Nondestructive Sensing Evaluation of Electrospun PVDF Fiber and Carbon Nanotube/Epoxy Composites Using Electro-Micromechanical Technique

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Electro-Micromechanical 시험법을 이용한 Electrospun PVDF Fiber 및 CNT 강화 Epoxy 복합재료의 비파괴 감지능 평가

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KEY WORDS: Sensing, Nondestructive evaluation, Electrospun PVDF, Carbon nanotube, Electro-micromechnical technique, Humidify sensor

ABSTRACT

Nondestructive sensing of electrospun PVDF web and multi-wall carbon nanotube (MWCNT)/epoxy composites were investigated using electro-micromechanical technique. Electrospinning is a technique used to produce micron to submicron diameter polymeric fibers. Electrospun PVDF web was also evaluated for the sensing properties by micromechanical test and by measurement electrical resistance. CNT composite was especially prepared for high volume contents, 50 vol% of reinforcement. Electrical contact resistivity on humidity sensing was a good indicator for monitoring as for multifunctional applications. Work of adhesion using contact angle measurement was studied to correlate acid-base surface energy between carbon fiber and CNF composites, and will study further for interfacial adhesion force by micromechanical test.

Nomenclature

$\Delta\rho$	: Change in electrical resistivity
ρ_v	: Electrical volume resistivity
ρ_c	: Electrical contact resistivity
L_{ec}	: Voltage contact length
A	: Cross sectional area
A_c	: Electrical contact area
R_c	: Electrical contact resistance

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1. INTRODUCTION

Recently, electrospinning process has been studying intensively in various nano-technological applications. Electrospinning is a process to easily produce polymeric fibers in the average diameter range of 100 nm–5 mm [1,2]. The average diameter of the fibers produced this way is at least one or two orders of magnitude smaller than the conventional fiber production methods like melt or solution spinning. Various polymers can be electrospinned into ultrafine fibers in solvent solution. Electrospinning was able to make polymer web without any expensive apparatus [3].

CNT was good electrical conductivity at low concentration of reinforcing materials [4,5]. The electro-micromechanical techniques have been used as economical nondestructive evaluation method for sensing. Electro-conductive polymer was evaluation of sensing and interfacial properties for electrical resistivity measurement using electro-micromechanical techniques [6,7]. Wettability is important surface properties of interface. The work of adhesion to solid surface can be measured directly using force measurement for dynamic contact angle [8]. In this study, nondestructive evaluation of electrospun PVDF web and high volume content of CNT composites using electro-micromechanical techniques.

2. EXPERIMENTAL

2. 1. Materials

Electrospun web for poly (vinylidene fluoride) (PVDF) (Aldrich, Mw: 180,000) was dissolved in N,N-dimethylformamide (DMF) (reagent Chemicals) as piezoelectric polymer sensor. CNT (Iljin Nanotech Co., Korea) as reinforcing and sensing materials were used and their average diameters were 20 nm, respectively. Epoxy resin (YD-127, Kukdo Chemical Co., Korea) based on diglycidyl ether of bisphenol-A was used as a matrix. Curing agent, KH-100 (aromatic amine, Kukdo Chemical Co., Korea) was used for high modulus properties.

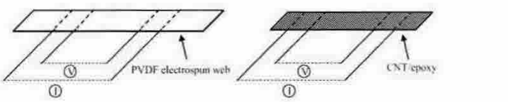

Fig. 1 Experimental scheme for electrical resistivity measurement of PVDF electrospun web and CNT composites

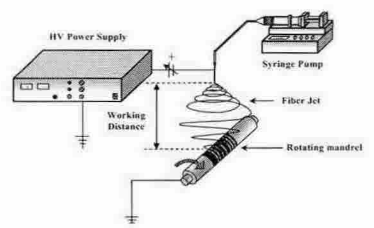

Fig. 2 Scheme of electrospinning set

2. 2. Specimen preparation

PVDF 25 wt% was dissolved in DMF and then heated at 80 °C for 2 hours to mix completely. Figure 2 shows the scheme of electrospun PVDF web. Machine controlling syringe pump was used to control uniform injection and PVDF nanofiber was winded in rotating mandrel or aluminum plate. Mixed PVDF solution was poured into syringe and fixed at syringe pump (KD Scientific Inc., KDS-100). Syringe pump speed was 10 mL/hour and needle diameter was 300 μm. Between needle and collector was 15 cm, whereas used voltage was 20 kV using high voltage power supply (Korea Switching, KSH-P100/01CD). Compressed CNT sheet by roller were dispersed in acetone-based epoxy solution by mechanical mixing and then infiltrated into CNT sheet. Acetone solvent was evaporated under low temperature in 35 oC for 2 hours and then cured at 150 oC for 4 hours.

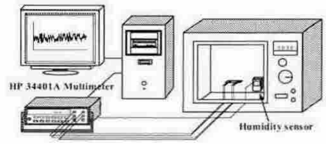

Fig. 3 Scheme of humidity test in the oven

2. 3. Electrical resistivity measurement

Figure 3 shows the scheme for measuring the electrical volume resistivity on the humidity. Electrical resistance of electrospun PVDF web and CNT was measured by four-point probe method. Electrical contact points were located with regular distance using copper wire and silver paste as a glue. Electrical resistivity was obtained from the measured electrical resistance, cross-sectional area of the nanocomposites, A_v, and electrical contact length, L_{ec} of the testing specimen connecting to copper wire. Testing speed were 0.5 mm/min. and load cell were 100 N. The composites and the multi-meter were connected electrically using a very thin 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.

2. 4. Dynamic Contact Angle Measurement

Dynamic contact angle of carbon fibers and CNT composites were measured using Wilhelmy plate technique (Sigma 70, KSV Co., Finland). Dipping liquids were used double distilled water, formamide, ethylene glycol, and diiodomethane. Dynamic contact angle, interfacial energies, donor and acceptor components, and polar and dispersive free energy terms of the fibers with various treated conditions were measured. Basic equation for Wilhelmy plate method is

$$F = mg + P\gamma_{LV}\cos\theta - F_b \qquad (3)$$

where F is total force, m is mass of plate, g is acceleration of gravity, F_b is buoyancy force, P is perimeter of fiber or plate, γ_{LV} is surface tension of liquid, and F-mg is equal to the measured force.

$$\gamma_L(1+\cos\theta) = 2\left(\gamma_S^{LW}\gamma_S^{LW}\right)^{\frac{1}{2}} + 2\left[\left(\gamma_S^{-}\gamma_L^{+}\right)^{\frac{1}{2}} + \left(\gamma_S^{+}\gamma_L^{-}\right)^{\frac{1}{2}}\right] \quad (4)$$

Where γ_L, γ_L^d, and γ_L^p are known for the test liquids and γ_S^p *and* γ_S^d can be calculated from the measured contact angles. Eventually the dispersive and acid-base components of both the fiber and matrix can be determined. It is possible to calculate the work of adhesion, W_{ad}, between the fiber and matrix at the interface using the following equation,

$$W_{ad} = 2\left[\left(\gamma_F^{LW}\gamma_M^{LW}\right)^{\frac{1}{2}} + \left(\gamma_F^{-}\gamma_M^{+}\right)^{\frac{1}{2}} + \left(\gamma_F^{+}\gamma_M^{-}\right)^{\frac{1}{2}}\right] \quad (5)$$

3. RESULTS AND DISCUSSION

3. 1. Sensing of PVDF electrospun fiber

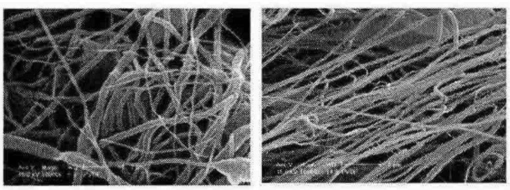

Fig. 4 FE-SEM photos of electrospun PVDF fiber for random state and more oriented cases

Figure 4 shows SEM image of electrospun PVDF fiber for random and orientation state by changing spinning conditions.

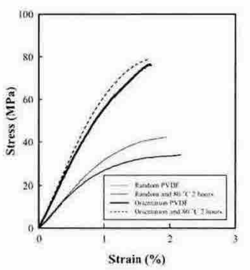

Fig. 5 Tensile properties of PVDF Web for random and orientation with temperature

Table 1. Tensile properties of PVDF Web for random and oriented cases with temperature

Type	Strength	Modulus	Elongation
Random	33.6 (2.4)	0.54 (0.02)	2.15 (0.27)
Oriented	43.3 (3.5)	0.64 (0.03)	1.92 (0.36)
Random, 80 °C	77.5 (3.6)	1.19 (0.02)	1.67 (0.15)
Oriented, 80 °C	79.6 (6.5)	1.51 (0.05)	1.59 (0.42)

Figure 5 and Table 1 show the tensile properties of random and oriented electrospun PVDF web with temperature. Tensile stress and modulus of orientation were higher than that of random state. Thermal treatment of tensile strength and modulus was higher than untreated.

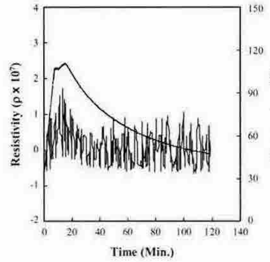

Fig. 6 The change in electrical resistivity of PVDF Web

Figure 6 shows the change in electrical resistivity of PVDF web with changing temperature. Temperature and electrical resistivity responded consistently.

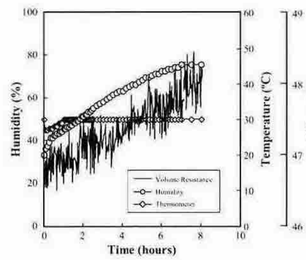

Fig. 7 The change in electrical Resistivity of PVDF Web for humidity

Figure 7 shows change in electrical resistivity of electrospun PVDF web with humidity. Temperature was set as constant degree 30°C. The electrical resistivity of electrospun PVDF web increased with increasing humidity proportionally. Electrical resistivity of electrospun PVDF web was possible using humidify sensor.

3. 2. Carbon Nanotube/epoxy composites

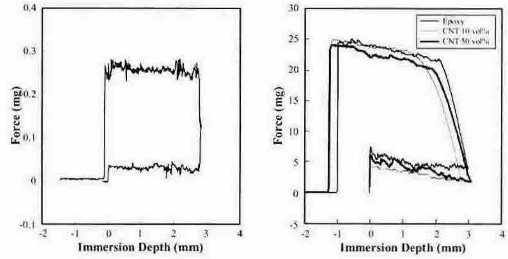

Fig. 8 Plots of contact angle for carbon fiber, epoxy matrix and CNT composites in double distilled water

Figure 8 shows plot of carbon fiber, epoxy matrix and CNT composites using contact angle method with double distilled water. Other three more solvents were also used to obtain work of adhesion. Figure 9 shows Plot of acid-base interaction *versus* work of adhesion for carbon fiber and epoxy matrix, epoxy matrix embedded CNT composites. Work of adhesion values of CNT 10 and 50 vol % were higher than epoxy-carbon fiber system whereas CNT 50 vol % composite was similar to CNT 10 vol % case. Thermodynamic work of adhesion between carbon fiber and epoxy matrix will be compared to adhesion force by micromechanical test, such as microdroplet test.

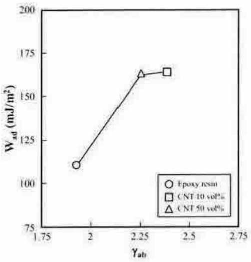

Fig. 9 Plot of work of adhesion for carbon fiber, epoxy and CNT composites 10 and 50 vol %

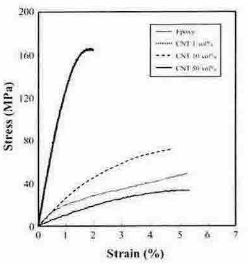

Fig. 10 Comparison of tensile properties for neat epoxy matrix and CNT composites 10 and 50 vol%

As a high CNT volume composites, added CNT volume fraction was over 10 and 50 wt%. Figure 10 shows the comparison of tensile properties for neat epoxy matrix and CNT composites 10 and 50 wt%. Tensile strength and modulus of CNT composites were much higher then neat epoxy case.

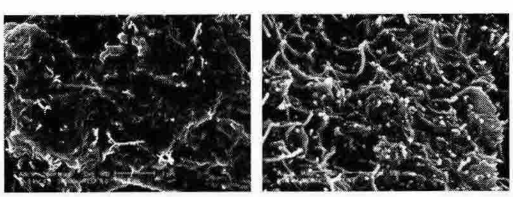

Fig. 11 Fracture surface of 1 vol% and 50 vol% CNT/epoxy composites

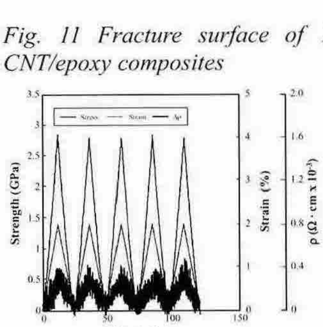

Fig. 12 Contact electrical resistivity of CNT 10 vol% composites under five cyclic loadings

Figure 11 shows the fracture surface of 1 and 50 vol% CNT/epoxy composites after tensile test. CNT was shown more in 50 vol% of CNT composites than the case of 1 vol%. Uniform distribution can be observed in 50 vol% case. Figure 12 shows contact resistivity of CNT 10 vol% composites under cyclic loading. Electrical resistivity can respond roughly consistently with applied stress-strain.

4. CONCLUSIONS

Electro-micromechanical technique was applied to electrospun PVDF web and CNT/epoxy composites to investigate sensing and stress transferring properties. Tensile properties of orientation electrospun PVDF web were higher than random state. Electrospun PVDF web was responded the sensing on temperature as well as humidity sensing proportionally. Higher volume content of CNT composites was prepared and showed significantly higher tensile strength and modulus than neat epoxy case. CNT composite was evaluated for humidity sensing and showed generally proportionality, whereas CNT composites also showed proportionality on temperature. Work of adhesion was correlated to acid-base interaction parameter. It is important that CNT composite is to get such a high volumetric content, over 50 vol%, than conventional 3-5 vol% CNT/epoxy composites despite high viscosity. Some new information on temperature sensing and stress transfer effect of carbon nanocomposites could be obtained from the electrical resistance measurement as a feasible new concept of the nondestructive evaluation.

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