Influence of Oxyfluorination on Geometrical Pull-Out Behavior of Carbon-Fiber-Reinforced Epoxy Matrix Composites

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Abstract: To improve the interfacial adhesion between carbon fibers and an epoxy matrix, carbon fibers were modified by oxyfluorination at different temperature conditions. Surface analyses of the oxyfluorinated carbon fibers were performed using scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and dynamic contact angle measurements. The interfacial shear strength (IFSS) of a single carbon fiber/epoxy matrix was studied by employing single-fiber pull-out tests to confirm the interfacial adhesion. The pull-out behavior of the fiber from the matrix was discussed based on the Greszczuk's geometrical model. Functional groups such as C-F, C-O, and COOH were present on the carbon fiber surfaces after oxyfluorination. Moreover, the presence of functional groups increased the surface polarity of the fibers, resulting in an increase in the IFSS owing to the improvement of the interfacial adhesive strength between the carbon fibers and the epoxy matrix.
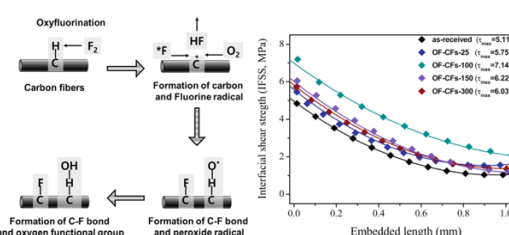
Keywords: carbon fiber, polymer-matrix composites (PMCs), surface treatments, oxyfluorination.

1. Introduction

The development of carbon materials has been studied in various fields by many researchers.[1-8] Among the well-known carbon materials, carbon fibers are the most widely used materials. Carbon fibers exhibit excellent properties such as good mechanical properties, high temperature resistance, and good electrical conductivity, and they are lightweight. Carbon fibers are the most important reinforcements used in polymeric matrix composites since specific properties can be achieved by combining carbon fibers and polymers.[9-14] These carbon fibers-reinforced polymer composites (CFRPs) exhibiting a high performance are widely applied in various fields such as aerospace defense, ships, automobiles, machine tools, sport equipment, transportation structures, power generation, as well as oil and gas industries.[15-26]

Mechanical properties of CFRPs are mainly determined by the interfacial adhesion between carbon fibers and matrix resins among various parameters. In other words, the interfacial properties of carbon fibers and matrix resins must be controlled for improving the mechanical properties of CFRPs. Hence, many researchers have focused on developing effective surface treatment methods to improve the interfacial strength.[27-29] Various surface treatment methods such as wet chemical, electrochemical, metal-coating, plasma, ozone treatment, fluorination, and oxyfluorination methods have been employed.[30-36]

In oxyfluorination, a dry chemical method, carbon fibers are treated to introduce polar group or active sites on a carbon fiber surface using oxygen-fluorine gas mixtures without employing any catalysts or initiators during a relatively short time. This method is more environmental friendly as compared to other methods. Using this method, the degradation of mechanical properties of carbon fibers can be minimized without damaging the surface-treated fibers under optimal processing conditions.[37-40]

Herein, the oxyfluorination method was employed to introduce polar functional groups or active sites on carbon fibers for achieving a stronger interfacial adhesion. The objective of this study is to evaluate the effect of oxyfluorination on the carbon fiber surface properties and the interfacial adhesion between carbon fibers and epoxy matrix. The surface properties of the carbon fibers were characterized using scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and dynamic contact angle measurements. The interfacial shear strength (IFSS) of the single carbon fiber/epoxy matrix was studied by performing single-fiber pull-out tests to confirm interfacial adhesion. The pull-out behavior of the fiber from the matrix is discussed based on the Greszczuk's geometrical model.

2. Experimental

2.1. Sample preparation

The epoxy resin used in this study was diglycidyl ether of bisphenol A (DGEBA, YD-128), which was supplied by the kukdo Chem.

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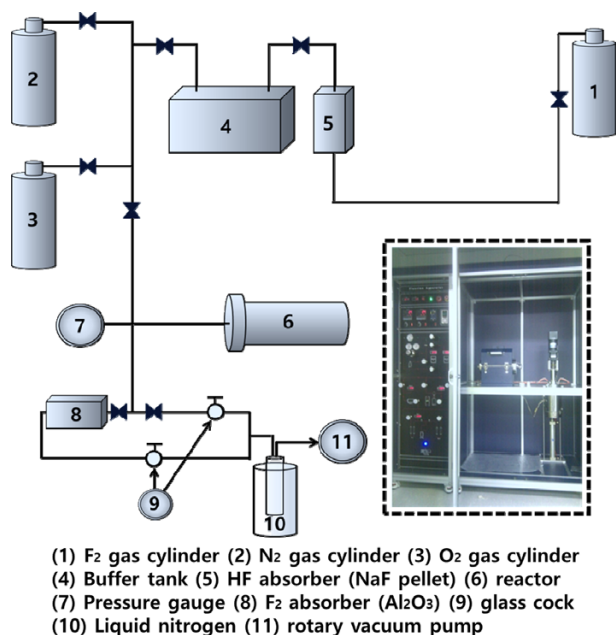
Figure 1. Schematic diagram and pictures of oxyfluorination reactor.

(1) F₂ gas cylinder (2) N₂ gas cylinder (3) O₂ gas cylinder (4) Buffer tank (5) HF absorber (NaF pellet) (6) reactor (7) Pressure gauge (8) F₂ absorber (Al₂O₃) (9) glass cock (10) Liquid nitrogen (11) rotary vacuum pump

Figure 2. Schematic diagram of specimen preparation and pull-out test.

Co., Korea. The carbon fibers used in this study were untreated and unsized polyacrylonitrile-based carbon fibers (TZ-307) supplied by Taekwang Ind., Korea. The average diameter of the carbon fibers was ~7 μm, and the typical tensile modulus and strength values were ~245 and 3.5 GPa, respectively.

Carbon fibers were treated by oxyfluorination at different temperature conditions using an oxyfluorination reactor. The schematic diagram and photographs of the reactor are presented in Figure 1. Oxyfluorination was conducted at 25, 100, 150, and 300 °C for 10 min. After oxyfluorination, the samples were degassed to remove unreacted gases. The untreated carbon fibers are named as as-received. The oxyfluorinated carbon fibers (OF-CFs) are referred to as OF-CFs-25, OF-CFs-100, OF-CFs-150, and OF-CFs-300, depending on the oxyfluorination temperature. The carbon fibers were embedded in the epoxy resin, and then semi-cured at room temperature for 24 h. Each specimen was prepared according to embedded length. The schematic diagram of the specimen preparation is presented in Figure 2.

2.2. Characterization

The morphologies of the OF-CFs were examined using SEM (Hitachi, Tokyo, Japan). The surface properties of the OF-CFs were characterized using XPS (ESCA210, VG Scientific Co., UK). The XPS spectra were collected using an MgK$_\alpha$ X-ray source (1253.6 eV). The pressure in the chamber was controlled below

5×10^{-8} Torr. Wide-angle X-ray diffraction (XRD, D2 PHASER, BRUKER, Germany) patterns of the OF-CFs were recorded with a rotation anode using CuK$_\alpha$ radiation (λ=0.15418 nm).

Dynamic contact-angle measurements of the carbon fibers were performed using a Krüss Processor Tensiometer K-100 with a fibers apparatus. 2 g of the CFs was packed into the apparatus and mounined onto the measuring machine. The characteristics of the four wetting liquids used for the contact-angle measurements are listed in Table 1. Details of this method were described in previous studies.[41,42]

A single fiber is embedded in resins and the debonding load for the pull-out of the single fiber from the resin is measured. IFSS (τ) is calculated using the following equation:[43,44]

$$\tau = \frac{F}{2\pi \cdot r_f \cdot L} \tag{1}$$

where F is the debonding load, r_f is the fiber radius, and L is the embedded length.

According to the Desarmot's proposition[45] on the basis of the Greszczuk's geometrical model,[46] the IFSS measured from the pull-out tests can be used for determining the maximum IFSS, τ_{max}, derived from the maximum debonding load, F_m, at L=0, using the following equation:

$$\tau_{max} = \left(\frac{F_{max}}{2\pi \cdot r_f}\right) \times \alpha \times [\coth(\alpha \cdot L_e) \times \cosh(\alpha \cdot L_e) - \sinh(\alpha \cdot L_e)] \tag{2}$$

where b_i, as defined by Greszczuk, is the effective thickness of the interface and R is the radius of the matrix. The parameters E_f, G_m, and r_f are the Young's modulus of the fiber, shear modulus of the matrix in the Greszczuk experiments, and fiber radius,

Table 1. Characteristics of wetting liquids used in this work^a

Wetting liquids	γ_L^d (mJ/m^2)	γ_L^p (mJ/m^2)	γ_L (mJ/m^2)	η (MPa·s)	ρ (g/cm^3)
n-Hexane	18.4	0	18.4	0.33	0.661
Water	21.8	51	72.8	1	0.998
Diiodomethane	50.4	0.4	50.8	2.8	3.325
Ethylene glycol	31.0	16.7	47.7	17.3	1.100

$^a\gamma_L^d$: London dispersive component of surface free energy. γ_L^p: specific component of surface free energy. γ_L: total surface free energy. η: viscosity. ρ: density.
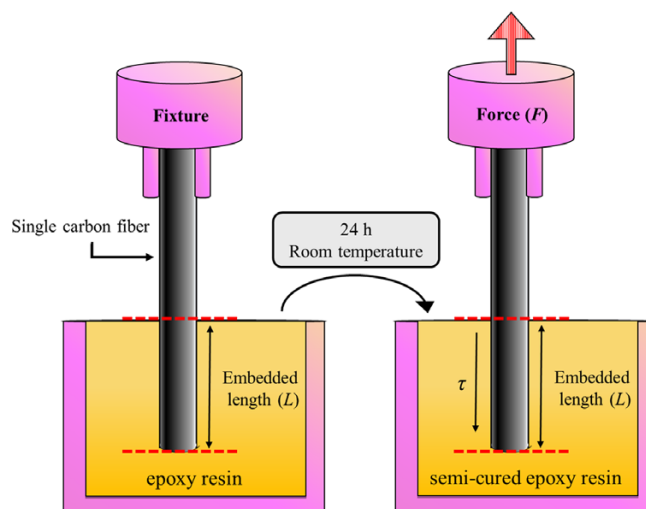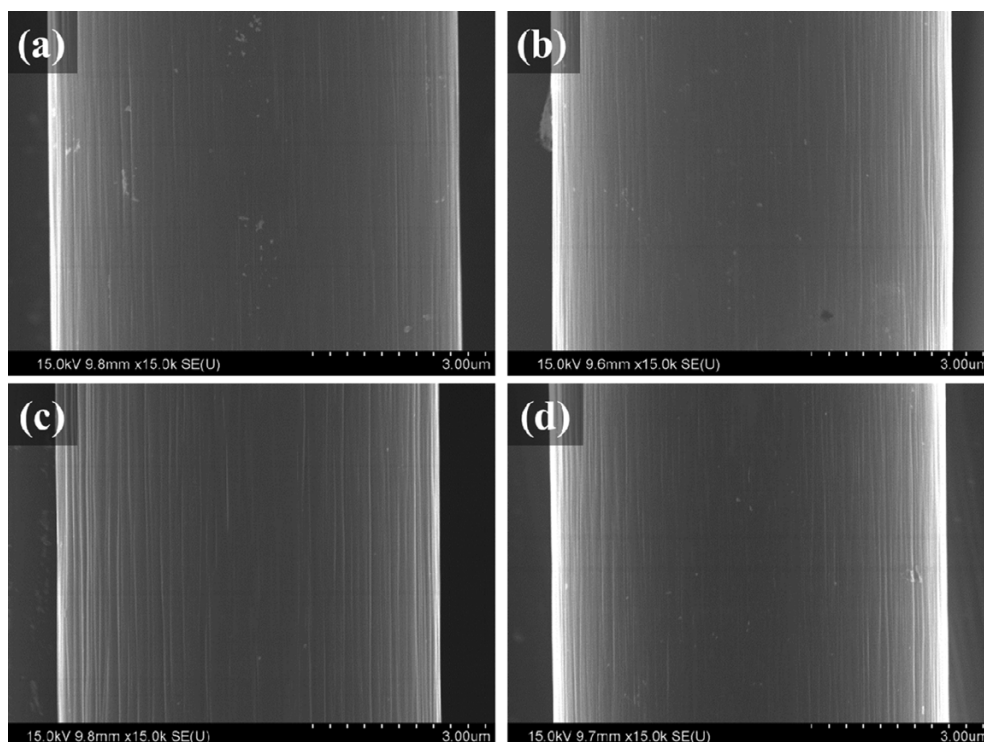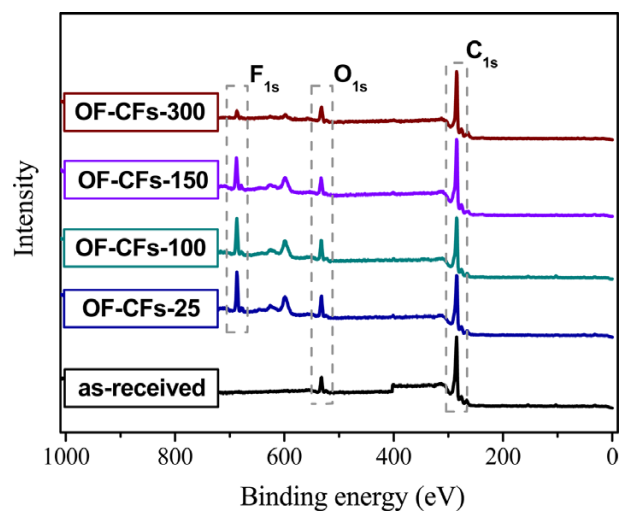
Figure 3. SEM pictures of oxyfluorinated carbon fibers; (a) as-received CFs, (b) OF-CFs-100, (c) OF-CFs-150, and (d) OF-CFs-300.

respectively. Therefore, α is a constant that depends on the nature of the fiber and matrix used.

3. Results and discussion

Figure 3 shows the SEM images of the surface oxyfluorinated carbon fibers ((a) as-received CFs, (b) OF-CFs-100, (c) OF-CFs-150, and (d) OF-CFs-300). At the SEM images, the considerable changes of the surfaces could not be observed. The diameter did not change either. From these results, it was confirmed that there was no damage of the carbon fibers by the oxyfluorination treatments. It is expected that the mechanical strength will not be decreased due to the damage of the carbon fibers. Consequently, it is thought that the effects of the functional group formation on the interfacial adhesion properties between reinforcements and matrix can be confirmed.

Figure 4 shows the XPS spectra of the as-received CFs and OF-CFs as a function of temperature. The XPS spectra show the oxyfluorination leads to a change in functional groups on the carbon fiber surfaces. First, there are only carbon (C_{1s}) and oxygen (O_{1s}) peaks in the XPS results of as-received CFs. On the other hand, the XPS results of all OF-CFs samples indicate the presence of carbon (C_{1s}), oxygen (O_{1s}), and fluorine (F_{1s}). The fluorine peaks of OF-CFs increased with an increase in the oxyfluorination temperature. The maximum value was obtained for the oxyfluorination sample OF-CFs-100. However, the fluorine peaks decreased in the OF-CFs-300. According to other reports, the fluorine functional groups on the carbon materials surfaces were removed at high temperatures above 300°C by forming CF_4 or C_2F_2 gases.[47-49] Therefore, the decrease of the fluorine peaks was probably caused by the high fluorination temperature. Hence, these XPS results mean that the oxyfluorination treatments can

Figure 4. XPS spectra of oxyfluorinated carbon fibers as a function of temperature.

modify the CFs surfaces by forming functional groups. Besides, this indicates that the oxyfluorination conditions employed in this study are appropriate for increasing the interfacial adhesion with matrix as well as the polarity of CFs surfaces.

Figure 5 shows High-resolution curve fitted C_{1s} peaks of the oxyfluorinated carbon fibers as a function of temperature. As Figure 5 shows, significant changes were observed in the OF-CFs compared to the as-received CFs. The C_{1s} spectra reveals the presence of three peaks consisting of graphitic carbon (C-C), carbony groups (C=O), and carboxy groups (COOH). In the CFs spectra, the ratio of graphitic carbon is observed higher than other functional groups. On the other hand, in the OF-CFs spectra, the ratio of graphitic carbon decreased, and the ratio of
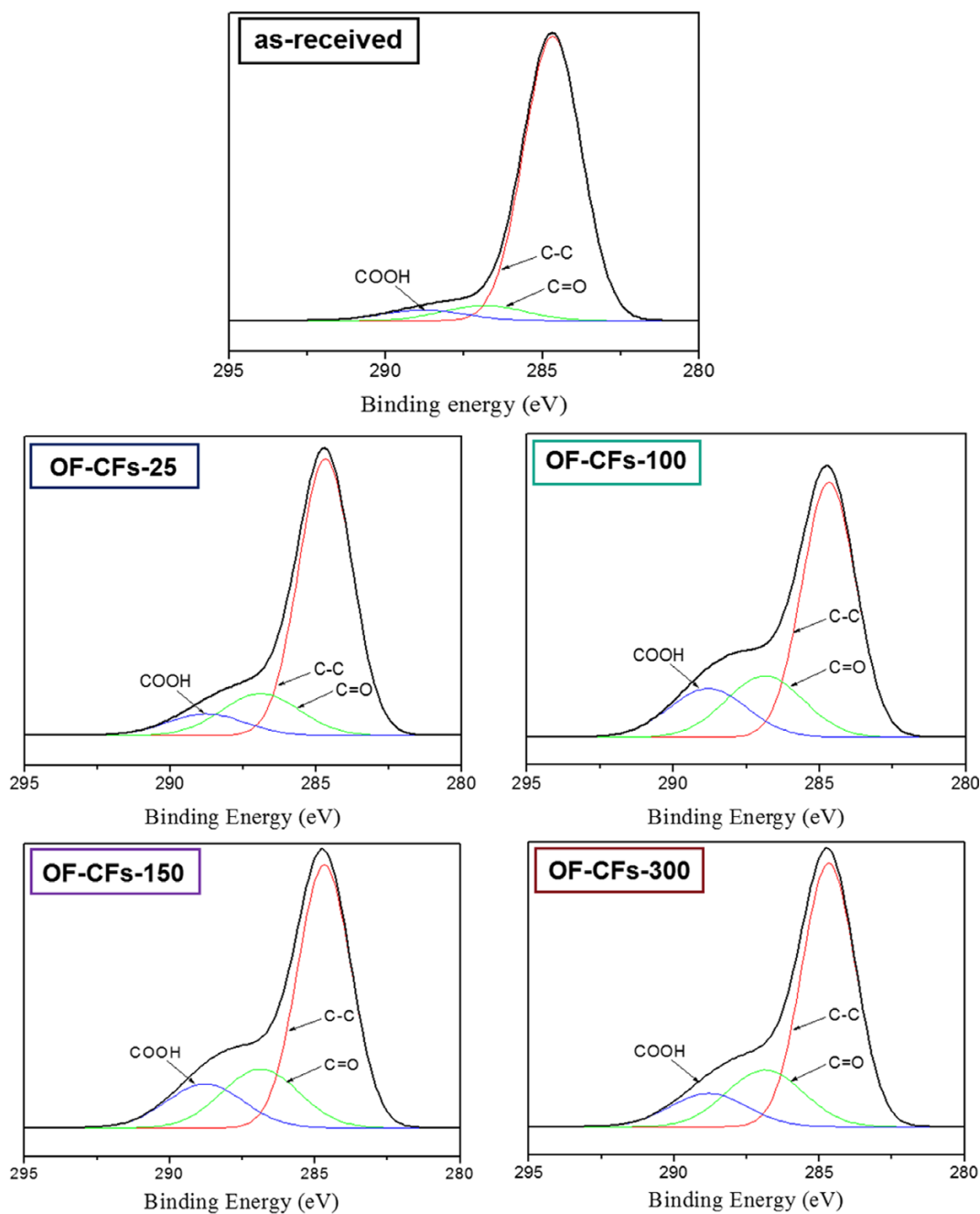
Figure 5. High-resolution curve fitted C_{1s} peaks of the oxyfluorinated carbon fibers as a function of temperature.

C=O and COOH groups increased. These results indicate that oxygen functional groups are introduced to the CFs surfaces through the oxyfluorination treatments. It seems likely that these oxygen functional groups increase the polarity of the surface of CFs. Besides, the polarity of the fibers is expected to improve the mechanical properties of the composites. The polarity of the CFs can be controllable through the oxyfluorination treatment.

The oxyfluorination mechanism of CFs illustrated in Figure 6. This chemical reaction results in achieving desired results with the surface analyses of OF-CFs. The mixed gas (F_2 and O_2) can introduces high amounts of functional groups on the fiber surfaces by the high reactivity of fluorine, and thereby obtaining an improved interfacial bonding force between the fibers and resins.

Figure 7 shows the XRD patterns of the as-received CFs and OF-CFs as a function of temperature. Almost no change in the graphitic structure is observed because only the CFs surface is oxyfluorinated. More specifically, all the oxyfluorinated carbon fibers, within error limits, exhibit almost the same 2θ value, interlayer distance (d_{002}), and FWHM as the as-received carbon fibers.

Figure 8 shows surface free energies of oxyfluorinated carbon fibers as a function of temperature. As shown in figure 8, the surface free energies of the carbon fibers tend to decrease with oxyfluorination treatments. On the other hand, the polar component (γ_S^p)of the surface free energy apparently increases at higher degrees of oxyfluorination. The character of C-F bonding is mainly influenced by the oxyfluorination temperature or
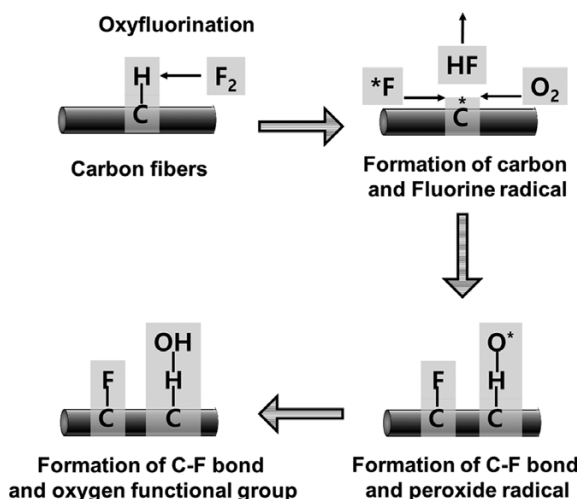
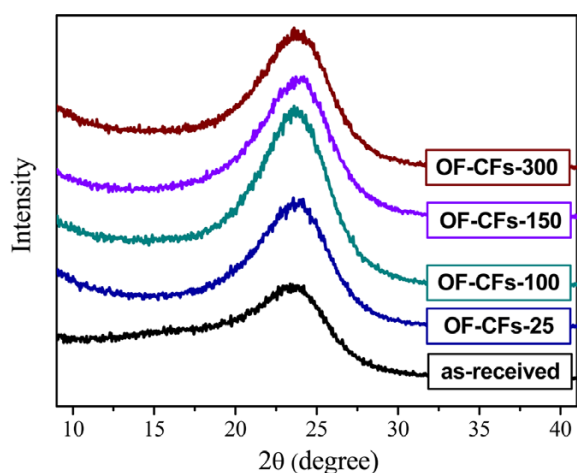**Figure 6.** A suggested oxyfluorination mechanism of carbon fibers.

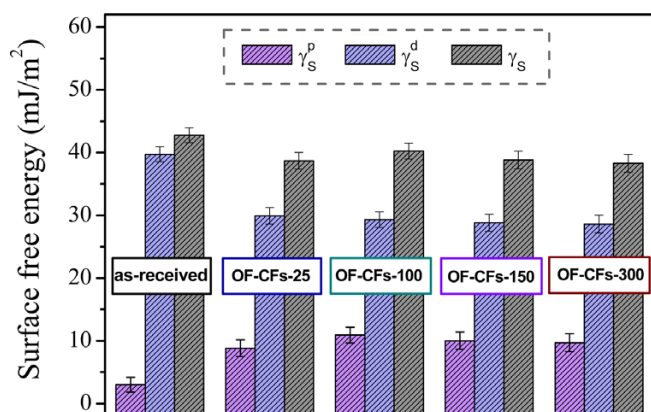**Figure 7.** XRD patterns of oxyfluorinated carbon fibers as a function of temperature.

Figure 8. Surface free energies of oxyfluorinated carbon fibers as a function of temperature.

the fluorine content. Hence, the oxyfluorination treatments can lead to a decrease in the dispersive component (γ_S^d) of the surface free energy by the damage of the graphitic character of the CFs surfaces.[50,51] Consequently, the increase in the polarity factor of the carbon fiber can improve the wettability to the epoxy matrix containing oxygen functional groups. Furthermore, the
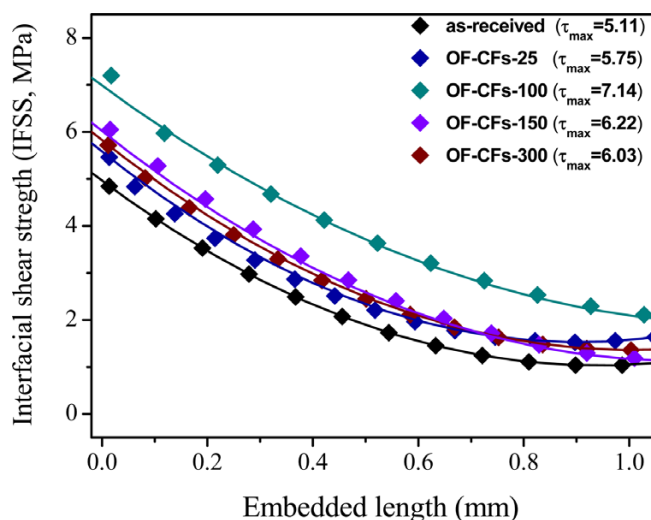

Figure 9. Geometrical pull-out behavior of oxyfluorinated carbon fibers-reinforced epoxy matrix composites.

improvement in wettability is expected to play an important role in increasing the interfacial adhesive between the fibers and the epoxy matrix.

Figure 9 shows the geometrical pull-out behavior and the IFSS values of oxyfluorinated carbon fibers-reinforced epoxy matrix composites. The geometrical pull-out behavior results as function of the embedded fiber length were obtained by the single fiber pull-out tests. All OF-CFs had higher IFSS values than as-received samples. Also, the IFSS values of OF-CFs showed a tendency to be enhanced according to increasing the oxyfluorination temperature. The maximum IFSS value is obtained for the OF-CFs-100. This result is similar to those of the carbon fiber surface analysis. The roughening and polarity of CFs surfaces affect interfacial adhesion and can be controlled by surface treatment.[52,53] Therefore, it seems likely that IFSS increased with an increase in the wettability of the CFs. The oxyfluorination can control the degree of adhesion. That is, the oxyfluorination can increases the polarity and the wettability of the CFs by forming oxygen functional groups on the CFs, thereby also
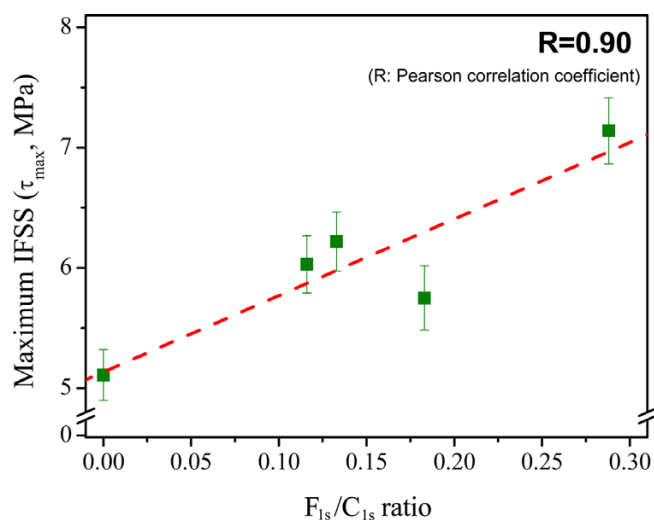

Figure 10. Dependence of interfacial shear strength (IFSS) on the F_{1s}/C_{1s} ratio of oxyfluorinated carbon fibers-reinforced epoxy composites.

improving the interfacial adhesion properties of the fibers.

Figure 10 shows the dependence of interfacial shear strength (IFSS) on the F_{1s}/C_{1s} ratio of OF-CFs. It has been reported that the mechanical properties of composites increased as appropriate functional groups are formed on the reinforcement surfaces.[54,55] Interestingly, the IFSS results are similar to the F_{1s}/C_{1s} ratio of OF-CFs according to the oxyfluorination treatments. The highest F_{1s}/C_{1s} ratio and the maximum IFSS values are indicated in the OF-CFs-100, which are significantly higher as compared with the as-received CFs. Consequently, these results show that the polarity and functional groups are the important factors in the adhesion between epoxy and carbon fiber. It could be hypothesized that the interfacial bonding force between the carbon fiber and the resin and the mechanical properties of the composites can be controlled by changing the oxyfluorination treatment conditions.

4. Conclusions

The influence of oxyfluorination on the surface properties of the OF-CFs and the geometrical pull-out behavior of carbon-fiber-reinforced epoxy matrix composites were examined. Through SEM, XPS, and surface free energy analysis, it was found that the CFs surfaces were successfully modified by the oxyfluorination treatments. The oxyfluorination increased the polarity and the wettability of the CFs by forming oxygen functional groups on the CFs, thereby also improving the interfacial adhesion properties of the fibers. Also, the IFSS values of OF-CFs showed a tendency to be enhanced at higher degrees of oxyfluorination. We confirmed that the interfacial bonding force between the carbon fiber and the epoxy resin and the mechanical properties of the composites can be controlled by changing the oxyfluonation treatment conditions.

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