Effect of Ni Plating on Mechanical Interfacial Properties of Carbon Fibers-reinforced Composites

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In recent years, carbon fibers have been used as reinforcing materials in high performance composite materials such as carbon fibers-reinforced plastics (CFRPs) and carbon-carbon composites. CFRPs are widely applied where high strength and stiffness, light weight, and creep resistance properties are essentially required. Major applications of CFRPs are in the high technologies, which includes aerospace and military engineering, and general engineering that includes engineering components such as gears, cams, and automobile bodies [1].

The mechanical properties of CFRPs are mainly controlled by the interfacial adhesion between fibers and matrix though it is also affected by the original properties of the fibers and matrix [2]. To achieve good adhesion between the fibers and matrix, the surfaces of reinforcements are usually modified by various methods such as oxidation in acid solutions [3], dry oxidation in oxygen [1], anodic oxidation [4], plasma treatment [5], mild fluorination [6], and electroplating in molten salt solutions [7].

The adhesion of electroplated metal/carbon fiber composites has been shown to be excellent where the metal coating is grown from the carbon fiber surfaces. In particular, polymer/metal interaction is strong, mainly due to the high metal surface energetics that allows extensive wetting with the polymer [8].

The objective of this study is to investigate the effects of surface properties on mechanical interfacial properties of electrolytically Ni-plated carbon fibers in a composites system.

For the present investigation, the reinforcement materials were continuous no-sized and no-treated PAN-based carbon fibers (12 K, TZ-307™) manufactured by Taekwang Industries, Ltd. in Korea. Prior to use, the surfaces of carbon fibers were cleaned in a Soxhlet extractor with distilled acetone. Epoxy resin, YD-128™ (supplied from Kukdo Chem. Co. of Korea), was used as the polymeric matrix.

The compositions of Ni salt solutions and operation conditions of Ni plating were listed in Table 1. A plating device was constructed for the continuous plating onto the fiber surfaces. The speed of Ni-plating was controlled, and it was

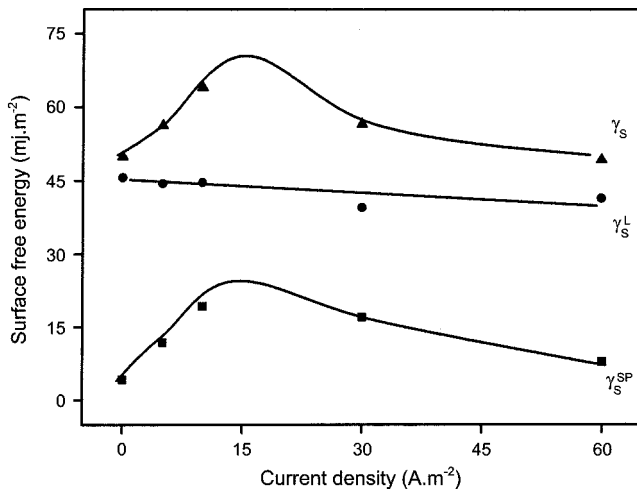**Table 1.** Composition and operating conditions of Ni-plating baths

	Electrolytical Ni-plating	
Composition	$NiSO_4 \cdot 6H_2O$	280 g/L
	$NiCl_2 \cdot 6H_2O$	40 g/L
	H_3BO_3	30 g/L
Conditions	pH	4.5-5.0
	Temperature (°C)	40-50
	Current density (A·m^{-2})	0-60

normally about 0.7 m·min^{-1}. Ni plating was performed with 5, 10, 30, and 60 A·m^{-2}.

Contact angle was used as a parameter to characterize the wetting performance and surface free energy of the surface-treated fibers. Contact angle measurement of carbon fibers was performed using a Krüss Processor Tensiometer K-100 (Krüss GMBH in Germany) with fiber apparatus, as shown in Figure 1. The test liquids used for contact angle measurements were n-hexane, deionized water, and diiodomethane.
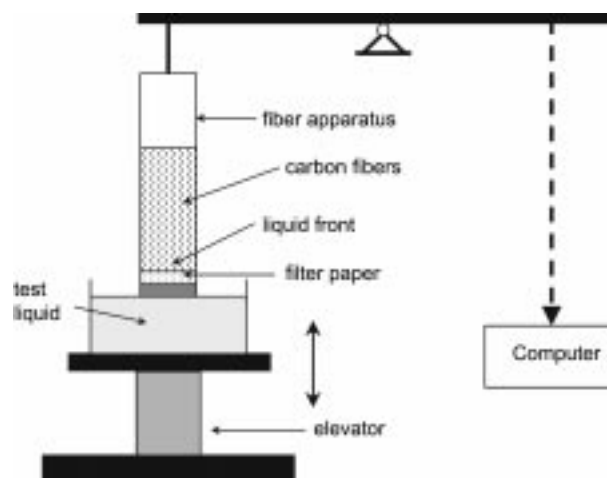
Fig. 1. Schematic diagram of the contact angle measurement method.

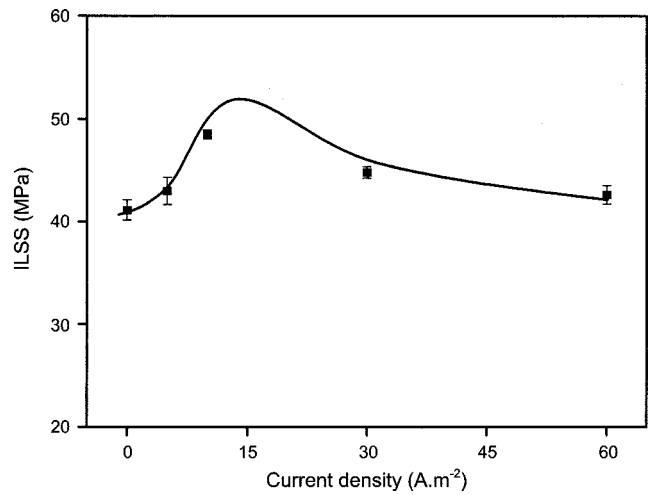**Fig. 2.** Surface free energy and their components of carbon fibers.

Fig. 3. ILSS of the carbon fibers-reinforced plastics as a function of the electrolytical Ni-plating current density.

The surface tensions of these liquids are known (surface tension of water, $\gamma_L = 72.8$ mJm^{-2}, polar component of the surface tension, $\gamma_L^{SP} = 51.0$ mJm^{-2}, and London dispersive component of the surface tension, $\gamma_L^{L} = 21.8$ mJm^{-2}. For diiodomethane $\gamma_L = 50.8$ mJm^{-2}, $\gamma_L^{SP} = 0.38$ mJm^{-2}, and $\gamma_L^{L} = 50.42$ mJm^{-2}).

The degree of adhesion at interfaces between fibers and matrix can be measured by a short-beam test (3-point) for the interlaminar shear strength of the mechanical interfacial properties according to the ASTM D2344 (cross head speed=2 mm/min, span-to-depth ratio=4:1).

The surface free energy of Ni-plated carbon fibers is shown in Figure 2. As seen in Figure 2, the Ni-plating on carbon fiber surfaces at the current density range of 5~60 A·m^{-2} lead to better wetting level than that of untreated carbon fibers. To improve the wettability, the surface free energy of the treated carbon fibers should be made larger than those of matrix in a real composite system [2]. In the case of 10 A·m^{-2} current density, the surface free energy, γ_S, reaches at a highest value, around 67 mJ·m^{-2}. Thus, it is expected that the degree of adhesion between metallized carbon fiber surfaces and epoxy resin can be enhanced, since surface free energy of the metallized carbon fibers does

Table 2. Chemical composition of Ni-plated carbon fibers

Current density (A·m^{-2})	Elemental compositions			Elemental ratio
	O_{1s} (%)	C_{1s} (%)	N_{1s} (%)	O_{1s}/C_{1s}
0	25.8	68.8	0.8	0.375
5	25.4	64.4	0.8	0.394
10	28.0	62.8	0.8	0.446
30	26.8	63.3	0.8	0.423
60	23.9	63.0	0.8	0.379

allow extensive wetting in the epoxy resin (45 mJ·m^{-2}).

Table 2 shows O_{1s}, C_{1s}, N_{1s} and O_{1s}/C_{1s} ratio. The O_{1s}/C_{1s} composition ratios of Ni-plated carbon fibers are increased until 30 A·m^{-2}, compared to that of untreated carbon fibers due to the deposition of more active forms, such as NiO, Ni(OH)$_2$, and Ni metal on the inactive carbon. In addition, the pattern of O_{1s}/C_{1s} ratios shows similar with that of surface free energy of Ni-plated carbon fibers. However, nitrogen of carbon fiber surfaces has no significant changes as the current density increases. From the XPS results, the carbon content of Ni-plated carbon fibers decreases when the fibers are plated with metallic nickel, whereas the oxygen and nickel contents of plated fibers are higher than those of untreated fibers. The active groups on the carbon fiber surfaces after Ni-plating lead to a change the polarity or functionality of fiber surfaces.

It is well known that resulting mechanical properties of composites are strongly depended on fiber/matrix interfacial adhesion due to the easiness of load transfer from one matrix to the others via the fibers. Figure 3 shows the interlaminar shear stress (ILSS) results of the Ni-plated CFRPs as a function of current density. All metallized CFRPs show higher ILSS value than that of untreated CFRPs. And, the maximum strength is found at the current density of 10 A·m^{-2}.

It is interesting to note that the ILSS results support the reliability of the data, since the tendencies in ILSS values seem to be very similar to tendencies in O_{1s}/C_{1s} or surface free energy. As a matter of fact, the relationship between ILSS and O_{1s}/C_{1s} and between ILSS and γ_S^{SP} are almost linear for all samples with different current densities, as shown Figure 4(a), (b). Therefore, the O_{1s}/C_{1s} ratio and γ_S^{SP} value can be explained as major governing factor in the adhesion of fiber/matrix in this system.

In conclusion, electrolytical Ni-plating on carbon fiber surfaces leads to the increase of the resulting mechanical inter-
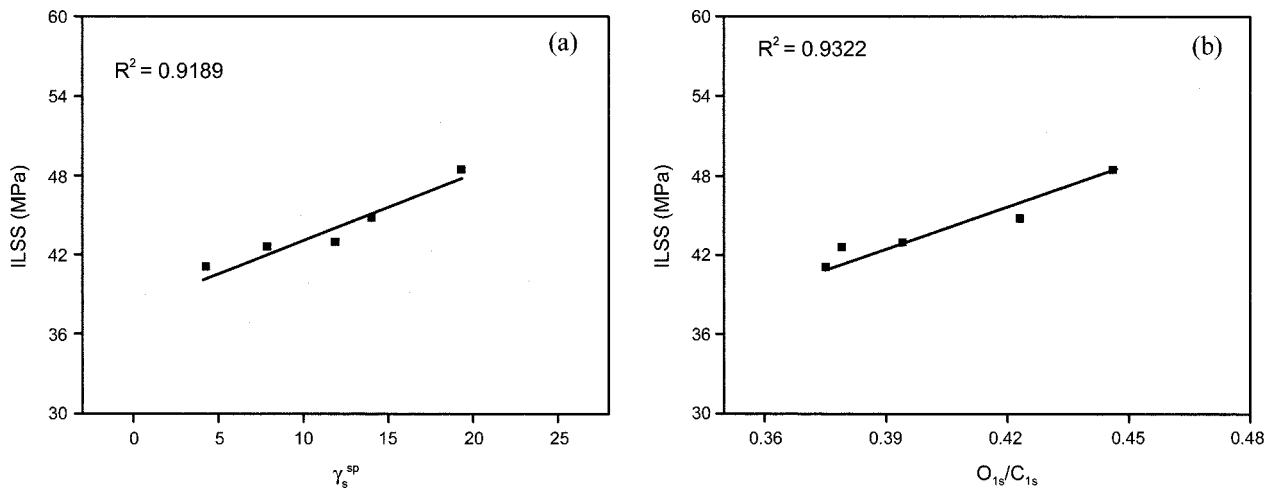
Fig. 4. Dependence of the ILSS on γ_S^{SP} (a) and O_{1s}/C_{1s} (b) of the carbon fiber surfaces (R=coefficient of regression).

facial properties in their composites. It is mainly due to the increase of surface free energy or surface oxygen ratio on Ni-plated carbon fibers.

References

[1] Donnet, J. B.; Bansal, R. C. "Carbon Fibers", 2 Ed. Marcel Dekker, New York, 1990.

[2] Park, S. J.; Jang, Y. S.; Rhee, K. Y. *J. Colloid Interface Sci.* **2002**, *254*, 383.

[3] Donnet, J. B.; Park, S. J. *Carbon* **1991**, *29*, 955.

[4] Bismarck, A.; Kumru, M. E.; Springer, J.; Simitzis, J. *Carbon* **1999**, *143*, 45.

[5] Paredes, J. I.; Martinez-Alonso, A.; Tascon, J. M. D. *Carbon* **2002**, *40*, 1101.

[6] Chang, Y.; Ohara, H. J. *J. Fluorine Chem.* **1992**, *57*, 169.

[7] Han, K. P.; Fang, J. L. *J. Appl. Electrochem* **1996**, *26*, 1273.

[8] Wu, S. "Polymer Interface and Adhesion." Marcel Dekker, New York, 1982.