Interfacial Properties and Curing Behavior of Carbon Fiber/Epoxy Composites using Micromechanical Techniques and Electrical Resistivity Measurement

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Micromechanical 시험법과 전기적 고유저항 측정을 이용한 탄소섬유강화복합재료의 계면 물성과 경화 거동에 관한 연구

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KEY WORDS : Micromechanical Techniques, Electrical Resistivity, Interfacial Shear Strength (IFSS), Electrodeposition (ED), Thermal Expansion Coefficient (TEC)

ABSTRACT

Logarithmic electrical resistivity of the untreated or thin diameter carbon fiber composite increased suddenly to the infinity when the fiber fracture occurred by tensile electro-micromechanical test, whereas that of the ED or thick fiber composite increased relatively broadly up to the infinity. Electrical resistance of single-carbon fiber composite increased suddenly due to electrical disconnection by the fiber fracture in tensile electro-micromechanical test, whereas that of SFC increased stepwise due to the occurrence of the partial electrical contact with increasing the buckling or overlapping in compressive test. Electrical resistivity measurement can be very useful technique to evaluate interfacial properties and to monitor curing behavior of single-carbon fiber/epoxy composite under tensile/compressive loading.

Nomenclature

τ_t, τ_c : Tensile/Compressive IFSS
α, β : Scale and shape parameters of Weibull distribution for aspect ratio
A : Cross-sectional area of the conductive fiber
L_{ec} : Eelectrical contact length of the fiber connecting to copper wires
R, ρ : Electrical resistance and resistivity

1. INTRODUCTION

Interfacial shear strength (IFSS) is an important factor to evaluate the mechanical properties in the fiber reinforced composites. The most common micro-mechanical techniques to evaluate IFSS include the single-fiber pullout test [1] and the fragmentation test [2] etc. The electrodeposition (ED) to improve IFSS is a process that a polymeric film is deposited on a carbon fiber surface from dispersions of colloid colloidal ion in double-distilled water [3]. During curing process, thermosetting matrix undergoes volume changes resulting from thermal expansion in composite, and matrix shrinkage produce significant residual stress at around fiber. Madhukar [4] studied correlation between matrix volume shrinkage and fiber tension resulting from residual stress as a function of the thermal history, and proposed optimum cure cycle in various fiber/thermosetting composites. Recently, several researchers had evaluated curing characteristics by the measurement of electrical resistance. Chung [5] measured electrical resistivity to evaluate curing characteristics and micromechanical properties. The relationship between residual stress and electrical resistivity change during curing was studied in single-carbon fiber/epoxy composite. And then, simultaneous micromechanical properties due to residual stress effect was investigated

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using electro-micromechanical test. In this work, micro-mechanical technique under tensile/compressive loadings and electrical resistivity measurement were used to evaluate interfacial properties and curing characteristics depending on curing temperature, matrix modulus and the surface treatments in single-carbon fiber/epoxy composites.

2. EXPERIMENTAL

2. 1. Materials

Carbon fibers with two diameters of 8 μm (Taekwang Industrial Co., Korea) and 18 μm (Mitsubishi Chemical Co., Japan) were used as conductive reinforcing fibers. Testing specimens were prepared with epoxy resin (YD-128, Kukdo Chemical Co., Korea). Epoxy resin is based on diglycidyl ether of bisphenol-A (DGEBA). Polyoxypropylene diamine (Jeffamine D-400 and D-2000, Huntzman Petrochemical Co.) was used as curing agents. Matrix modulus was controlled by adjusting relative proportion of D-400 *versus* D-2000. Polybutadiene–maleic anhydride (PBMA, Polyscience Inc.) was used as a polymeric coupling agent to improve IFSS by ED.

2. 2. Methodologies

2. 2. 1. ED Treatment: Fig. 1 exhibited ED system for carbon fiber surface treatment. Carbon fiber acted as the anode, whereas an aluminum plate was the cathode. After the anode and the cathode were immersed into 0.5 wt.% PBMA aqueous electrolyte solution, 3 voltages were supplied to both electrodes by power supply. Typical coating time was set up for 10 minutes. After ED was treated, carbon fibers were dried at room temperature without further thermal treatment.

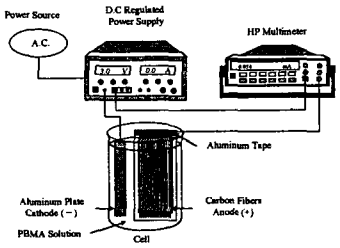

Fig. 1 ED system for carbon fiber surface treatment

2. 2. 2. Measurements of Mechanical and Electrical Properties of Fibers: About thirty specimens were measured at 20 mm gauge length for each fibers. Universial testing machine (UTM, LR-10K, Lloyd Instrument Ltd.) was used to measure the single-fiber tensile strength. Electrical resistance was measured at 32 mm in distance between two voltage contacts using digital multimeter.

2. 2. 3. Preparation of Testing Specimens: Three-type composite specimens were used in this experiment. Fig. 2(a) is a testing specimen to evaluate IFSS using two-fiber tensile fragmentation test. Fig. 2(b) and (c) are single-carbon fiber composites to measure the electrical resistivity under tensile/compressive tests. Testing composites were precured at 80 °C for 1 hour and then postcured at 120 °C for 1 hour.

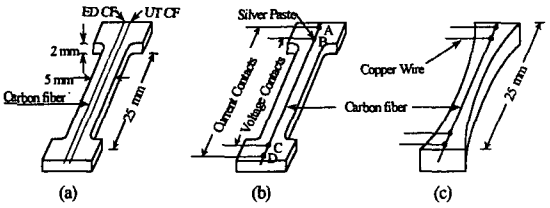

Fig. 2 Three-type testing composites.

2. 2. 4. Measurement of IFSS and Residual Stress: IFSS of carbon fiber/epoxy composite depending on curing temperature, matrix modulus and the surface treatment was measured by tensile/compressive test. Tensile IFSS, τ_t, was determined using Drzal equation [3]. By introducing Weibull distribution for aspect ratio, IFSS was exhibited in the form as follows:

$$\tau_t = \frac{\sigma_{ft}}{2 \cdot \alpha} \cdot \Gamma\left[1 - \frac{1}{\beta}\right] \tag{1}$$

Where α and β are scale and shape parameters of Weibull distribution for aspect ratio (l_c/d), σ_{ft} is the fiber tensile strength using Weibull weakest link rule, and Γ is gamma function. According to the compressive profile, compressive IFSS, τ_c, based also on the force balance,

$$\tau_c = \frac{\sigma_{fc} \cdot d}{2 l_c} \tag{2}$$

where critical length l_c is the original length of the fiber, is σ_{fc} is the fiber stress at the point where the interfacial stress is insufficient to induce further fragmentation. Residual stress was generated by matrix shrinkage due to TEC difference between fiber and matrix during curing process. Residual stress can be obtained by a following equation as [6],

$$\sigma_{residual} = (\alpha_m - \alpha_f)\,\Delta T \cdot E(\varepsilon) \tag{3}$$

Where $E(\varepsilon)$ is the elastic modulus resulted from the measures stress/strain response of composite, and α_m and α_f are thermal expansion coefficient of matrix and fiber.

2. 2. 5. Electrical Resistivity Measurement: In fig. 3, a HP34401A digital multimeter was used to measure electrical resistance during curing or tensile/compressive

electro-micromechanical test. Testing speed and load cell were 0.5 mm/minute and 100 kg_f in tensile test and 2 mm/minute and 10KN in compressive test, respectively. Electrical resistance was measured by four-point probe method, and silver paste was used as electrically connecting glue at 4 junctions to maintain electrical contact between the fiber and leading wire (fig. 2(b)). Total electrical resistance (R_{Tot}) between B and C may include R_c based on the contact resistance by silver paste beside R_f due to the electrical resistance by the fiber as follows:

$$R_{Tot} = R_c + R_f \quad (4)$$

Since the value of R_c is negligibly small due to very high conductivity of silver paste comparing to R_f, it can be considered that the voltage developed between junction B and C becomes nearly fiber resistance,

$$R_{Tot} \cong R_f \quad (5)$$

Electrical resistivity (ρ) was obtained from the measured electrical resistance (R).

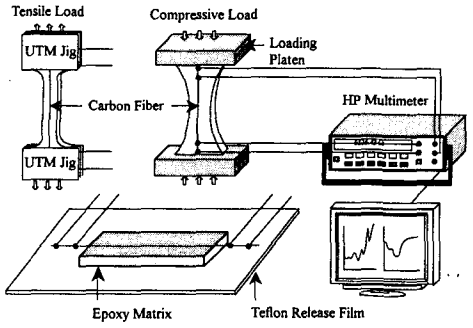

Fig. 3 Experimental system for the measurement of electrical resistance

3. RESULTS AND DISCUSSION

3. 1. Material Properties: Table 1 shows the mechanical and electrical properties of carbon fiber comparing with other fibers. Electrical resistivity of 8 μm carbon fiber was higher than that of 18 μm case due to intrinsic structure of fiber material.

Table 1 Intrinsically electrical and mechanical properties for conductive fibers

Fiber	Diameter (μm)	Electrical Resistance (Ω)	Electrical[1] Resistivity (×10⁻³Ω·cm)	Tensile[2] Strength (MPa)	Elastic Modulus (GPa)
Carbon	8	1.19×10^4 (570)[5]	18.6 (0.9)	2878	175
Carbon	18	1.57×10^3 (120)	12.5 (1.0)	1753	201
SiC[3]	138	0.34×10^3 (10)	156.8 (5.3)	3613	162
Steel[4]	280	0.57 (0.07)	1.09 (0.14)	1461	193

1, 2) Measured at 32 mm in voltage contacts and 20 mm in gauge length, respectively.
3) Manufactured by Textron Co.
4) No. 1 of guitar string (Segovia Instruments Co., Korea)
5) Parenthesis is standard deviation.

Table 2 shows TEC, matrix modulus and IFSS depending on the curing temperature and curing agent composition. TEC decreased as curing temperature increased or matrix modulus increased. It might be because the curing degree and cross-linking density were improved.

Table 2 TEC, matrix modulus and IFSS as a function of various matrix conditions

Ratio of[1] Curing Agents	Curing Temp. (°C)	TEC[2] (10^{-6}°C^{-1})	Matrix Modulus (GPa)	IFSS[3] (MPa)
2.7 : 0.3	100	77.4	1.73	25.2
2.7 : 0.3	120	69.1	1.85	31.5
2.7 : 0.3	140	64.3	1.92	35.3
2.5 : 0.5	120	81.8	1.08	28.0
3.0 : 0.0	120	53.6	2.19	26.3

1) Mixing composition of Jeffamine D400 versus D2000
2) Thermal expansion coefficient was measured at 80℃ for 15 min.
3) Measured by tensile fragmentation test

3. 3. Curing Behavior of SFC: Fig. 4 shows behavior of electrical resistivty depending on curing temperature carbon and steel fiber with or without epoxy matrix. Electrical resistivty decreases as curing temperature in a bare carbon fiber, whereas it increased in a bare steel fiber. It might be due to different fiber structure. In both carbon and steel fiber/epoxy composites, electrical resistance difference (ΔR) is very high compared to two bare fibers. It might be because of residual stress due to matrix shrinkage during curing process.

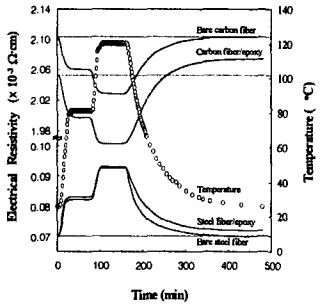

Fig. 4 Behavior of electrical resitivity depending on curing temperature in two bare fibers and SFCs

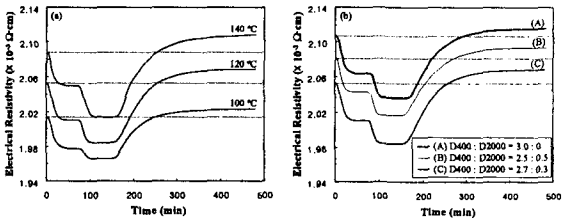

Fig. 5 Electrical resistivity on (a) curing temperature and (b) matrix modulus during curing

Fig. 5 exhibits electrical resistivity behavior of single carbon fiber/epoxy composite depending on the curing temperature and matrix modulus. Electrical resistivity

difference (ΔR) increased as curing temperature increased. It might be because the curing degree increased at high temperature. In fig. 5(b), ΔR of condition (A) with optimum composition is the largest in same curing temperature, whereas that of condition (B) is the smallest.

3. 3. Interfacial Properties by Tensile/Compressive Electro-micromechanical Test: Fig. 6 shows IFSS between the untreated and ED carbon fiber/epoxy composites by tensile/compressive tests. IFSS of ED case was higher than that of the untreated case in both tests. It might be due to electrical polymer coating layer with chemical or hydrogen bondings.

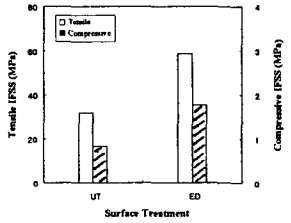

Fig. 6 Comparison of IFSS between the untreated and ED cases using tensile/compressive test.

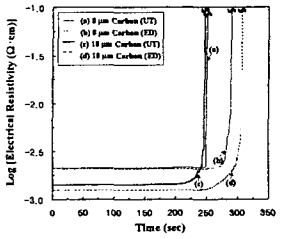

Fig. 7 Logarithmic electrical resistivity of SFC under tensile test

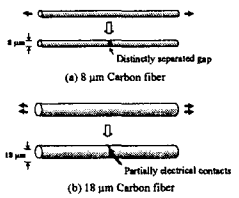

Fig. 8 Schematic model for a fiber breakage with 2 diameters

Fig 7 shows the comparison of logarithmic electrical resistivity depending on the ED treatment in both single 8 and 18 μm carbon fiber composites using tensile electro-micromechanical test. Logarithmic electrical resistivity of the untreated carbon fiber composites increased comparatively suddenly compared to the ED cases. It might be because of the retarded fracture time due to the improved interfacial adhesion. When tensile stress was transferred from matrix to fiber by the external deformation, ED carbon fiber could be endured well against the applied tensile stress and could not be broken easily. When a fiber was broken for the first time, the logarithmic electrical resistivity increased abruptly to the infinity in the case of thin 8 μm carbon fiber composite. On the other hand, the electrical resistivity exhibited smooth increment in the thicker 18 μm carbon fiber composite, and finally the electrical resistivity reached to the infinity. It might be due to the fiber diameter effect by a very abrupt change of the electrical resistivity occurred for thinner 8 μm carbon fiber composite than the thicker 18 μm case.

Fig. 8 exhibited two schematic models for the fiber fracture modes of thin 8 μm and thicker 18 μm carbon fibers in terms of the size effect of fiber diameter. Carbon fiber fracture of 8 μm in diameter shows the complete disconnection, whereas the break of 18 μm carbon fiber shows the maintenance of partial electrical contacts. It was considered that the break of thick 18 μm carbon fiber might be kept on contacting electrically until further strain level comparing to 8 μm case.

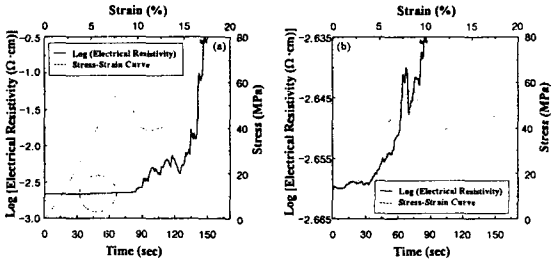

Fig. 9 Logarithmic electrical resistivity of a SFC under compressive load

Fig. 9 shows logarithmic electrical resistivity of single-carbon fiber/epoxy composite by compressive electro-micromechancial test. Fig. 9(a) exhibited total behavior of logarithmic electrical resistivity, and fig. 9(b) was magnified with initial part in fig. 9(a). Significant change of logarithmic electrical resistivity change due to fiber fractures was observed in the initial stage. Change of logarithmic electrical resistivity was large in latter stage. It might be due to changing contacting distance between fiber fractures. The trend of logarithmic electrical resistivity for single carbon fiber/epoxy composite by compressive test is different significantly from that by tensile test.

3. 4. Comparison of IFSS and Various Parameters: Fig. 10 shows correlation of IFSS and other parameters in single-carbon fiber/epoxy composites, such as curing temperature and matrix modulus. As curing temperature increase, other parameters except TEC increased. It is considered that residual stress gave effect on the IFSS and electrical resistivity difference. With increasing matrix modulus, TEC decrease whereas other parameters such as IFSS, electrical resistance difference (ΔR), and residual stress increased, and then decreased. It is due to the optimum matrix modulus condition for the maximum

performance of composites. It might be due to the optimum matrix modulus condition for the maximum performance of composite.

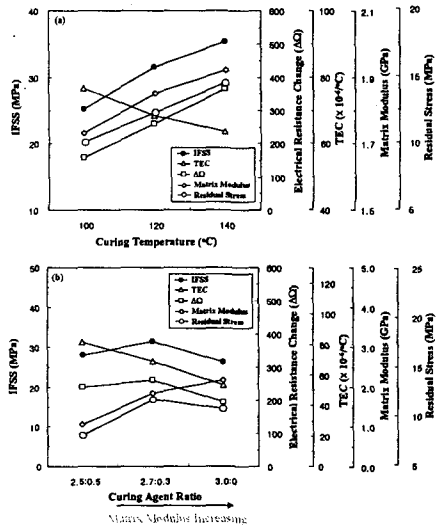

Fig. 10 IFSS and other parameters depending on the (a) curing temperature and (b) matrix modulus

4. CONCLUSIONS

IFSS of the ED composite exhibited higher than the untreated case. It is might be due to the electrically and firmly adsorbed polymeric coating, as well as hydrogen and chemical bonding. logarithmic electrical resistivity of the untreated or thin fiber case increased suddenly to the infinity, whereas the ED or thick fiber case increased broadly to the infinity in SFC. It might be because of the retarded fracture time by improved interfacial adhesion and fiber diameter effect. Electrical resistivity decreases with increasing curing temperature in a bare carbon fiber without epoxy matrix, whereas it increased in a bare steel fiber. It is might be due to different intrinsic structure of materials. In both carbon and steel fiber/epoxy composites, electrical resistance difference (ΔR) between initial and final steps is very high compared to two bare fibers. It might be because of residual stress due to matrix shrinkage during curing process. In tensile test, of single-carbon fiber composite, a sudden increase of electrical resistance exhibited due to electrical disconnection by the fiber fracture, whereas in compressive test the stepwise increase of electrical resistance change was observed due to the occurrence of the partial electrical contact with increasing the buckling or overlapping. As curing temperature increased, TEC decreased, whereas IFSS, electrical resistivity difference, and residual stress increased due to increasing the curing degree by high temperature. In controlling curing agent formulation, IFSS and other parameters such as electrical resistance difference (ΔR) and residual stress is largest at optimum curing agent composition, whereas that of brittle matrix is smallest..

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