

산소-불소처리된가 탄소섬유 강화 복합재료의 기계적 계면특성에 미치는 영향

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Effect of Oxy-Fluorinated Carbon Fiber Surfaces on Mechanical Interfacial Properties of Carbon Fibers-reinforced Composites

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Key Words : carbon fibers-reinforced composites, oxy-fluorination, surface properties, mechanical interfacial properties

ABSTRACT

In this work, the effects of oxy-fluorination on surface characteristics of carbon fibers were investigated in mechanical interfacial properties of carbon fibers-reinforced composites. The surface properties of the carbon fibers were determined by X-ray photoelectron spectroscopy (XPS), FT-IR and contact angle measurements. And their mechanical interfacial properties of the composites were studied in interlaminar shear strength (ILSS) and critical stress intensity factor (K_{IC}). As experimental results, the F_{1s}/C_{1s} ratio of carbon fiber surfaces was increased by oxy-fluorination, due to the development of the oxygen containing functional groups. The mechanical interfacial properties of the composites, including ILSS and K_{IC} , had been improved in the oxy-fluorination on fibers. These results could be explained that the oxy-fluorination was resulted in the increase of the adhesion between fibers and matrix in a composite system.

1. INTRODUCTION

The surface modification of carbon materials is of great importance in a wide variety of fields, such as structural application, biomedicine, electrochemistry, microelectronics, and thin-film technology. Surface modification is accomplished through different types of treatment: thermal treatment, wet chemical or electrochemical oxidation, plasma treatment, ion or cluster bombardment, covalent linkage of biomolecules, ect. The ultimate goal of these treatments is to change the surface chemistry and microstructure of the material and thus modulate a number of properties: biocompatibility, roughness, reactivity, conductivity [1-3].

Especially, the modification of carbon fiber surfaces has been the goal of many efforts in the field of composites, as the ultimate performance of these advanced materials is influenced by the quality of the

fiber/matrix interface.

In the case of carbon fibers, the oxygen-containing fluorination treatment has been one of the methods newly studied as a surface modification that offers several advantages over other treatment. One primary advantage is that the mechanical properties of the fiber are not significantly degraded if optimum conditions are modified. Other important advantages are related to concerns about the development of more environmentally-friendly processes [4-6].

However, the studies on improving the fibers/matrix adhesion for a given surface treatment are well understood in the literature. Therefore, in this work, a direct oxy-fluorination 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 Interlaminar shea strength (ILSS) and critical stress intensity factor (K_{IC}) test.

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2. EXPERIMENTAL

2.1 Materials and Sample Preparation

The fibers used in this work were polyacrylonitrile (PAN)-based carbon fibers (12K, TZ-307) 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 was 11500-13500 cps at 25 °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 DGEBA and DDM were shown in Figure 1.

Carbon fibers were subjected to fluorination or oxy-fluorination in different conditions. The reactor was removed from the cooling bath after purging fluorine with nitrogen. The fluorine pressure was 0.2 ~ 1 MPa and the nominal reaction time was 10 min at the treatment temperature. Table 8 listed the experimental fluorination conditions of carbon fibers studied.

Unidirectional carbon fibers-epoxy matrix composites were prepared by continuous impregnation of the fibers using a drum winding technique for manufacturing prepregs with subsequent hot-pressing. Specimens were prepared from laminates composed of 22 plies and fabricated in a hot-press at 150 °C and 7.4 MPa for 150 min with a vacuum bagging method. The fiber volume fraction of bulk specimens was about 50% ($\pm 2\%$), and the specimens were cut into test specimens to

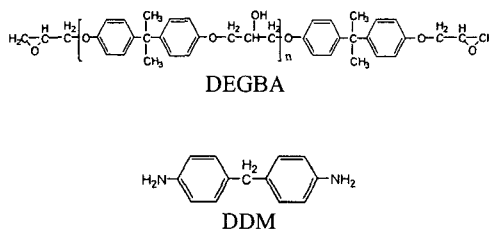


Figure 1. Chemical structures of DGEBA and DDM.

Table 1 Fluorinated Reactive Conditions of the Carbon Fibers Used

Specimens	F ₂ /O ₂ mixtures (%)	Fluorination temperature (°C)	Fluorination pressure (MPa)
No treatment	-	-	-
CFO-RT	50/50	25	0.2
CFO-100	50/50	100	0.2
CFO-300	50/50	300	0.2
CFO-400	50/50	400	0.2

carry out mechanical testing.

2.2. Surface properties

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

The potential chemical activity of surface functional groups on SiC 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 & Braun 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 interfacial properties

Interlaminar shear strength (ILSS) was conducted by three-point short-beam bending test method to estimate the interfacial adhesion strength of the composites, according to ASTM D 2344. The distance between supports divided by the thickness of specimens, L/d=5, and the crosshead speed was fixed at 2.0mm min⁻¹. 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 1mm min⁻¹.

3. RESULTS AND DISCUSSION

3.1 Surface properties

Table 2 shows the pH and acid value of oxy-fluorinated carbon fiber surfaces. The results exhibit that the surface properties of oxy-fluorinated carbon fibers show a slight excess of acidic properties, while the

Table 2 pH and Acid Values of the Carbon Fibers Studied

Specimens	pH	Acid value (meq.g ⁻¹)
No treatment	7.02	15
CFO-RT	6.95	18.5
CFO-100	6.94	22.1
CFO-300	6.94	20.3
CFO-400	6.95	18.4

fluorinated carbon fibers do not change the values. This is probably due to the formation of acidic groups, such as carboxyl, carbonyl, and hydroxyl groups, on the carbon fiber surfaces, resulting from the use of oxidizer for fluorination, which play a major role in increasing the degree of fluorination or fluorine content on carbon fibers.

It is well known that H-bonding has a considerable influence on the -OH stretching vibration in carbon fibers, which is observed at wave number of 3100~3700 cm^{-1} . In this work, FT-IR spectroscopy is also applied to observe the effect of F_2 or F_2/O_2 mixture gases on carbon fiber surfaces. Fig. show the FT-IR results of carbon fibers with oxy-fluorination, respectively. As a result, the carboxyl/ester groups ($\text{C}=\text{O}$) at 1632 cm^{-1} and hydroxyl group (O-H) at 3450 cm^{-1} are observed both the fluorinated carbon fibers. Moreover, the oxy-fluorinated carbon fibers have a higher peak intensity than that of the fluorinated ones and especially the intensity of O-H group of the fibers exhibits the highest at the oxy-

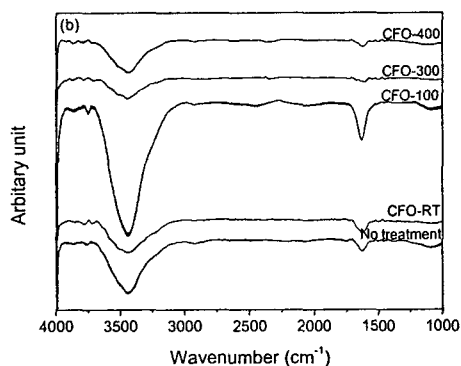


Figure 2. FT-IR spectra of oxy-fluorinated carbon fibers as a function of temperature.

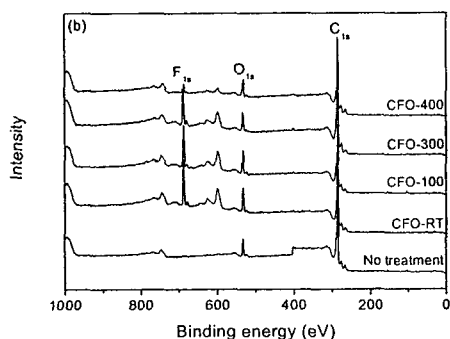


Figure 3. XPS spectra of oxy-fluorinated carbon fibers as a function of temperature.

Table 3. Compositions of the Carbon Fibers Studied by XPS Measurements

Specimens	XPS			
	[unit: at%]			
	C_{1s}	F_{1s}	O_{1s}	$\text{O}_{1s}/\text{C}_{1s}$
As-received	88.38	-	9.59	0.109
CFO-RT	74.21	13.56	10.93	0.147
CFO-100	67.72	19.50	9.27	0.154
CFO-300	79.96	10.64	8.06	0.100
CFO-400	76.93	8.91	10.13	0.132

fluorination temperature of 100 °C. Also, the peak intensity of O-H group is increased with increasing the content of oxygen in the case of oxy-fluorinated carbon fibers, as shown in Figure 2. These results affect the surface characteristics of the fibers, resulting in improving the interfacial adhesion between fibers and matrix, due to the increase of specific polarity and the formation of H-bonding of oxy-fluorinated carbon fiber surfaces.

Wide scan spectra in the binding energy range 0~800 eV are obtained to identify the surface elements present and carry out a quantitative analysis. XPS wide scan spectra of the oxy-fluorinated carbon fiber specimens are shown in Figure 3. The intensity scale factor for the oxy-fluorinated carbon fibers are higher than that of the as-received carbon fiber specimen. The XPS spectra show distinct carbon, oxygen and fluorine 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. As expected, the fluorine peak intensity of the oxy-fluorinated carbon fibers is also increased according to the fluorination temperature and oxygen content.

Quantitative peak analysis is carried out to determine the surface element concentrations. The resulting surface element concentrations of the oxy-fluorinated carbon fiber specimens are listed in Table 3. It is found that the surface carbon concentrations of the as-received and CFO-100 carbon fiber specimens are 88.38 at% and 67.72 at%, respectively. A lower surface carbon concentration in the CFO-100 carbon fiber specimen compares to that of the as-received specimen can be attributed to the bonding of oxygen or fluorine on the carbon surfaces produced by the oxy-fluorination. The surface fluorine concentration ranges of the surface oxy-fluorinated carbon fiber specimens are 8.91~19.50 at%. The higher fluorine concentration on the CFO-100 specimen (19.50 at%) surfaces can be also attributed to the surface oxy-fluorination of the fibers. The surface concentration of oxygen in the CFO-RT specimen is relatively similar to that of the as-received carbon fiber.

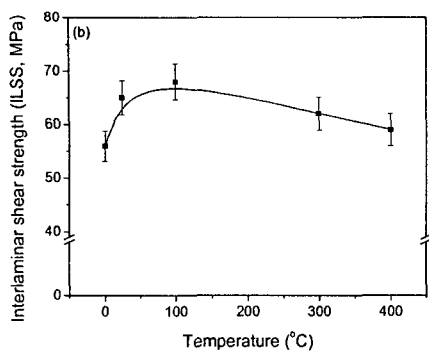


Figure 4. Interlaminar shear strength (ILSS) oxy-fluorinated carbon fibers-reinforced composites.

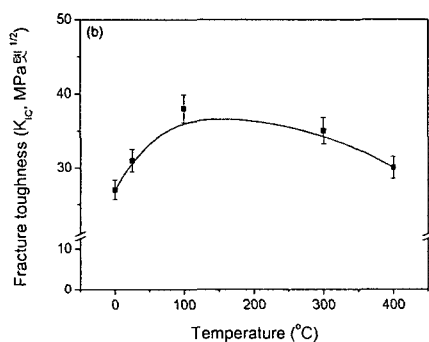


Figure 5. Fracture toughness (K_{IC}) oxy-fluorinated carbon fibers-reinforced composites.

The broad carbon peak that is observed in the binding energy range from 281 to 293 eV, due to the several carbon-based surface functional groups which have different binding energies[7].

3.2 Mechanical interfacial properties

Figure 4 shows the results of ILSS for the carbon fibers-reinforced composites. As a result, a good relationship between the characters of oxy-fluorinated carbon fiber surfaces and the resulting fiber-matrix adhesions on mechanical interfacial properties of the composite is existed in this experimental condition. That is, ILSS value is increased with increasing the wettability of the fibers for the degree of adhesion at interfaces due to the oxy-fluorination, resulting from increasing the polarity and oxygen functional groups of the fiber surfaces. And the maximum strength value of ILSS is obtained at the oxy-fluorinated carbon fiber specimen, CFO-100. This result is in good agreement with surface analyses of the carbon fibers studied.

Figure 5 shows the results of fracture toughness (K_{IC}) for the composites according to the fluorine content (F/C). Good relationships are shown between the fluorine content and the resulting fracture toughness of

the composites. That is, the value of K_{IC} is increased with increasing the fluorine content on carbon fiber surfaces.

4. CONCLUSION

In this work, the effects of oxy-fluorination on surface characteristics of carbon fibers were investigated in mechanical interfacial properties of carbon fibers-reinforced composites. The surface properties of the carbon fibers were determined by X-ray photoelectron spectroscopy (XPS) and FT-IR measurements. And their mechanical interfacial properties of the composites were studied in interlaminar shear strength (ILSS) and critical stress intensity factor (K_{IC}). As experimental results, the F_{1S}/C_{1S} ratio of carbon fiber surfaces was increased by oxy-fluorination, due to the development of the oxygen containing functional groups. The mechanical interfacial properties of the composites, including ILSS and K_{IC} , have been improved in the oxy-fluorination on fibers. These results could be explained that the oxy-fluorination is resulted in the increase of the adhesion between fibers and matrix in a composite system.

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