論文

전기저항측정 및 미세역학시험법을 이용한 탄소나노섬유/튜브 및 전기방사된 나노섬유/에폭시 복합재료의 계면특성 및 감지능 연구

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Interfacial Properties and Sensing of Carbon Nanofiber/Tube and Electrospun Nanofiber/Epoxy Composites Using Electrical Resistance Measurement and Micromechanical Technique

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ABSTRACT

Nondestructive damage sensing and load transfer mechanisms of carbon nanotube (CNT) and nanofiber (CNF)/epoxy composites have been investigated by using electro-micromechanical technique. The electrospun PVDF nanofibers were also prepared as a piezoelectric sensor. The electro-micromechanical techniques were applied to evaluate sensing response of carbon nanocomposites by measuring electrical resistance under an uniform cyclic loading. Composites with higher volume content of CNT showed significantly higher tensile properties than neat and low volume% CNT composites. CNT composites showed humidity sensing within limited temperature range. CNF composites with smaller aspect ratio showed higher apparent modulus due to high volume content in case of shorter aspect ratio. Thermal treated electrospun PVDF nanofiber showed higher mechanical properties than the untreated case due to crystallinity increase, whereas load sensing decreased in heat treated case. Electrospun PVDF nanofiber web also showed sensing effect on humidity and temperature as well as stress transferring. Nanocomposites and electrospun PVDF nanofiber web can be applicable for sensing application.

초 록

탄소나노튜브 및 탄소나노섬유/에폭시 복합재료의 비파괴 손상감지능 및 응력전달 메카니즘이 전기-미세기계적 실험법을 통하여 조사되었다. 전기-미세기계적 실험법은 균일한 반복하중 하에서 전기저항을 측정함으로써 탄소나노복합재료의 감지반응을 평가하는 것이다. 큰 탄소섬유 부피 분율이 있는 복합재료가 에폭시 자체나 작은 부피 분율에 비하여 매우 큰 인장강도 특성을 보여주었다. 탄소나노섬유 복합재료는 제한된 온도범위 내에서 습도 감지능을 보여주었다. 형상비가 작은 탄소나노섬유 복합재료는 많이 첨가된 부피량에 기인하여 보다 큰 겉보기 탄성계수를 보여 주었다. 열처리된 전기 방사된 PVDF 나노섬유는 증대된 결정화에 기인하여 미처리의 경우보다 큰 기계적 특성을 보여 주었으며, 그 반면에 응력 감지능은 열처리의 경우에 감소를 보여 주었다. 전기 방사된 나노섬유는 또한 응력전달 뿐만 아니라 습도 및 온도에 대한 감지능도 나타내었다. 탄소나노튜브, 탄소나노섬유 및 전기 방사된 PVDF 나노섬유는 나노복합재료의 다기능에 응용할 수 있을 것이다.

Key Words: 감지능(sensing), 탄소 나노섬유/튜브(carbon nanofiber/tube), 전기방사 PVDF 나노섬유(electrospun PVDF nanofiber), 전기저항측정(electrical resistance measurement), 미세역학시험법(micromechanical technique)

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1. Introduction

Recently, carbon nanomaterials (CNMs) such as single-wall carbon nanotube (SWCNT), multi-wall carbon nanotube (MWCNT), and carbon 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 for multi-functional purpose [1-3]. Carbon nanocomposites have high stiffness, strength and good electrical conductivity at relatively low concentrations of reinforcing CNM. Electrical and mechanical properties of CNM reinforced polymer composites depend on many factors seriously, such as inherent properties of CNM, the degree of dispersion, orientation, interfacial adhesion, aspect ratio, fiber shape and adding content, etc. Especially, the degree of dispersion is well known as one of the very important factors to control many uniform properties. Experimentally-observed percolation threshold values strongly depend on the aspect ratio of the reinforcement. CNMs or aligned buckypapers could be used for achieving the desirable mechanical orientation in composite materials [4-5]. Recently new method was developed to fabricate bucky nanocomposites which was preformed SWNT to be dispersed in water-based suspension with the aid of surfactant and sonication [6]. Electrospinning has been recognized as an efficient technique for producing polymer nanofibers as polymer electrolyte [7]. Thermal treatment electropsun PVDF nanofiber can improve physical properties and dimensional stability [8].

The electro-micromechanical technique [9-12] has been studied as an economical nondestructive evaluation (NDE) method for damage sensing, the characterization of interfacial properties, and nondestructive behavior because conductive fiber can act as a sensor in itself as well as a reinforcing fiber. In this work, contact resistance and sensing effect were evaluated for CNT, CNF, electrospun PVDF nanofiber reinforced composites by electrical resistance measurement. Especially, high volume CNT composites and feasible humidity sensing was also evaluated for nanocomposites.

2. Experimental

2.1 Materials

CNT (Iljin Nanotech Co., Korea) and CNF (Applied Science Inc. U. S. A.) as reinforcing and sensing materials were used and their average diameters were 20 nm and 150 nm, respectively. Another type of CNF in the range of 50-200nm range was specially supplied from Applied Science Inc. (U. S. A.) with different aspect ratio. 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. Diethyltoluene (KH100, Kukdo Chemical Co. Ltd.) with 30 wt% was used as curing agent for CNT composites. For CNF composites, toughened epoxy matrix was controlled by changing the ratio of Jeffamine D400 and D2000 (polyoxypropylene diamine, Huntsman Petrochemical Co.) in the curing mixture. Electrospun poly(vinylidene fluoride) (PVDF) (Aldrich, M_w: 180,000) was used in N, N-dimethylformanide (DMF) (Reagent Chemicals) and acetone solution as piezoelectric polymer sensor.

2.2 Methodology

2.2.1 Preparation for CNT or CNF composites

For CNT composites with a high volume content of 50 vol%, CNT was compressed using a roller to make film type thin sheet. To reduce the viscosity of epoxy plus curing agent, acetone was mixed with same amount of epoxy and then was infiltered and poured into CNT sheet. Four copper wires were fixed through thin sheet specimens. After evaporating acetone from the specimen at room temperature for 2 hours, the nanocomposite sheet was cured at 150 °C for 4 hours in the oven. Specimen in strip shape was prepared with 2 mm in width, 30 mm in length and 0.3 mm in thickness, respectively. For 1 vol% CNT composite, 1 vol% CNT was mixed with methanol and dispersed under ultrasonic process for 2 hours. Epoxy resin was added and processed with ultrasonic process for 2 more hours. Curing agent KH100 was added and dried in oven at 60 °C for 4 hours to remove solvent. Specimen in strip shape was prepared with 2 mm in width, 30 mm in length and 0.5 mm in thickness, respectively. Prepared specimen was cured at 150 °C for 2 hours.

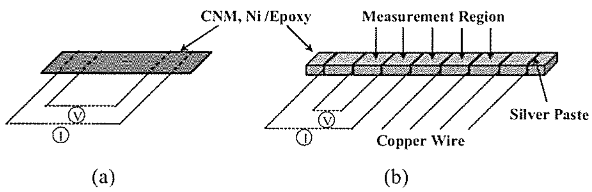

Fig. 1 Experimental scheme for the electrical volume resistivity measurement (a) CNT composite; and (b) CNF composite.

CNF were dispersed in ethanol-based epoxy solution by sonication for 2 hours, and then solvent was evaporated under sonication at 35 °C for 6 hours. Dispersion process was processed using sonication (Crest Ultrasonic Co.). Residual ethanol solvent was eliminated using vacuum oven at 60 °C for 3 days. After epoxy mixture was poured into the mold, epoxy was precured at 80 °C for 2 hours and then postcured at 120 °C for 2 hours. Chosen CNF contents were 0.5 vol% by considering viscosity of mixed solution for both types A and B, respectively.

2.2.2 Electrospinning Process

Figure 2 shows scheme of electrospinning process using PVDF. PVDF with 20 wt% was dissolved in DMF plus 20 wt% acetone solution and then heated at 80 °C for 2 hours to mix completely. Machine controlling syringe was used to control uniform injection and PVDF nanofiber was winded in rotating mandrel or plate aluminum sheet. Mixed PVDF solution was poured into syringe and fixed at syringe pump. Working distance between needle and collector was set as 15 cm, whereas used voltage was set as 20 kV using High voltage power supply (Korea Switching, KSH-P100/01CD). Speed of syringe pump (KD Scientific Inc., Model: KDS100) was 10 mL/hour and diameter of used needle was 300 μm.

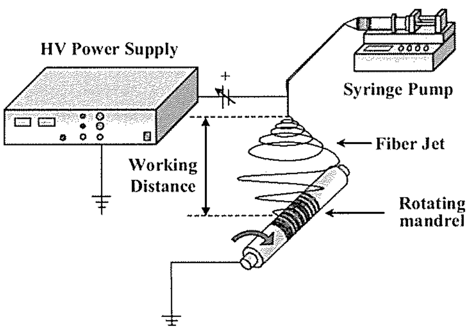

Fig. 2 Scheme of electrospinning of PVDF.

2.2.3 Electrical resistivity measurement

Figure 3 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_{el} of the testing specimen connecting to copper wire. 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 (HP34401A) were connected electrically using thin copper wires. 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_V, and electrical contact length, L_{el} of the testing fiber connecting to copper wire. The relationship between electrical volume resistivity, ρ_V and electrical volume resistance, R_V is as follow:

$$\rho_V = \left(\frac{A_V}{L_{el}}\right) \times R_V \qquad (\Omega \cdot cm) \tag{1}$$

The electrical contact resistivity, ρ_c *is as follow:*

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

where, A_c and R_c are electrical contact area and electrical contact resistance, respectively. To obtain statically meaningful data, each 4 specimens were used at least.

2.2.4 Cyclic loading and humidity sensing tests

Cyclic loading test was performed using the mini-tensile machine (H1KS, Hounsfield Equipment Ltd., U.K.) with a multimeter to measure electrical resistivity simultaneously under uniform 5 cyclic tensile and compressive loadings. Load cell of 100 N was used with testing speed of 0.5 mm/minute. Humidity sensing test was performed in the oven by fixing temperature at 30 °C. Humidify range was set from about 15 to 55 % due to the limited oven facilities.

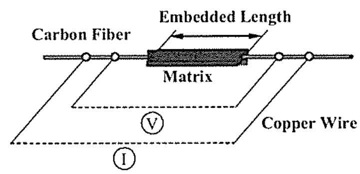

Fig. 3 Scheme of cyclic loading test.

3. Results and Discussion

3. 1 Sensing of carbon nanotube (CNT)/epoxy composites

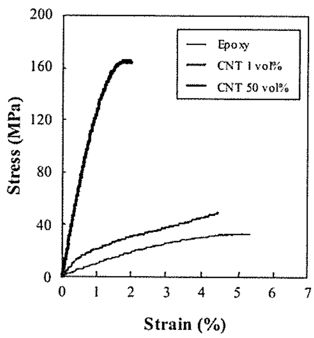

Fig. 4 Comparison of tensile properties of CNT composites and epoxy matrix.

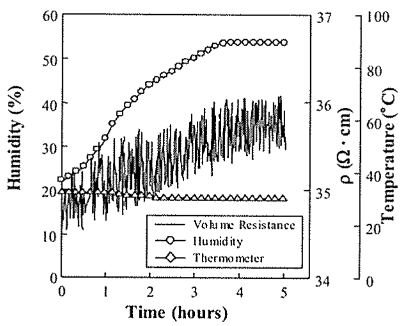

Fig. 5 The change in electrical resistance on humidity of CNT nanocomposite.

Table 1 Mechanical properties of CNT composites and neat epoxy matrix under tensile test

Type	Tensile Strength (MPa)	Tensile Modulus (GPa)	Elongation (%)
Neat Epoxy	30.2 (4.3)[a)]	0.3 (0.2)	5.4 (1.3)
1vol% CNT	47.2 (4.2)	4.3 (0.4)	4.4 (2.1)
50 vol% CNT	168.0 (3.6)	11.4 (0.5)	2.1 (3.6)

1) S. D. (Standard deviation)

Table 1 and Figure 4 show the comparison of tensile properties for neat epoxy matrix and high and low volume content CNT composites. Tensile strength and modulus of 50 vol% CNT composites were much higher than neat epoxy and 1 vol% nanocomposites as expected. For load bearing purpose, volume content should be over 20 vol%. However, conventional nanocomposites by mixing method cannot be prepared due to high viscosity by added nanomaterials as reinforcement. To solve such high viscosity properties, CNT sheet was prepared by using compressing roller and compared with conventional 1 vol% composites and neat epoxy.

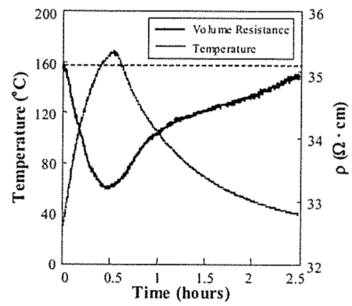

Fig. 6 Change in electrical resistivity for CNT nanocomposite with increasing temperature.

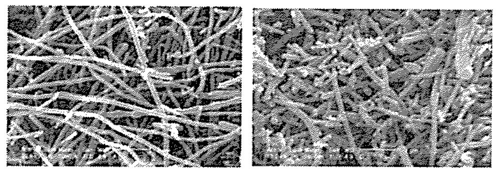

Fig. 7 SEM photos of two different aspect ratio carbon nanofibers (a) Type A; and (b) Type B.

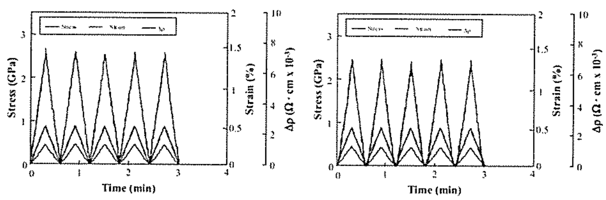

Fig. 8 Electrical resitivity of two of CNF composites of different aspect ratio under uniform cyclic loading.

Uniformity of reinforcement carbon nanomaterials is very important for stress transferring application. Based on brittleness of epoxy matrix, neat epoxy specimen was broken before necking, whereas CNT composite showed necking due to the fracture toughness by the nano-sized reinforcement.

Figure 5 shows the change in electrical resistance on humidity of CNT composite under constant temperature, 30 °C. When the humidity increases, the electrical resistance also increases, although there are some noise level. Electrical resistance on humidity change will be evaluated continuously further for humidify sensing using different CNMs.

Figure 6 shows the electrical resistivity with changing temperature using CNT composite. Electrical resistance was responded reversely well with temperature profile due to inherent thermal properties of CNT and internal and residual stress between CNT and epoxy matrix as described in our previous works [11].

3. 2 Sensing of carbon nanofiber (CNF)/epoxy composites

Figure 7 shows two different carbon nanofiber. Different aspect ratio can contribute to differing volume content.

Figure 8 shows the results of five uniform cyclic loading of two different aspect ratio CNF composites, respectively. Their reaching time was similar to each other. Figure 9 shows apparent modulus and their electrical resistivity. Since short aspect ratio, type B has more CNF content than type A case, stress transferring effect for type B showed higher apparent modulus. Likewise, type B has more opportunity of electrical connection than longer aspect type A case.

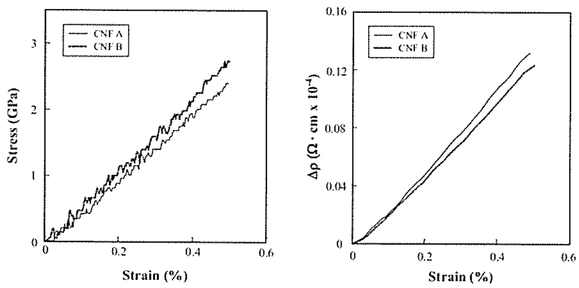

Fig. 9 Comparison of apparent modulus for high and low aspect ratio.

3.3 Sensing of electrospun PVDF nanofiber web

Electrospinning is an useful technique to produce nanofiber webs using many different types of materials. Since electrospun nanofiber webs have nanoporous structure, they can have a potential application for a polymer electrolyte or a sensor. PVDF nanofiber web can be also used as one of polymer electrolyte binders.

Table 2 Mechanical properties of untreated PVDF nanofiber under 3 different thermal treatments

Type	Tensile Strength (MPa)	Tensile Modulus (GPa)	Elongation (%)
Untreated PVDF	41.5 (2.2)[1)]	0.9 (0.4)	3.1 (5.~1)
150 °C for 2 hrs	82 (2.6)	1.6 (0.3)	2.6 (3.7)
160 °C for 2 hrs	93.4 (4.5)	1.8 (0.4)	2.3 (3.2)

·1) S. D. (Standard deviation)

Table 2 and Figure 10 show the comparison of mechanical properties of the untreated PVDF and thermal treated PVDF nanofiber webs. Thermal treated PVDF nanofiber web showed much higher tensile strength and modulus than the untreated PVDF case. It can be due to the increased crystallinity of PVDF [8]. On the other hand, higher temperature might may lose sensing capability despite of an increase of mechanical property.

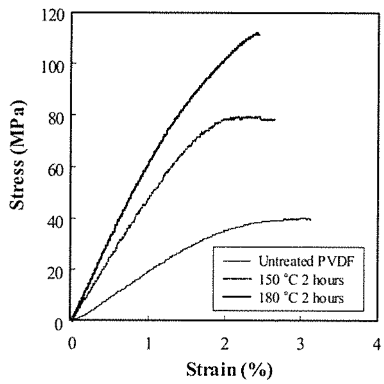

Fig. 10 Comparison of the untreated and thermal treated PVDF nanofiber web.

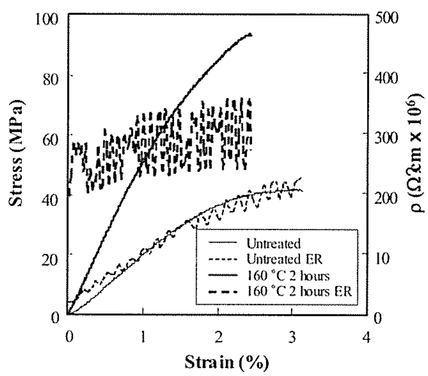

Fig. 11 Electrical resistivity for electrospun PVDF nanofiber web with increasing stress.

Figure 11 shows the electrical resistivity with applying stress for two different electrospun PVDF nanofiber webs. For untreated PVDF nanofiber web, the electrical resistivity was responded proportionally well with the temperature profile due to inherent thermal properties of PVDF nanofiber web as described in our previous works [11].

On the other hand, heat treated at 160 C for 2 hours case, electrical resistance was much less responded with wider noise. under applied load.

Sensing evaluation with different PVDF nanofiber types will be studied further including actuation study. Further actuation studies using above CNT, CNF, and elctrospun PVDF nanofiber web will be performed for detecting deformation change continuously.

4. CONCLUSIONS

Nondestructive damage sensing and load transfer mechanisms of carbon nanotube (CNT) and nanofiber (CNF)/epoxy composites have been investigated using electro-micromechanical technique. Electrospun PVDF nanofibers were also prepared to evaluate the feasible piezoelectric sensor. Electro-micromechanical techniques were applied to obtain the sensing response of carbon nanocomposites by measuring electrical resistance and interfacial evaluation. High volume CNT composites showed significantly higher tensile properties than neat and low volume CNT composites. CNT composites showed humidity sensing observed within limited range and temperature response. CNF composites with smaller aspect ratio showed higher apparent modulus due to high volume content in case of shorter aspect ratio. Electrospun PVDF nanofiber/epoxy composites showed sensing effect on stress transferring. Dispersion and surface modification can be very important parameters to obtain improved mechanical and electrical properties of CNMs for multifunctional applications.

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