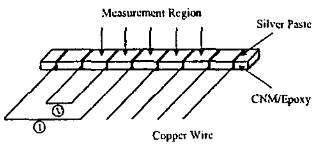

Figure 1 Experimental scheme for the electrical volume resistivity measurement

2.2. Methodologies

2.2.1. Specimen Preparation: Dispersion process using sonication (Crest Ultrasonic Co.). CNMs were dispersed in methanol-based epoxy solution by sonication for 2 hours, and then solvent was evaporated under sonication at 35 °C for 6 hours. Residual solvent was eliminated using vacuum oven at 60 °C for 3 days. Selected three CNT and CNF contents were 0.1, 0.5 and 2 vol%, respectively. CB contents were 2 vol% for the comparison.

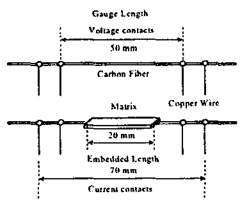

Figure 2 Schematic figures for cyclic loading test.

2.2.2. Measurement of Electrical Resistivity: Figure 2 shows the experimental scheme for the electrical volume resistivity measurement. Electrical resistance of carbon nanocomposites with volume fraction was measured by four-point probe method. Electrical contact points were located with regular distance using copper wire and silver paste. Electrical volume resistivity was obtained from the measured electrical volume resistance, cross-sectional area of the carbon nanocomposites, A_v, and electrical contact length, L_{ec} of the testing specimen connecting to copper wire.

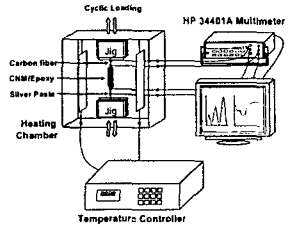

Figure 3. Scheme for electro-micromechanical test in temperature controlling chamber

Testing speed and load cell were 0.5 mm/min. and 100 N, respectively. After a testing specimen was fixed into the UTM grip, the composite and the multi-meter 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:

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

The electrical contact resistivity, ρ_c is as follow:

$$\rho_c = A_c \times R_c \quad (\Omega \cdot cm^2) \tag{2}$$

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

Table 1 Weight change between before and after thermal treatment

Thermal Treated Temperature	Type	CNT	CNF	CB
500 °C	Before (g)	0.2000	0.2000	0.2032
	After (g)	0.0850	0.1984	0.1160
	Δ (wt%)	57.5	0.8	42.9
400 °C	Before (g)	0.2002	0.1025	0.3521
	After (g)	0.1987	0.1016	0.3360
	Δ (wt%)	0.9	0.9	4.6
300 °C	Before (g)	0.2009	0.1038	0.3405
	After (g)	0.2000	0.1030	0.3366
	Δ (wt%)	0.5	0.8	1.2

2.2.3. Thermal Treatment and Thermal Test: Among 3 CNMs, typically CNT was thermally treated at 500 °C for 1 hour to modify the fiber surface and any impurity on the CNT surface was removed. Dispersion process was similar to the untreated case. As shown in Figure 3, heating chamber was set up with the mini-tensile /compressive machine and electrical resistivity measurement equipment (HP34401A Multimeter). Temperature range was room temperature up to 68 °C due to the limitation of heating facilities. Table 1 shows the mass decrease after TGA test for 3 CNMs. After 500 °C heating, steep decrease occurred and in this work 400 °C for 1 hour was applied as the thermal treatment.

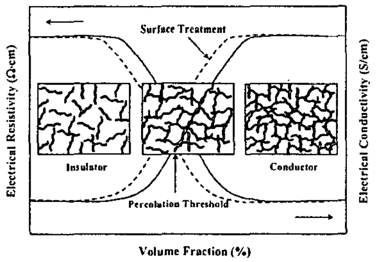

Figure 4. Scheme of percolation threshold

Table 2. Volumetric resistance of the untreated CNT, CNF, and CB with increasing temperature

Type (MΩ)	Mean	Temperature (°C)							
		30	40	50	60	70	80	90	100
CNT 0.5wt%	AVE.	0.64	0.65	0.64	0.63	0.61	0.61	0.59	0.58
	S.D.[1)]	0.06	0.06	0.06	0.06	0.05	0.05	0.05	0.04
	COV[2)]	8.7	8.6	9.4	9.2	8.3	8.8	7.8	7.2
CNF 0.5wt%	AVE.	6.26	7.10	7.35	7.48	8.07	9.56	11.34	13.37
	S.D.	1.15	2.40	2.26	1.81	1.40	1.41	0.23	0.68
	COV	18.4	33.7	30.8	24.2	17.3	14.8	2.1	5.1
Carbon Black 2wt%	AVE	5.26	5.65	6.36	6.56	6.87	7.64	8.93	9.88
	SD	0.43	0.39	0.59	0.43	0.29	0.50	0.90	1.46
	COV	8.2	7.0	9.2	6.5	4.3	6.5	10.0	14.8

Table 3. Volumetric resistance of the thermal treated CNT, CNF, and CB with increasing temperature

Type (MΩ)	Mean	Temperature (°C)							
		30	40	50	60	70	80	90	100
CNT 0.5wt%	AVE.	2.32	2.32	2.31	2.35	2.29	2.24	2.21	2.16
	S.D.[1)]	0.34	0.43	0.42	0.39	0.42	0.36	0.40	0.35
	COV[2)]	14.6	18.7	17.8	16.4	18.1	16.2	18.1	16.4
CNF 0.5wt%	AVE.	11.79	10.62	11.44	11.14	12.04	11.53	10.32	10.32
	S.D.	1.27	2.72	2.40	2.35	1.90	1.88	3.09	3.11
	COV	10.8	25.6	20.9	21.1	15.8	16.4	29.9	30.1
Carbon Black 2wt%	AVE	6.53	7.32	9.71	9.97	11.33	11.44	11.32	11.86
	SD	2.49	1.55	2.15	1.80	1.91	2.68	2.47	3.90
	COV	38.1	21.2	22.2	18.0	16.5	23.5	21.8	32.9

3. RESULTS AND DISCUSSION

3.1. Thermal and temperature effect on volumetric electrical resistivity: Figure 4 shows the scheme of percolation threshold as a function of adding CNMs contents. There can be critical percolation threshold concentration for electrical resistivity. With functionalization or surface treatment on CNMs, percolation threshold might be shifted to a certain degree to obtain improved performance of CNM/epoxy composites. Table 2 and Table 3 show the volumetric electrical resistivity for untreated cases for 3 different CNMs with increasing temperature. After temperature increased, in CNF and CB cases the electrical resistivity increased, whereas CNT decreased slightly. It is because thermal treatment effect appeared differently due to their inherent properties and aspect ratio etc. Figure 5 shows the change in electrical resistance of untreated and thermal treated CNT, CNF, and CB with increasing temperature.

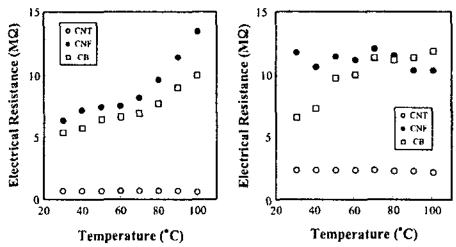

Figure 5. The change in electrical resistance of CNT, CNF, and CB with increasing temperature

Figure 6 shows stress/strain sensing for the untreated and thermal treated for (a) 30 °C and (b) 60 °C, respectively. Electrical resistivity was responded well against stress/strain application for all cases.

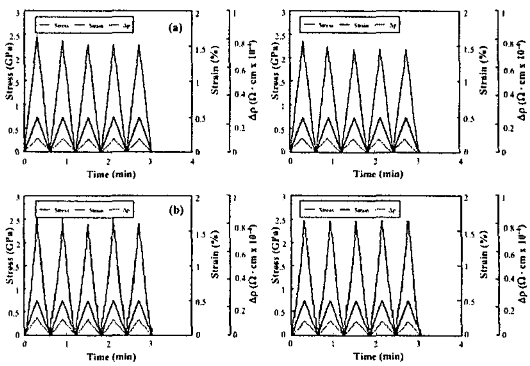

Figure 6 The maximum stress of the untreated and thermal treated CNT/epoxy composite for 0.5 vol%: (a) 30 °C; and (b) 60 °C under 5 uniform cyclic loading

3.2. Thermal and temperature effect on electrical resistivity for electro-micromechanical test: Figure 7 shows the direct comparison of apparent modulus and ρ-stress curve of CNT/epoxy composite with 0.5 wt% CNT content for (a) untreated and treated at 30 °C; (b) untreated and treated at 60 °C; (c) 30 °C and 60 °C for the untreated case; (d) 30 °C and 60 °C for the treated case. Thermal treated case showed higher apparent modulus and electrical resistivity than the untreated case for both temperatures. At higher temperature case apparent modulus was lower than lower temperature, whereas ρ exhibited to be lower, i.e., higher conductive. It might be because electron hopping due to possible band theory.

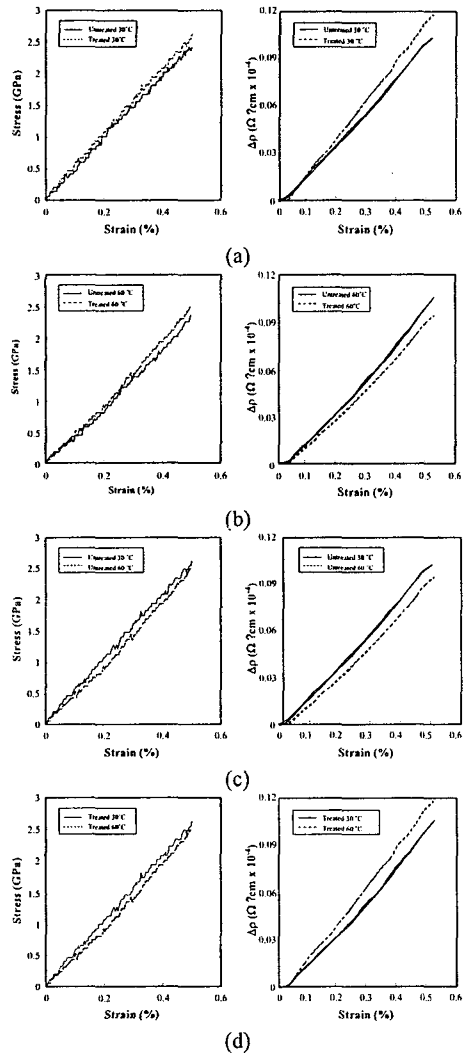

Fig. 7 Direct comparison of apparent modulus and Δρ-stress curve of CNT/epoxy composite with 0.5 wt% CNT content for (a) Untreated and treated at 30 °C; (b) Untreated and treated at 60 °C; (c) 30 °C and 60 °C for the untreated case; (d) 30 °C and 60 °C for the treated case

4. CONCLUSIONS

Electro-micromechanical technique was applied to thermal treated CNMs composites to investigate improved properties for CNMs/epoxy composites. At the same volume fraction the electrical volume resistivity, ρ_v and the coefficient of variation (COV) indicated the degree of dispersion of CNMs composites. CNT composites were the lowest among three CNMs. Homogeneous dispersion and improved interfacial interaction could be keying parameters for better damage monitoring and mechanical performance as well. Thermal treatment and temperature affected on apparent modulus and electrical properties on nanocomposites due to different inherent properties of each CNMs. Some new information on temperature sensing and stress transfer effect of thermal treated carbon nanocomposites could be obtained from the electrical resistance measurement as a feasible new concept of the nondestructive evaluation.

ACKNOWLEDGMENT: This work was financially supported from '*Center for Nanostructured Materials Technology*' of the '*21st Century Frontier R&D programs*' by Ministry of Science and Technology, through Engineering Research Institute (ERI), Gyeongsang National University, 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) U. D. Weglikowska, J. M. Benoit, P. W. Chiu, R. Graupner, S. Lebedkin, S. Roth, *Current Applied Physics* 2, 2002, 497-501.

(11) D. Tasis, N. Tagmatarchis, V. Georgakilas, C. Gamboz, M. R. Soranzo, M. Prato, *CHIMIE*, 6, 2003, 597-602.