플라즈마 처리가 탄소섬유강화 복합재료의 기계적특성에 미치는 영향

오진석* · 이재락* · 박수진*

Effect of Plasma Treatment on Mechanical Properties of Carbon Fibers-reinforced Composites

Jin-Seok Oh[*], Jae Rock Lee[*], and Soo-Jin Park[*]

Key Words : carbon fibers-reinforced composites, oxygen plasma treatment, surface properties, mechanical properties

ABSTRACT

In this work, effects of oxygen plasma on surface characteristics of carbon fibers were investigated in mechanical properties interfacial of carbon fibers-reinforced composites. The surface properties of the carbon fibers were determined by acid/base values, FT-IR, and X-ray photoelectron spectroscopy (XPS). Also, the mechanical properties of the composites were studied in and critical stress intensity factor (K_{IC}) and critical strain energy release rate mode II (G_{IIC}) measurements. As experimental results, the O_{1S}/C_{1S} ratio of the carbon fiber surfaces treated by oxygen plasma was increased compared to that of untreated ones, possibly due to development of oxygen-containing functional groups. The mechanical properties of the composites, including K_{IC} and G_{IIC} had been improved in the oxygen plasma on fibers. These results could be explained that the oxygen plasma was resulted in the increase of the adhesion of between fibers and matrix in a composite system.

1. INTRODUCTION

Carbon fibers are of potential importance nowadays due to their technological applications. Microstructure of carbon fibers is such that they have both high modulus and strength. Various types of chemicals have been intercalated in the fibers in the past to improve their mechanical properties. Carbon fibers, when used without surface treatment, produce composites with low interlaminar shear strength (ILSS). This has been attributed to weak adhesion and poor bonding between fibers and matrix [1,2].

Thus, all the carbon fibers are given a surface treatment. These treatments increase the surface active sites and then improve bonding between the fibers and the resin matrix. Generally, the oxidative methods for the modification of such non-polar carbon fiber surfaces include oxidation in different plasmas, oxidation in air, electrochemical oxidation using carbons as an anode in various electrolytes, and wet chemical methods, such as immersing in phosphoric acid or boiling in nitric acid and intercalation [3,4].

However, the studies on improving the fibers/matrix adhesion for a given surface treatment are well understood in the literature. Therefore, in this work, plasma tratment condition is applied to modify the surface characteristics of carbon fibers. Especially, the oxygen gas is used as fibers. And the replacement between the oxygen content and the fiber/matrix adhesion of the composites is investigated using a combination of surface analysis and critical stress intensity factor (K_{IC}) and critical strain energy release rate mode II (G_{IIC}) test.

2. EXPERIMENTAL

2.1 Materials and Sample Preparation

The fibers used in this work were polyacrylonitrile (PAN)-based carbon fibers (12K, TZ-607) manufactured by Taekwang of Korea. The epoxy resin used as a matrix was diglycidylether of bisphenol-A (DGEBA, YD-128 supplied from Kukdo Chem. Co. of Korea). Epoxide equivalent weight was 185-190 g.eq^{-1} and the viscosity

*
Advanced Materials Division, Korea Research Institute of Chemical Technology

was 11500-13500 cps at 25℃. Diaminodiphenylmethane (DDM, purchased from Aldrich Co.) was selected as a hardener and methylethylketone (MEK) was used to reduce the high viscosity of DGEBA. The chemical structures of DEGBA and DDM were shown in Figure 1.

Plasma processing (ATMOSTM-Mulit, Plasmart in Korea) for the carbon fibers were carried out using atmospheric pressure and radiofrequency for Ar/O2 (O2 1%) mixed gas. The radiofrequency generating Ar/O2 mixture plasma was at 300 W and 13.56 MHz.

Unidirectional carbon fibers-epoxy matrix composites were prepared by continuous impregnation of the fibers using a drum winding technique for manufacturing prepreg with subsequent hot-pressing. Specimens were prepared from laminates composed of 22 plies and fabricated in a hot-press at 150℃ and 7.4
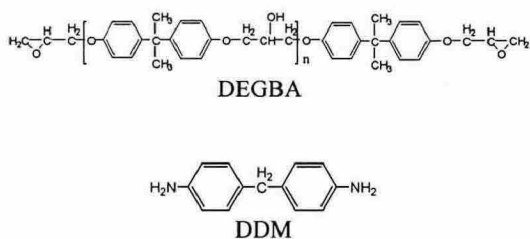

DEGBA

DDM

Figure 1. Chemical structures of DEGBA and DDM.

MPa for 150 min with a vacuum bagging method. The fiber volume fraction of bulk specimens was about 50% (±2%), and the specimens were cut into test specimens to carry out mechanical testing.

2.2. Surface properties

The surface property changes of the carbon fibers before and after plasma treatment were characterized by the following techniques;

The potential chemical activity of surface functional groups on plasma treated carbon fibers can be determined by measuring the pH according to the ASTM E-70 and by measuring acid-base values using the Boehm's method on the basis of adsorption of 0.1 N NaOH and HCl standard solutions.

The FT-IR instrument used was a Hartman & Brawn Model Bomen MB 102 Spectrophotometer. The scan range was 400 to 4000 cm^{-1}.

The X-ray photoelectron spectroscopy (XPS) experiment was performed using a VG Scientific ESCA LAB MK-Ⅱ spectrometer equipped with a Mg-K α X-ray source. The base pressure in the sample chamber was controlled in the range of 10^{-8} to 10^{-9} torr.

2.4. Mechanical properties
Mechanical properties of the composites were

investigated using two types of testing method, namely critical stress intensity factor (K_{IC}) and critical energy release rate mode II (G_{IIC}).

An analytical expression for critical stress intensity factor (K_{IC}) of unidirectional composites can be characterized by single edge notched (SEN) test in three-point flexure. Notches were cut using a diamond-coating saw, approximately half the depth of specimen. The three-point bending test was conducted using Instron Model Lloyd LR-5K mechanical tester according to the ASTM E-399. A span-to-depth ratio 4:1 and crosshead speed of 1 mm·min^{-1}

The critical energy release rate mode II (G_{IIC}) in end-notch flexure (ENF) tests was conducted by cross-head speed of 1mm.min^{-1} according to the ASTM D-5528. A span-to-depth ratio 4:1.

3. RESULTS AND DISCUSSION

3.1 Surface properties

Table 1 shows the experimental surface properties of the carbon fibers treated by oxygen plasma. The results of pH show that the surface properties of untreated carbon fibers are a slight excess of basic properties. This is probably due to the existence of basic groups on the fiber surfaces through high manufacturing treatment time. Both the pH and the acid values of plasma treated carbon

Table 1 pH and Acid-Base Values of the Carbon Fibers Studied

Specimens	pH	Acid value [meq·g^{-1}]	Base value [meq/g]
No treatment	7.02	15.0	20.2
CFP - 2	6.95	35.0	20.1
CFP - 4	6.94	65.1	20.1
CFP - 8	6.94	32.5	20.1
CFP - 16	6.95	36.7	20.1

Table 2. Compositions of the Carbon Fibers Studied by XPS Measurements

				[unit: at%]
Specimens	XPS			
	C_{1S}	N_{1S}	O_{1S}	O_{1S}/C_{1S}
As-received	74.3	1.4	24.3	0.327
CFP-2	73.5	1.4	25.1	0.342
CFP -4	68.8	0.7	30.6	0.445
CFP -8	72.1	1.4	26.5	0.368
CFP -16	69.7	1.5	28.9	0.414

fibers acidity to that of the untreated fibers, and indicate that the treatment time at 4 min provides an optimum condition to the surface acidity of the fibers.[5]

Fig. 2 shows the FT-IR results of plasma treated carbon fiber specimens. As a result, the oxygen functional groups (C=O, COOH, and C-O) at 1600-1800 cm^{-1} and hydroxyl group (O-H) at 3450 cm^{-1} are increased in the plasma treated carbon fibers. Moreover, the hydrocarbon group (CH) at 2980 cm^{-1} is decreased with increasing the treatment time. This result affects the surface characteristics of the fibers, resulting in improving the interfacial adhesion between the fibers and the matrix resins, due to the increase of oxygen functional groups on carbon fiber surfaces.

Wide scan spectra in the binding energy range 0~1000 eV are obtained to identify the surface elements present and carry out a quantitative analysis. XPS wide scan spectra of the plasma treated carbon fiber specimens are shown in Fig. 3. The intensity scale factors for the plasma treated carbon fibers are higher than that of the as-received carbon fiber specimen. The XPS spectra show distinct carbon and oxygen peaks, representing the
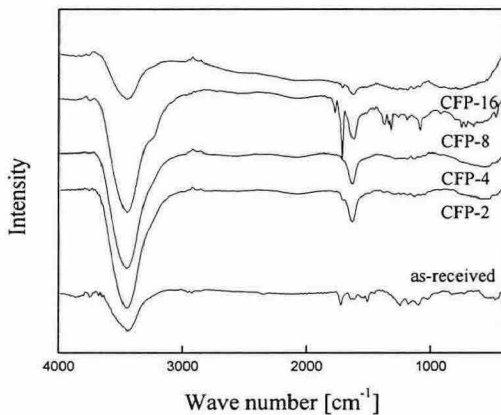

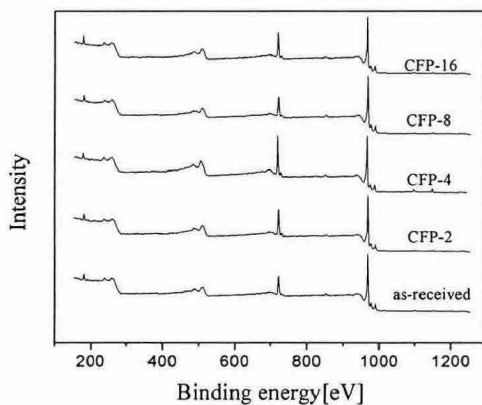**Fig. 2. FT-IR spectra of the plasma treated carbon fibers.**

Fig. 3. XPS spectra of plasma treated carbon fibers.

major constituents of the carbon fibers investigated. Relatively weak peaks of other major elements, such as nitrogen are also observed. No other major elements are detected from wide scan spectra on the surface of the carbon fibers. The resulting surface element concentrations of the plasma treated carbon fiber specimens are listed in Table 2. It is found that the surface carbon concentrations of the as-received and CFP-4 carbon fiber specimens are 74.3 at% and 68.8 at%, respectively. A lower surface carbon concentration in the CFP-4 carbon fiber specimen compares to that of the as-received specimen can be attributed to the bonding of oxygen on the carbon surfaces produced by the plasm treatment. The surface concentration of oxygen in the CFP-4 specimen is relatively similar to that of the as-received carbon fiber. The broad carbon peak that is observed in the binding energy, due to the several carbon-based surface functional groups which have different binding energies[6].

3.2 Mechanical behaviors

The critical stress intensity factor (K_{IC}), which is one of the fracture toughness parameters, describes the state in the vicinity of the tip of a crack as a function of specimen geometry, the crack geometry and the applied load on the basis of linear elastic fracture mechanics (LEFM). For the SEN bending specimens, the value of K_{IC} is calculated using the Eq. (1).[7,8]

$$K_{IC} = \frac{P \cdot L}{b \cdot d^{3/2}} \cdot Y \qquad (1)$$

where, P is the load obtained from the load-deformation curve, L the span between the supports, Y the geometric factor described in ASTM E 399, and b and d the specimen width and thickness, respectively.

Expressions for the calculation of mode-II critical strain energy-release rate (G_{IIC}) are calculated by the following Eq. (2) [9]

$$G_{IIC} = \frac{9a^2 p \Delta a}{2w(2L^3 + 3a^3)} \qquad (2)$$

where, P is the load, a crack, L half-span length, and W width

Fig. 4 shows the results for K_{IC} and G_{IIC} of the plasma treated carbon fibers-reinforced composites. As a result, the effect of fiber surface treatment conditions and the resulting fiber-matrix adhesion on composite mechanical properties produce noteworthy relationships. Thus, the K_{IC} increases with increasing the G_{IIC} for the degree of adhesion at interfaces. The maximum strength values of 274.4 MPa/cm$^{1/2}$ and 1.29 kJ/m^2 are attained at the
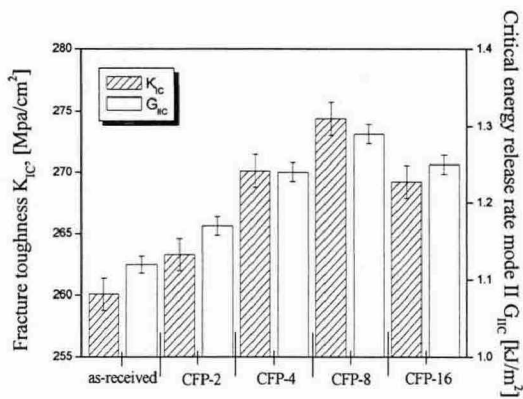
Fig. 4. K_{IC} and G_{IIC} of plasma treated carbon fibers-reinforced composites.

plasma treatment time at 4 min. Therefore, we suggest that additional energy to extend the interfacial crack at this condition is attributed to increasing the interfacial adhesion between fiber and matrix.

From a good linearity of the results, it is found that there is a strong correlation between surface functionality of the fibers and mechanical properties of the composites. Consequently, plasma treatment leads to an increase of interfacial bonding at interfaces between fibers and matrix resins. This is due to the increase of acidic functional groups on carbon fiber surfaces, which is resulted in the improvement of acid-base intermolecular interaction of the composites.

4. CONCLUSION

In this work, the O_{1s}/C_{1s} ratio of the carbon fiber surfaces treated by oxygen plasma was increased compared to that of untreated ones, possibly due to the development of oxygen-containing functional groups. The mechanical properties of the composites, including K_{IC} and G_{IIC} had been improved in the oxygen plasma on fibers. These results could be explained that the oxygen plasma was resulted in the increase of the adhesion between fibers and matrix in the composite systems.

References

1. M. M. Schwartz, "Composite Materials Handbook", 2th ed., McGraw-Hill, New York, 1992.
2. J. B. Donnet and R. C. Bansal, "Carbon Fibers", 2th ed., Marcel Dekker, New York, 1990.
3. S. J. Park, M. H. Kim, J. R. Lee, and S. Choi, "Effect of Fiber-polymer Interactions on Fracture Toughness Behaviors of Carbon Fiber–reinforced Epoxy Matrix Composites," *Journal of Colloid and Interface* Science, Vol. 228, 2000, pp. 287-291.
4. N. Dilsiz, E. Ebert, W. Weisweiler, and G. Akovali, "Effect of Plasma Polymerization on Carbon Fibers Used for Fiber/Epoxy Composites" *J. Colloid Interface Sci.,* 170, 241-248 (1995).
5. H. P. Boehm, "Chemical Identification of Surface Groups," *Advances in Catalysis*, Vol. 16, 1966, pp. 179-225.
6. N. M. D. Brown, J. A. Hewitt, and B. J. Meenan, "X-ray-induced beam damage observed during X-ray photoelectron spectroscopy (XPS) studies of palladium electrode ink materials" *Surf. Interface Anal.,* Vol. 18, 1992, pp.187-198.
7. A. A. Griffith, "The Phenomena of Rupture and Flow in Solids," *Philosophical Transactions of the Royal Society of London, Series A*, Vol. 221, 1920, pp. 163-198.
8. S. J. Park and Y. S. Jang, "Interfacial Characteristics and Fracture Toughness of Electrolytically Ni-plated Carbon Fiber-reinforced Phenolic Resin Matrix Composites," *Journal of Colloid and Interface Science*, Vol. 237, 2001, pp. 91-97.
9. P. Compston, P. Y. B. Jar, P. J. Burchill, and K. Takahasi, "The Effect of Matrix Toughness and Loading Rate on the Mode II Interlaminar Facrture Toughness of Glass-Fiber/vinyl-ester Composites," *Composites Science and Technology*, Vol. 61, 2001, pp. 321-333