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Surface and Mechanical Interfacial Properties of Oxyfluorinated Carbon Fibers-reinforced Composites

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Abstract

In this work, the effect of a direct oxyfluorination on surface and mechanical interfacial properties of PAN-based carbon fibers is investigated. The changes of surface functional groups and chemical composition of the oxyfluorinated carbon fibers are determined by FT-IR and XPS measurements, respectively. ILSS of the composites is also studied in terms of oxyfluorination conditions. As a result, FT-IR exhibits that the carboxyl/ester groups (C=O) at 1632 cm^{-1} and hydroxyl group (O-H) at 3450 cm^{-1} are observed in the oxyfluorinated carbon fibers. Especially, the oxyfluorinated carbon fibers have a higher O-H peak intensity than that of the fluorinated ones. XPS result also shows that the surface functional groups, including C-O, C=O, HO-C=O, and C-F_x after oxyfluorination are formed on the carbon fiber surfaces, which are more efficient and reactive to undergo an interfacial reaction to matrix materials. Moreover, the formation of C-F_x physical bonding of the carbon fibers with fluorine increases the surface polarity of the fibers, resulting in increasing ILSS of the composites. This is probably due to the improvement of interfacial adhesion between fibers and matrix resins.

***Keywords :** Oxyfluorination, Surface properties, Mechanical interfacial properties, Surface polarity*

1. Introduction

Carbon fibers are widely used as reinforcements in composites, especially in composites with epoxide matrices and of potential importance due to their real applications. They combine a high stress factor and strength with a low density, which has led to their increasing use in high performance construction materials [1, 2].

To improve the fiber/matrix adhesion of the composites, it is necessary to increase the surface polarity of fiber surfaces, which can be related to more sites for hydrogen bonding and possibility for mechanical interlocking between the fiber materials and the surrounding polymeric matrix, resulting in improving good stress transfer from the matrix materials to the filling fiber materials [3].

One of methods to increase the surface polarity of carbon fibers is their surface oxidation [4, 5], which introduces hydrophilicity to the fiber surfaces. And, it has been also found that fluorine reacts well with carbon materials in the presence of gaseous HF or O_2 [6].

Therefore, in this work, different oxyfluorination conditions are applied to modify the surface properties of carbon fibers by using a direct oxyfluorination. Especially, the O_2 gas is used as a replace of HF catalyst for oxyfluorination of the fibers. And the relationships between the degree of oxyfluorination and the physicochemical properties of the carbon fibers are studied in the combination of surface analyses and mechanical interfacial properties of the composites.

2. Experimental

2.1. Materials and Sample Preparation

The carbon fibers studied in this work were untreated and unsized polyacrylonitrile (PAN)-based high strength fibers, TZ-307 (12 K) manufactured by Taekwang of Korea. The average diameter of these carbon fibers was approximately 7 μm, and typical tensile strength and modulus were about 3.5 GPa and 245 GPa, respectively.

Epoxy resins used in this study was diglycidylether of bisphenol-A (DGEBA, YD-128 supplied from Kukdo Chem. Co. of Korea), which had an epoxide equivalent weight of 187 $g·eq^{-1}$ and a viscosity of about 5000 cps at 25°C. Diaminodiphenylmethane (DDM) supplied from Aldrich Chem. Co. was selected as a hardener and methylethylketone (MEK) was used to reduce a high viscosity of the DGEBA.

Carbon fibers were subjected to oxyfluorination in different conditions. The oxyfluorination reaction was performed with F_2, O_2, and N_2 gases in a batch reactor made from nickel with an outer electric furnace, as shown in Fig. 1. After evacuation, the fluorine and oxygen mixtures (F_2/O_2 gases)

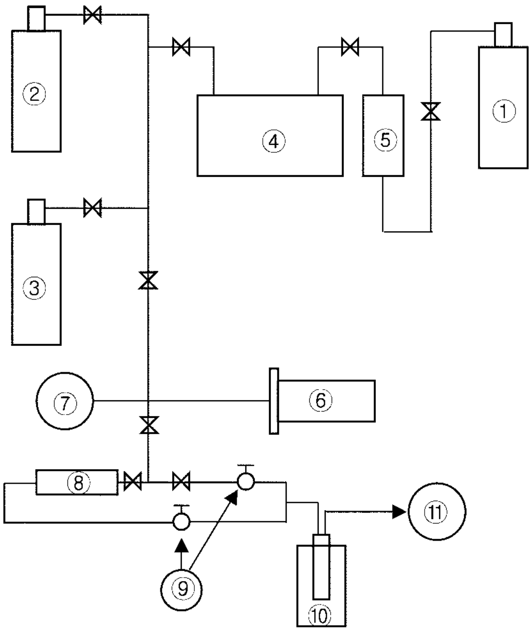

Fig. 1. Schematic diagram of the oxyfluorination reactor: ① F_2 gas cylinder, ② N_2 gas cylinder, ③ O_2 gas cylinder, ④ Buffer tank, ⑤ HF absorber (NaF pellet), ⑥ Reactor, ⑦ Pressure gauge, ⑧ F_2 absorber (Al_2O_3), ⑨ Glass cock, ⑩ Liquid nitrogen, ⑪ Rotary vacuum pump.

were introduced to the reactor at room temperature, and then the reactor was heated to the treatment temperature. After reaction, the samples were cooled to room temperature, and then the reactive gases were purged from the reactor with nitrogen. In the case of the reaction at room temperature, the reactor was cooled and evacuated in a cooling bath prior to charging fluorine. The reactor was removed from the cooling bath after purging fluorine with nitrogen. The fluorine pressure and nominal reaction time were 0.2 MPa and 10 min at the fluorination temperatures of 25, 100, 300, and 400°C, respectively.

Unidirectional composite laminates were prepared by continuous impregnation of the fibers using a drum winding technique for manufacturing prepregs with subsequent hot pressing [7]. And, the laminates made with 32 plies of prepregs were fabricated in a hot-press at 7.4 MPa at 150°C for 150 min with a vacuum bagging method in a conventional composite processing [8]. The quantities of fibers in the test specimens were determined by combustion of the polymer matrix of the test specimens for 1 h at 400°C in air. Before and after combustion, the weight of the specimens was measured with a balance, with an accuracy of 0.01 mg. The fiber content as percentage by volume (V_f) (vol%) was calculated with the following eq. (1):

$$V_f = \{(W_f/r_f)/(W_f/r_f+W_r/r_r)\} \times 100(\%) \qquad (1)$$

where W_f is the weight proportion of carbon fibers, r_f (=1.80/cm^3) is the density of carbon fibers, W_r is the weight proportion of resins and r_r is the density of resins (was calculated from the unreinforced test specimens).

The fiber volume fraction of bulk specimens was about 52% (±0.2%) for all composites

2.2. Surface analyses

To investigate the occurrence of surface chemical reaction on carbon fiber surfaces, the infrared spectra of the oxyfluorinated carbon fibers were measured with a FT-IR spectroscopy (Digital FTS-80, Bio-Rad).

The X-ray photoelectron spectroscopy (XPS) of fiber surfaces 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. 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 the ASTM D 2344. The distance between supports divided by the thickness of specimens (L/d) was 5, and the crosshead speed was fixed at 2.0 mm/min.

3. Results and Discussion

It is well known that H-bonding has a considerable influence on the -OH stretching vibration in carbon fibers, which is observed at the wave number of 3100~3700 cm^{-1}. In this work, FT-IR spectroscopy is also applied to observe the effect of oxyfluorination on carbon fiber surfaces. Fig. 2 shows the FT-IR results of oxyfluorinated carbon fiber specimens. As a result, the carboxyl/ester groups (C=O) at

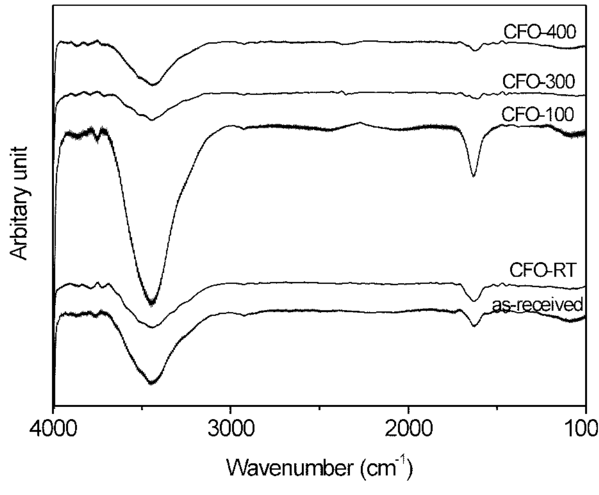

Fig. 2. FT-IR spectra of oxyfluorinated carbon fibers as a function of oxyfluorination temperature.

1632 cm^{-1} and hydroxyl group (O-H) at 3450 cm^{-1} are observed at the oxyfluorinated carbon fibers. Moreover, the oxyfluorinated carbon fibers have higher peak intensity than that of the low temperature oxyfluorinated ones and especially the intensity of O-H group of the fibers exhibits the highest at the oxyfluorination temperature of 100°C. 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 specific polarity and the formation of H-bonding of oxyfluorinated carbon fiber surfaces [9].

Consequently, the oxyfluorination of carbon fibers probably occurs more efficiently when the surface is acidic rather than basic in nature. During oxyfluorination, however, the surface becomes less acidic due to the formation of C-F bond and hydroxide radical. In addition, when F_2 is used as an oxidizing agent, it is reduced to give the basic F^- ion. Therefore, the presence of oxygen in the reaction mixtures acidifies the surface and makes it kinetically more approachable to F_2 molecules [10].

It is well known that XPS has been used as a powerful analytical technique to evaluate the surface compositions of the carbon fibers [11]. XPS analysis is, therefore, performed in order to obtain information about the surface compositions (up to a sample depth of about 10 nm) and binding characteristics of the carbon fibers for all fluorinated fiber systems studied. Although different features, such as preferential sputtering, atomic mixing, fiber diameter effects, and roughness of surface, can affect the treatment profiles, the ion sputtering is performed in the present studies for comparative purposes on the carbon fiber samples where such effects are expected to be very similar [12, 13].

The broad scan XPS spectra of the oxy-fluorinated carbon fibers are shown in Fig. 3. According to the literature, the carbon fibers have 1.7% N and 3.8% O for the surface of the PAN-based fibers [14]. Therefore, in most fluorinated fibers, oxygen and nitrogen are found on the outer surface, and newly added fluorine is also observed in the fluorinated carbon fibers regardless of fluorination techniques.

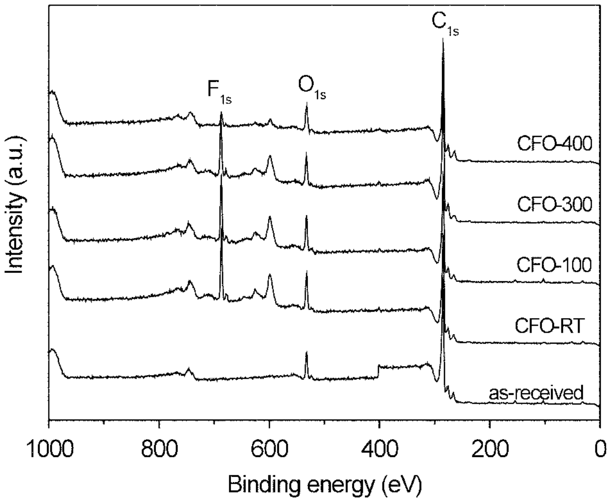

Fig. 3. Full range XPS spectra of oxy-fluorinated carbon fibers as a function of oxyfluorination temperature.

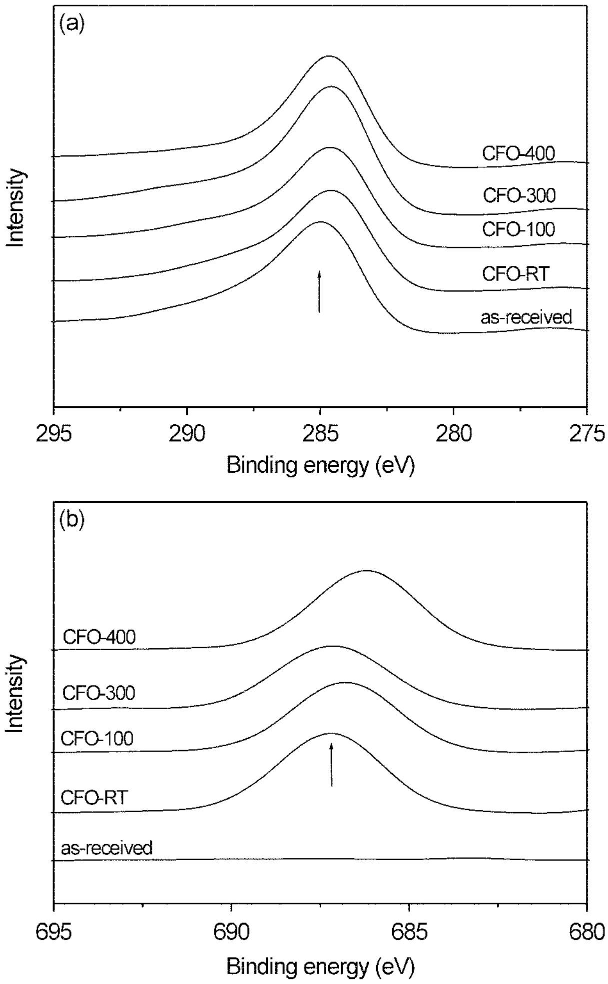

Fig. 4. C_{1s} and F_{1s} narrow scan XPS spectra of oxyfluorinated carbon fibers as a function of oxyfluorination temperature: (a) C_{1s} spectra and (b) F_{1s} spectra.

Fig. 4(a) shows narrow scan spectra of the C_{1s} region of oxyfluorinated carbon fibers. The binding energy of the C_{1s} peak for the as-received carbon fibers is 285 eV, representing the most graphitic carbons. The difference between the FWHM values of the as-received and the oxyfluorinated carbon fibers at room temperature, CFO-RT is 0.65 eV. A higher FWHM value is found for the CFO-100 sample presumably due to the surface oxy-fluorination. And, Fig. 4(b) also shows narrow scan spectra of the F_{1s} region for the oxyfluorinated carbon fibers. Due to the surface oxyfluorination, a higher FWHM value and a shoulder at a higher binding energy range of 686.7~688±0.1 eV is observed for the oxyfluorinated carbon fiber specimens.

Therefore, a reaction mechanism of direct oxyfluorination

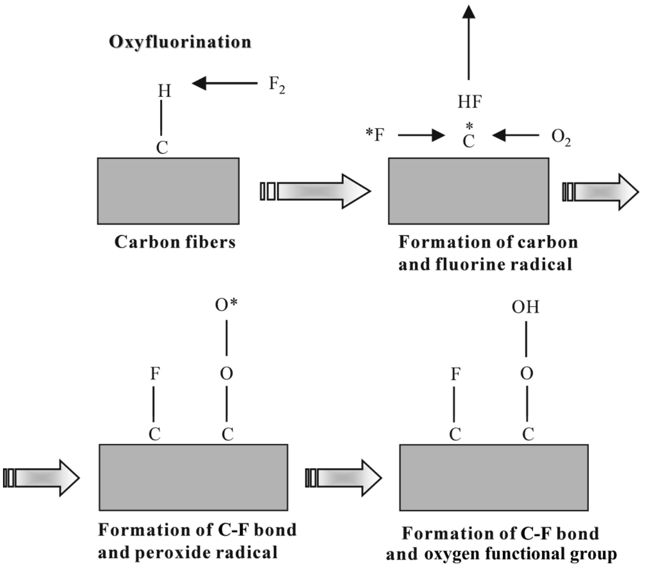

Fig. 5. A suggested reaction mechanism of oxyfluorination carbon fibers with F_2/O_2 gas mixtures.

of carbon fibers with F_2 and O_2 gas mixtures can be considered, as shown in Fig. 5. This mechanism can produce a desirable result of surface analyses of oxyfluorinated carbon fibers. That is, the F_2/O_2 mixtures introduce much more contents of oxygen functional groups on carbon fiber surfaces, leading to an improvement of interfacial adhesions in the fibers-reinforced composites [15].

Mechanical properties of composites are determined by not only these properties of the reinforcement and the matrix but also the interfacial properties between them, since load stress transfers from one matrix to the others *via* the fiber [16]. Especially, the interfacial shear strength (ILSS) is very important for the strength of brittle matrix composites such as carbon fibers-reinforced composites, and it is changed drastically by surface treatment that increase interfacial surface areas and surface functional groups [17].

In this work, the degree of adhesion at interfaces between oxyfluorinated carbon fibers and matrix resins was measured by the short-beam flexural test for ILSS of the composites using the following eq. (2).

$$ILSS = \frac{3P}{4bd} \qquad (2)$$

where P is the load at moment of break, b the width of the specimen, and d the thickness of the specimen.

Fig. 6 shows the results of *ILSS* for the carbon fibers-reinforced composites. A good relationship between the characters of oxyfluorinated 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 oxyfluorination, which can be attributed to the increasing of surface polarity of the fibers. And the maximum strength value of ILSS is obtained at the oxy-fluorinated carbon fiber sample condition at 100°C (CFO-100).

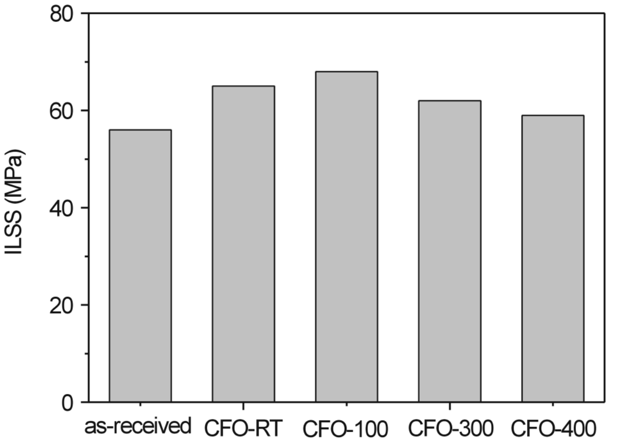

Fig. 6. Interlaminar shear strength (ILSS) of oxy-fluorinated carbon fibers-reinforced composites.

4. Conclusion

From the results of surface analyses, it was found that the surface oxygen containing functional groups, such as C-O, C=O, HO-C=O, and C-F_x after oxyfluorination were formed on carbon fiber surfaces. Mechanical interfacial properties of the composites were improved with increasing the fluorine and oxygen content on carbon fiber surfaces. This was probably due to the introduction of fluorine and oxygen functional groups and the formation of bulk phase on carbon fibers, which was effective in altering their surfaces to polarity. Consequently, a direct oxyfluorination of carbon fibers was proven to be one of the useful methods to increase the surface polarity and to improve the oxygen functional groups on carbon fiber surfaces, leading to the increase of the mechanical interfacial properties in the resulting fibers-reinforced composites.

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