Effect of Atmospheric Plasma Treatment of Carbon Fibers on Crack Resistance of Carbon Fibers-reinforced Epoxy Composites

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Abstract

In this work, the effects of atmospheric oxygen plasma treatment of carbon fibers on mechanical interfacial properties of carbon fibers-reinforced epoxy matrix composites was studied. The surface properties of the carbon fibers were determined by acid/base values, Fourier-transform infrared spectrometer (FT-IR), and X-ray photoelectron spectroscopy (XPS) analyses. Also, the crack resistance properties of the composites were investigated in critical stress intensity factor (K_{IC}), and critical strain energy release rate mode II (G_{IIC}) measurements. As experimental results, FT-IR of the carbon fibers showed that the carboxyl/ester groups (C=O) at 1632 cm^{-1} and hydroxyl group (O-H) at 3450 cm^{-1} were observed for the plasma treated carbon fibers, and the treated carbon fibers had the higher O-H peak intensity than that of the untreated ones. The XPS results also indicated that the O_{1S}/C_{1S} ratio of the carbon fiber surfaces treated by the oxygen plasma led to development of oxygen-containing functional groups. The mechanical interfacial properties of the composites, including K_{IC} (critical stress intensity factor) and G_{IIC} (critical strain energy release rate mode II), were also improved for the oxygen plasma-treated carbon fibers-reinforced composites. These results could be explained that the oxygen plasma treatment played an important role to increase interfacial adhesions between carbon fibers and epoxy matrix resins in our composite system.

Keywords : *Oxygen plasma, Critical stress intensity factor, Critical strain energy release rate*

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 resulting 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 [1-4].

Therefore, the surface treatment is necessary for all carbon fibers, which increases the surface active sites and then improve bonding strength 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 under various electrolytes, and wet chemical methods, such as immersing in phosphoric acid or boiling in nitric acid and intercalation [5-7]. Among those, the interaction of the plasma treatment with carbon surfaces produces highly active species, such as free radicals, ions and metastable species, depending on nature of the gases used in the plasma zone. Many authors [8-10] have reported that an oxygen plasma treatment leads to the increase of oxygen containing functional groups on the carbon surfaces. The oxygen plasma on carbon fibers has been also reported to enhance the properties of polarity [8-9].

The studies on improving the fibers/matrix adhesion for a given surface treatment are well understood in the literatures [5-7]. Therefore, in this work, a innovative atmospheric plasma treatment is applied to modify the surface characteristics of carbon fibers. Especially, the oxygen gas is employed for the carbon fibers. And the relationship between the oxygen content and the fiber/matrix adhesion of the composites is investigated using a combination of surface analyses, critical stress intensity factor (K_{IC}), and critical strain energy release rate mode II (G_{IIC}) tests.

2. Experimental

2.1. Materials and sample preparation

The fibers used in this work were polyacrylonitrile (PAN)-based carbon fibers (12 K, TZ-607) produced by Taekwang of Korea. The average diameter of these carbon fibers was approximately 7 μm, and typical tensile modulus and strength were c.a. 245 GPa and 3.5 GPa, respectively. The epoxy resin used as a matrix was diglycidylether of bis-
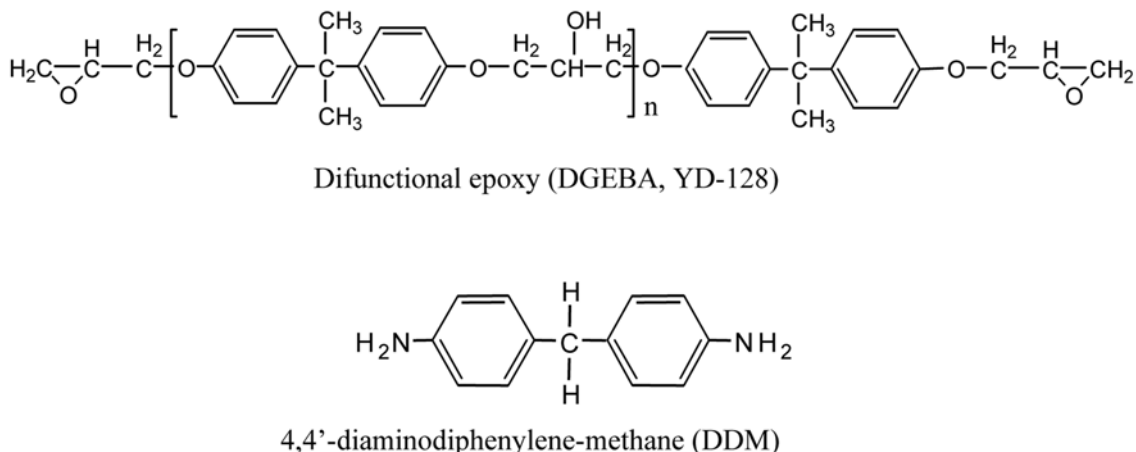
Fig. 1. Chemical structures of DEGBA and DDM.

phenol-A (DGEBA, YD-128 supplied from Kukdo Chem. Co. of Korea). Epoxide equivalent weight was 185-190 g.eq^{-1} and the viscosity was 11500-13500 cps at 25 $^{\circ}$C. 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 Fig. 1.

Plasma processing (ATMOS^{TM}-Mulit, Plasmart in Korea) for the carbon fibers was carried out using atmospheric pressure and radiofrequency for Ar/O$_2$ (O$_2$ 1%) mixed gas. The schematic diagram of the atmospheric pressure plasma device was shown in Fig. 2 [11]. The radiofrequency generating Ar/O$_2$ mixture plasma was at 300 W and 13.56 MHz. The flow rate of Ar/O$_2$ mixed gas was 5 l/min, and the plasma treatment speed and distance between electrodes were 5 mm/s. The weight of carbon fibers samples was about 1.0 g. The number of times for oxygen plasma

treatment varied between 0, 2, 4, 8, and 16 min, namely as-received, CFP-2, 4, 8, and 16.

Unidirectional carbon fibers-epoxy matrix composites were prepared by continuous impregnation of the fibers using a drum winding technique for home-made prepreg with subsequent hot-pressing [12]. Specimens were prepared from laminates composed of 22 plies and fabricated in a hot-press at 150 $^{\circ}$C and 7.4 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 measure the mechanical properties.

2.2. Surface properties

The surface properties 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 could be determined by measuring the pH according to the ASTM E-70 and by measuring acid-base values using the Boehm's method[13] on the basis of adsorption of 0.1 N NaOH and HCl standard solutions. In case of an acidic value, about 1.0 g of sample was added to 100 ml of 0.1 N NaOH solutions and shaken for 24 h. After filtration with a nylon membrane filter, the mixture was titrated with 0.1 N HCl standard solutions, using 0.01 M phenolphthalein solution as an indicator.

The FT-IR instrument used was a Hartman & Brawn Model Bomen MB 102 Spectrophotometer. The scan rate ranged from 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 Kα X-ray source. The base pressure in the sample chamber was controlled in the range of 10^{-8} to 10^{-9} torr.

2.3. Crack resistance

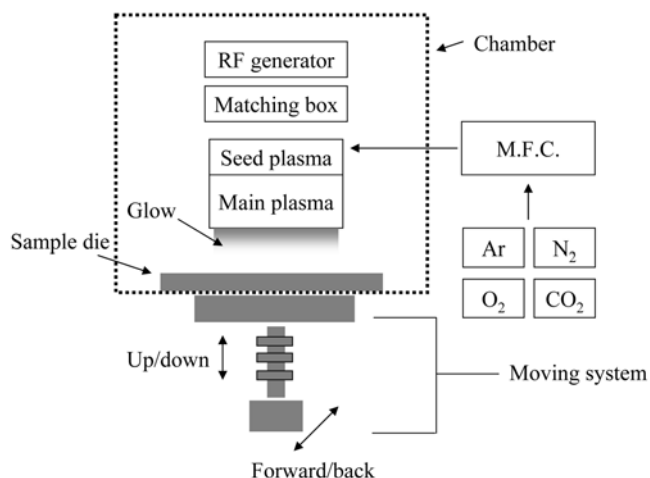Mechanical interfacial properties of the composites were

Fig. 2. Schematic diagram of the atmospheric pressure plasma device.

investigated using two types of testing method, namely critical stress intensity factor (K_{IC}) and critical energy release rate mode II (G_{IIC}) [14-15].

An analytical expression for critical stress intensity factor (K_{IC}) of unidirectional composites could be characterized by single edge notched (SEN) tests 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 of 4:1 and crosshead speed of 1 mm·min^{-1} was used.

The critical energy release rate mode II (G_{IIC}) in end-notch flexure (ENF) tests was conducted by cross-head speed of 1 mm·min^{-1} according to the ASTM D-5528. A span-to-depth ratio was 4:1. All of experiments were done under room temperature and humidity 60%, and the error range of the mechanical values was ± 0.2.

3. Results and Discussion

3.1. Surface properties

Table 1 summarizes the 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. Acid value of all the plasma treated carbon fibers is higher than that of the as-received one. Optimum condition to the surface acidity of the fibers was observed at the treatment time of 4 minutes [16].

Fig. 3 shows the FT-IR results of plasma treated carbon fiber specimens. As a result, the intensities of 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 for the plasma treated carbon fibers. Moreover, the hydrocarbon group (CH) at 2980 cm^{-1} 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 [17].

Wide scan spectra in the binding energy range 0~1000 eV

Table 1. pH and Acid-Base Values of the Carbon Fibers Studied
[unit: meq/g]

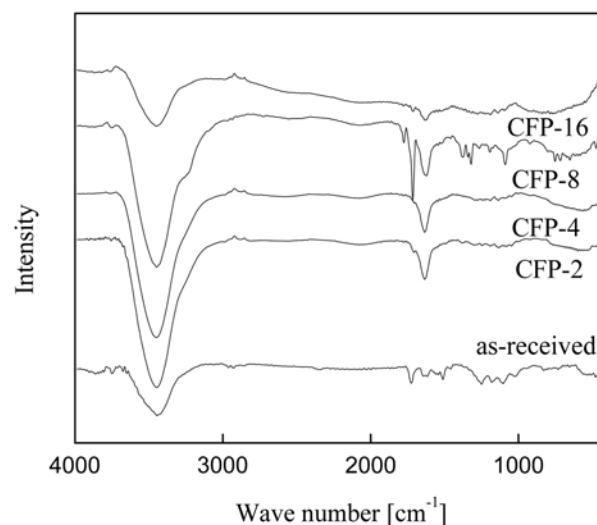| Specimens	pH	Acid value	Base value
As-received	7.2	15.0 ± 0.1	21.2 ± 0.2
CFP-2	6.95	35.0 ± 0.3	20.1 ± 0.2
CFP-4	6.94	65.1 ± 0.2	20.1 ± 0.1
CFP-8	6.94	32.5 ± 0.2	20.1 ± 0.1
CFP-16	6.95	36.7 ± 0.1	20.1 ± 0.2

Fig. 3. FT-IR spectra of the carbon fibers with and without plasma treatments.
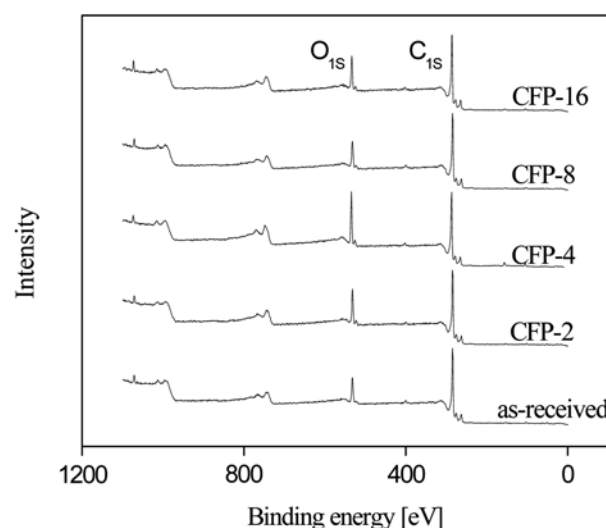

Fig. 4. XPS spectra of the carbon fibers with and without plasma treatments.

are obtained to identify the present surface elements and carry out a quantitative analysis. XPS wide scan spectra of the plasma treated carbon fiber specimens is shown in Fig. 4. The intensity scale factor for the plasma treated carbon fibers is higher than that of the as-received carbon fiber specimen. The XPS spectra show distinct carbon (285 eV) and oxygen (532 eV) peaks, representing the 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 [18, 19]. The resulting surface element concentrations of the plasma treated carbon fiber specimens are listed in Table 2. It is found that the surface

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

carbon concentration of the as-received and CFP-4 carbon fiber specimens is 74.3 at% and 68.8 at%, respectively. A lower surface carbon concentration in the CFP-4 carbon fiber specimen compared to that of the as-received specimen can be attributed to the bonding of oxygen on the carbon surfaces produced (C-O, C=O, C-OH) by the plasma treatment. While the CFP-4 specimen exhibits a maximum value at 30.6% oxygen concentration compared to that of as-received one [20, 21].

3.2. Crack resistance

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) [13, 14].

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

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 critical strain energy-release rate mode-II (G_{IIC}) are calculated by the following Eq. (2) [14, 15].

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

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

Fig. 5 shows the results for critical stress intensity factor (K_{IC}) and critical strain energy-release rate mode-II (G_{IIC}) results for plasma treated carbon fibers-reinforced composites. Error rang of the mechanical values 0.3%. As a result, the effect of fiber surface treatment conditions and the resulting fiber-matrix adhesion on mechanical interfacial properties of the composites produces noteworthy relation-
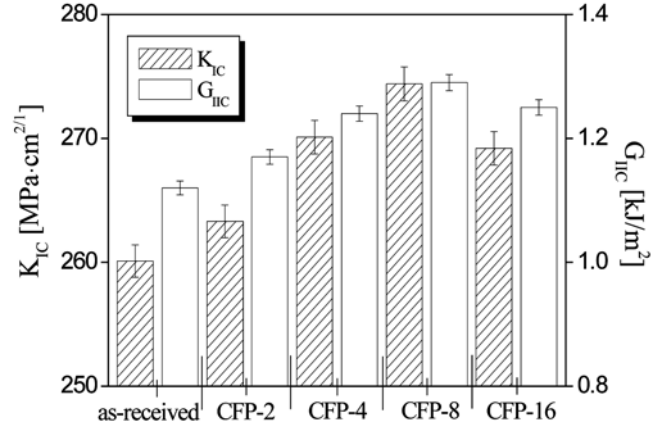

Fig. 5. K_{IC} and G_{IIC} of the carbon fibers-reinforced composites with and without plasma treatments.

ships. 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 exhibited under the plasma treatment time of 4 min. It is found that there is strong correlation between surface functionality and mechanical properties. As above mentioned, this is a consequence of the improving of acidic oxygen functional groups on fibers, resulting in growing fibers-matrix physical adhesion of the composites. Therefore, we suggest that the additional energy to extend the interfacial crack at this condition is attributed to the increasing the interfacial adhesion between fibers and matrix resins.

The plasma treatment leads to an increase of interfacial bonding at interfaces between fibers and basic matrix resins. This is due to the increase of acidic functional groups on carbon fiber surfaces, resulting in the improvement of acid-base intermolecular interaction of the composites.

4. Conclusions

In this work, the effects of atmospheric oxygen plasma treatment of carbon fibers on mechanical interfacial properties of carbon fibers-reinforced epoxy matrix composites was studied. As experimental results, FT-IR result showed that the carboxyl/ester groups (C=O) at 1632 cm^{-1} and hydroxyl group (O-H) at 3450 cm^{-1} were observed in the plasma treated carbon fibers, and the treated carbon fibers had the higher O-H peak intensity than that of the untreated ones. The XPS results also indicated that the O_{1S}/C_{1S} ratio of the carbon fiber surfaces treated by the oxygen plasma increased compared to that of untreated ones, possibly due to the development of oxygen-containing functional groups. The mechanical interfacial properties of the composites, including K_{IC} and G_{IIC}, were also improved in the oxygen plasma-treated carbon fibers-reinforced composites. These results

could be explained that the oxygen plasma treatment led to an increase of interfacial adhesions between carbon fibers and epoxy matrix resins composite system.

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