DISPERSION EVALUATION AND INTERFACIAL SENSING OF CARBON FIBER/CNT-PHENOLIC COMPOSITES USING ELECTRO-MICROMECHANICAL TECHNIQUE

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1 Introduction

Phenols are aromatic compounds with one or more hydroxyl group attached [1], and it has high heat resistance and excellent dimensional stability, accordingly phenols are produced as basic materials in a variety of industries, such as aerospace industry, transportation industry, insulation materials [2]. Carbon fibers present extremely high strength and modulus, good stiffness, and creep resistance etc., have been widely employed as the reinforcing material in the high performance resin composites which have been extensively used in many industrial fields [3]. It is significant to develop the composite reinforced by carbon fiber with good mechanical properties, which are governed by both the composed components and the interface between them.

The increasing importance of composite materials in many application fields, has determined the necessity to describe with great accuracy their overall mechanical behavior. Due to their high specific stiffness and strength as well as their outstanding fatigue performance, fiber reinforced polymers (FRPs) have become irreplaceable materials for structural component design. Interfacial adhesion is attributed to the interfacial chemical bonds form and interaction between the polar groups on the surface of the reinforcing carbon fiber and the active groups present in the phenol matrix resin.

In this research optimum dispersion conditions of CNT in phenolic matrix for self-sensing as well as the concentration threshold of CNT-phenolic composites were investigated by volume resistivity measurements. The work of adhesion between a carbon fiber and CNT-phenolic composite material was higher than it was for neat phenolic resin. These results were consistent with microdroplet pull-out tests of interfacial shear strength in that microdroplet of CNT-phenolic composite exhibited higher IFSS.

2 Experimental

2.1 Materials

Carbon fiber (T700S, Korea and Toray Inc., Japan) was used as reinforcing fiber with average diameter of around 8μm. Multi-wall carbon nanotube (CNT, IlJin Nanotech Co., Korea) as reinforcing whereas as self-sensing material. Phenol (SC–1008, Monsanto Chemical Co., Korea) based on phenolic resole resin was used as matrix. Acetone (Dae Jung Chemical, Co.) was used for dispersion solvent of CNT.

2.2 CNT dispersion process in phenol

Figure 1 shows the fabrication process of the CNT-phenolic composites. The phenolic resin was mixed in acetone solvent before adding CNT. Next sonication of the CNT and phenol mixture was performed for additional 12 hours. The phenol solution, with the embedded CNT was then dispersed in a sealed beaker for 6 hours. Next the CNT dispersive solvent in the phenol solution was removed by evaporation under sonication at 35 °C for 3 days. The process of this dispersion is outlined schematically in Figure 2.

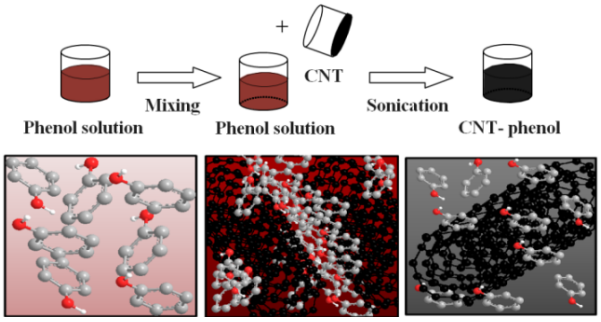

Fig.1. Schematic model of CNT dispersed in phenol

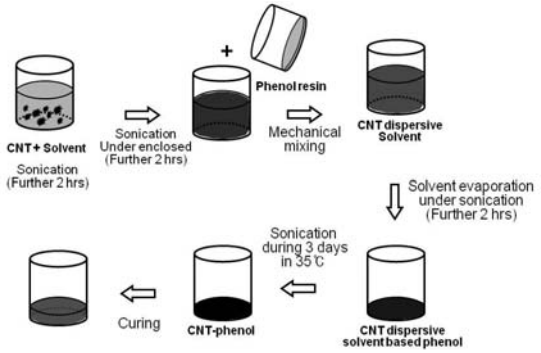

Fig.2. Schematic diagram of the fabrication process

2.3 Interfacial shear strength measurement

Figure 3 shows test systems of apparent modules test and microdroplet test. The IFSS between carbon fiber and CNT-phenolic composites was measured by microdroplet pull-out test. One of the major advantages of microdroplet technique is that the value of forces at the moment of debonding can be measured. The IFSS was calculated from the measured pullout force, F which can be calculated using the following equation, by extrapolation and liner regression.

$$\tau = \frac{F}{\pi D_f L} \qquad (1)$$

where D_f and L are fiber diameter and fiber embedded length in the matrix, respectively.

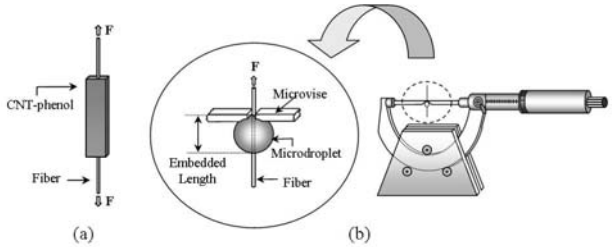

Fig.3. Interfacial properties measurement

2.4 Electrical resistance measurements

Figure 4 shows gradient specimens of electrical resistance test using two and four-point methods. Contact resistance was measured using gradient specimen. Electrical contact was made using copper wires located at gradually-increasing spacing. The contact resistance at an interface is highly sensitive to both the microstructure and the nanostructure. The contact resistance between the copper wires and the CNT-phenolic composites was first determined using the two-point method with the electrical gap set to zero by extrapolation and liner regression.

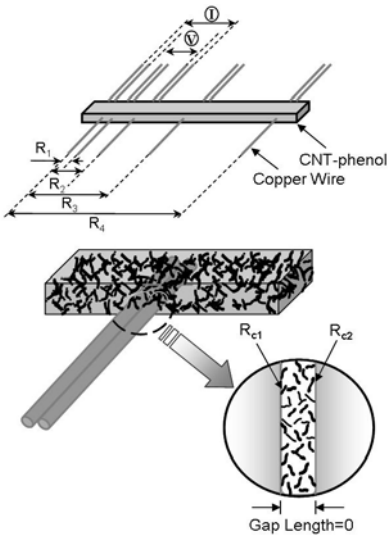

Fig.4. Schematic diagram of gradient specimen

2.5 Wettability and surface energy measurement

Dynamic contact angles of carbon fiber and CNT-phenolic composites were measured using Wilhelmy plate technique (Sigma 70, KSV Co., Finland). Four dipping liquids double purified water, formamide, ethylene glycol and diiodomethane were used. Dynamic contact angle, surface energies, donor and acceptor components, polar and dispersive free energy terms of carbon fiber with different conditions and CNT-phenolic composites were measured. The wettability between a liquid and a solid surface can be roughly determined by measuring the contact angle between a droplet of liquid in thermal dynamic equilibrium with a horizontal surface. The viscosity of phenolic resin can also affect the interfacial adhesion measurement. The basic equation for the WPM measurements is:

$$F = mg + P\gamma_{LV}\cos\theta - F_b \qquad (2)$$

A commonly-used approach in considering solid surface energies is to express them as a sum of dispersive and polar components which can influence the work of adhesion, W_a between the surface of the reinforcement material and the matrix. To determine the polar and dispersive surface free energies, the Owens-Wendt equation is used, expressed as:

$$W_a = \gamma_L(1+\cos\theta) = 2\left(\gamma_S{}^d \gamma_L{}^d\right)^{\frac{1}{2}} + 2\left(\gamma_S{}^p \gamma_L{}^p\right)^{\frac{1}{2}} \quad (3)$$

3 Results and Discussion

3.1 CNT dispersion process in phenolic solution

The electrical resistance curve was divided into three stages. At the beginning of dispersion, the CNTs were largely deposited in the bottom of the beaker, resulting in a lower value of electrical resistance. During the second stage dispersion, the CNT in the phenolic solution progresses (but still in a somewhat tangled state) causing a rather sudden increase in electrical resistance. In the third stage the CNTs becomes sufficiently dispersed so as to produce a CNT network with a high contact density and the resistance again decreases.

3.2 Contact resistance measurement

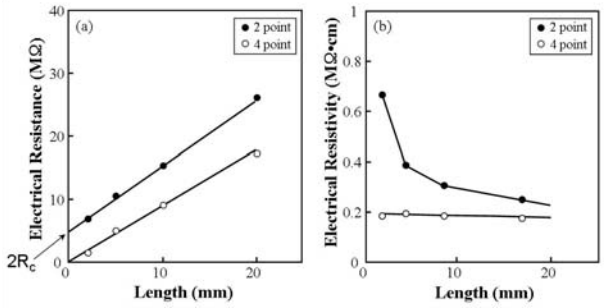

Fig.5. Electrical properties measurement

The Figure 5 shows the results of electrical measurement using two-point and four-point probe methods. Figure 5(a) shows the electrical resistance values which measured by two methods. The curve of two-point probe method can show the contact resistance value indirectly, from the linear fit of resistance against CNT gap length, $2R_c$ is obtained which is the intercept. However, the extended line of four-point method results nearly passes through origin. It is for the reason that the four-point probe method can measure the effective resistance without interfered by the contact resistance. Figure 5(b) shows the result of the electrical resistivity values measured using above two methods. The electrical resistivity that is calculated using four-point probe method data are similar, whereas the results of two probe method data exhibit errors. It is because the contact resistance dominates the overall resistance in the calculation process.

3.3 Comparison of mechanical properties

Figure 6 shows the tensile and compressive test curves of pure phenol and CNT-phenolic composites. In tensile test case, tensile modulus of CNT-phenol composites was higher than phenol due to the increased stiffness of composites. The compressive strength increased significantly in CNT-phenolic composites case, even the concentration is just 0.3 vol% for the composites. The inherent property of CNT was dominant in the CNT-phenolic composites, mechanical property was improved because of the accumulated loading stress in Broutman specimen.

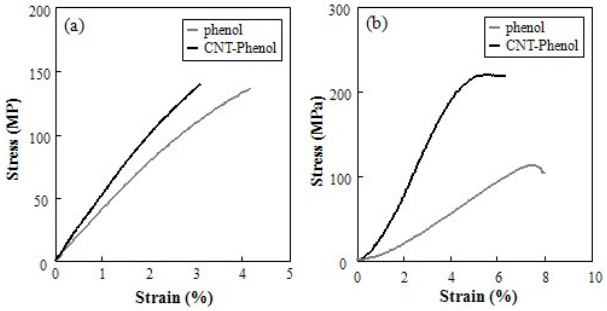

Fig.6. Mechanical properties of CNT-phenol composites

3.4 Interfacial properties

From curves of cyclic tensile test using carbon fiber reinforced phenol and CNT-phenolic composites. Both of phenol and CNT-phenolic composites exhibited good reinforcement effect during cyclic tensile test.

Figure 7 shows stress-strain curves and apparent modulus of bare carbon fiber and carbon fiber reinforced phenol or CNT-phenol composites. The reinforcing effect was measured indirectly by apparent modulus, which is the modulus of single carbon fiber embedded in the matrix. As expected, apparent modulus of carbon fiber embedded matrixes were higher than bare carbon fiber, and CNT-phenol composites exhibited a higher apparent modulus than neat phenol due to the better stress-

transferring and reinforcement effects of CNT-phenol composites. The CNT-phenol matrix is more rigid than neat phenol.

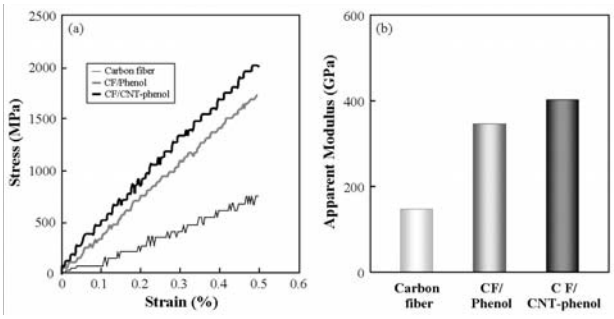

Fig.7. Stress-strain curves and apparent modulus

Microdroplet test shows the optical photos of pull-out patterns of carbon fiber with neat phenol and the CNT-phenol composite microdroplet. In neat phenol case, microdroplet exhibited pulling-out pattern due to limited interfacial adhesion between carbon fiber and neat phenol. The fiber was just fractured in CNT-phenol composites case even embedded with same size microdroplet. It is due to increased interfacial adhesion between carbon fiber and CNT-phenol composites.

3.5 Contact angle and wettability

Dynamic contact angle test for carbon fiber, neat phenol plate and CNT-phenol composites were measured. CNT-phenol composites exhibits hydrophobic properties, and the advancing contact angle of neat phenol was lower. It means that there were different surface energies based on the CNT microstructure. This enhancement in advancing contact angle was contributed to the combined effects of CNT microstructure on the surface of CNT-phenol composites, thus leading to the hydrophobicity of the CNT-phenol composites.

Table 1. Interfacial properties between fiber and matrix

Type	γ_S^{LW}	γ^-	γ^+	γ_S^T	γ^d	γ^p	W_a [1] (mJ/m^2)	S [2] (mJ/m^2)
Carbon fiber	17.9	4.2	0.1	19.3	10.3	9.6	~	~
Phenolic	37.3	0.9	1.5	39.6	41.5	4.4	57.3	16.6
CNT-phenolic	42.7	0.3	1.8	44.2	45.4	1.9	61.1	19.8

[1] W_a between a single carbon fiber and matrixes
[2] Spreading coefficient between a single carbon fiber and matrixes

Table 1 shows acid-base interaction and polar-dispersion surface energy components of carbon fibers, phenol and CNT-phenol composites. Work of adhesion between carbon fiber and CNT-phenol composites was higher than carbon fiber and phenol, implying that the interfacial adhesion between carbon fiber and the CNT-phenol composites was better.

4 Conclusions

Electro-micromechanical tests combined with wettability test were investigated to obtain the interfacial properties of carbon fiber reinforced phenol/CNT-phenolic composites. The optimum CNT dispersion condition with a solvent for maximizing self-sensing in a phenolic resin was determined. Contact resistance of CNT-phenolic composites was obtained using gradient specimen with two and four-point methods. Carbon fiber reinforced CNT-phenolic composites showed higher interfacial adhesion and apparent modulus than neat phenol. CNT microstructure caused hydrophobic property of CNT-phenolic composites.

Acknowledgments

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