

# The Physicochemical Characteristics of Modified Carbon Fibers by Fluorination

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**Abstract**—The surface of PAN-based carbon fiber was directly modified with fluorine-oxygen mixtures at room temperature. The surface characteristics of the modified fiber were determined by using X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), and dynamic contact angle analyzer. The surface free energy was also calculated with the Owens-Wendt geometric mean method using water and methylene iodide contact angle. The surface of carbon fiber was changed into hydrophilicity by the formation of semicovalent C-F bond and C-O bond depending on reaction conditions and the surface free energy of oxyfluorinated fiber was significantly increased.

Key words: Carbon Fiber, Fluorination, X-ray Photoelectron Spectroscopy (XPS), Surface Modification

## INTRODUCTION

Although many studies are being performed in order to improve the mechanical properties of carbon fibers [Yang et al., 1999; Sea et al., 1995] surface treatment of the carbon fibers is also being widely used for enhancing the bond between fibers and the matrix in composites. To improve the fiber matrix adhesion, it is necessary to increase the surface polarity, to create more sites for hydrogen bonding and to increase the possibility for covalent linking between the fiber material and the surrounding polymer matrix by achieving good stress transfer from the matrix material to the filling fiber material. Possible surface treatments include anodization [Fukunaga et al., 1999; Delamar et al., 1997; Alexander et al., 1995], plasma treatment [Montes-Moran et al., 2001; Köster et al., 2000; Bogoeva-Gaceva et al., 1997], and solution [Wu et al., 1995] and gas-phase oxidation [Lee et al., 2001]. Rhee and co-worker reported that the mechanical properties of carbon fiber-mesophase pitch composites were affected by surface treatment of carbon fiber [Rhee et al., 1987].

Recently, fluorine gas has been used as a surface treatment for many kinds of organic and inorganic plastic materials [Park and Kim, 1999], because of its very high reactivity [Chong et al., 1992]. In particular, direct fluorination using fluorine gas is a dry process that requires a relatively simple device compared with such methods as anodization. It has been widely studied in the fields of energy conversion materials containing carbon as well as surface treatment of carbon fiber [Tressaud et al., 2002; Gupta et al., 2001; Nakajima, 2000; Fukunaga et al., 2000]. In order to improve surface wettability of carbon fiber, fluorine gas or fluorine-nitrogen mixture as the fluorinating agent has been selected. On the other hand, oxyfluorination using fluorine-oxygen mixtures was proved to be a very attractive method to develop hydrophilicity of polymer surface [Khari-tonv, 2002; Toit, 1999; Schonherr et al., 1998]. We investigated the hydrophilicity of oxyfluorinated carbon fiber as a new approach to carbon fiber surface treatment and found that through this treat-

ment, wettability of the surface of surface modified carbon fibers increased drastically without any weakness compared with that of raw carbon fiber in tensile strength.

In this study, we mainly investigated the effect of the ratio of fluorine/oxygen mixtures and the reaction gas pressure on the wettability of oxyfluorinated PAN-based carbon fiber which could be determined using X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), and dynamic contact angle analyzer.

## EXPERIMENTAL

### 1. Materials and Fluorination Reaction

The high tensile strength polyacrylonitrile (PAN)-based carbon fibers (FT300 6000-99) were obtained from Torayca Inc. and exposed to the fluorine-oxygen mixtures for 30 min with changing the mole fraction of oxygen (0.1-0.9) and the reactant gas pressure (5-80 kPa) in a reactor from which all traces of oxygen had been removed at room temperature. The fiber bundles were introduced in a nickel reactor having a Teflon gasket. Prior to oxyfluorination, samples were dried under vacuum at 60 °C for 24 h. Fluorine gas (99.8% purity) was supplied by Messer Griesheim GmbH. The major impurity component was nitrogen and the amount of hydrogen fluoride was under 0.01 mol%. Trace amounts of hydrogen fluoride in the fluorine gas were removed by the sodium fluoride pellets heated at 100 °C.

### 2. Contact Angle Measurement

The contact angles of water and methylene iodide on the surface of oxyfluorinated carbon fibers were measured by CAHN (DCA-315) Dynamic Contact Angle Analyzer. Since the contact angles for single monofilaments were too small to detect, we used bundle type for measurement. Average contact angles for water and methylene iodide were used to calculate the surface free energy of the oxyfluorinated and unmodified carbon fibers by using the Owens-Wendt geometric mean method. The surface tensions of water and methylene iodide used are given in Table 1. To check the reproducibility, each sample was measured 12 times and the average value was obtained by omitting the largest and smallest ones. All contact

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**Table 1. Liquid surface tensions of water and methylene iodide**

Solution	Surface tension (mN/m)		
	$\gamma^T$	$\gamma^d$	$\gamma^p$
Water	72.8	22.1	50.7
Methylene iodide	50.8	44.1	6.7

$\gamma^T$ : total surface tension

$\gamma^d$ : dispersive surface tension

$\gamma^p$ : polar surface tension

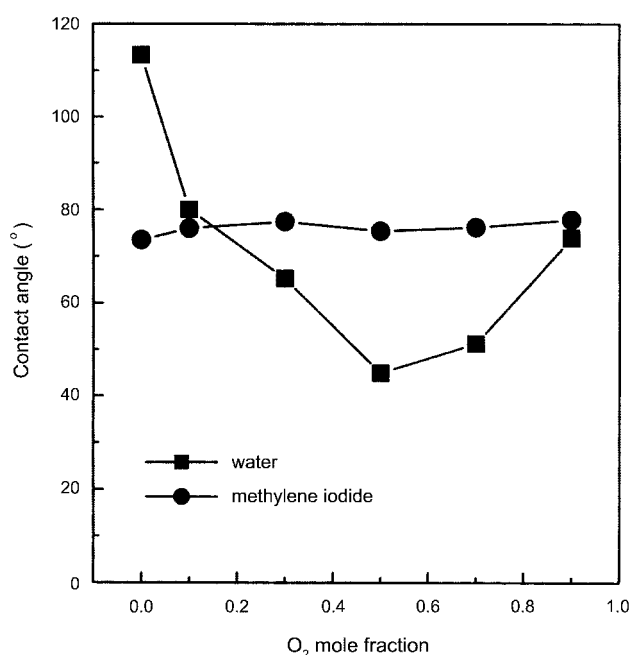
angles reported here were the average values and they had good the reproducibility with errors below 3%. Experiments were performed in an air-conditioned room at 25 °C.

### 3. X-ray Photoelectron Spectroscopy (XPS) and X-ray Diffraction (XRD)

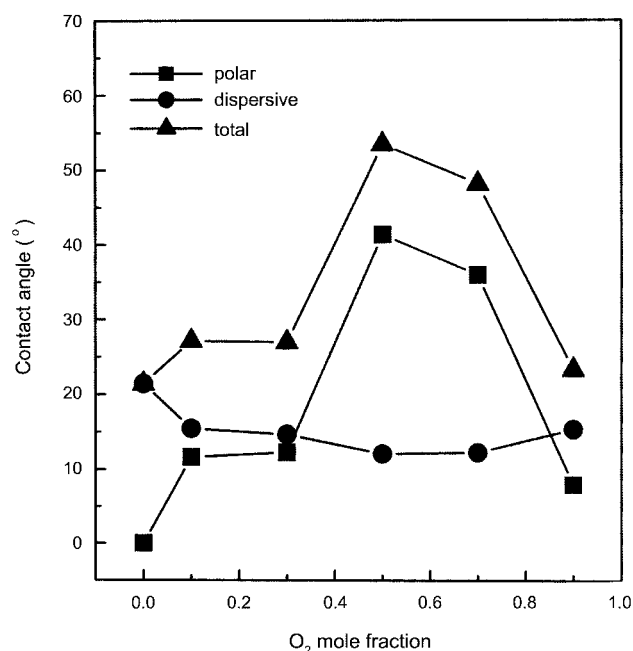
The changes of chemical species on the surface of fibers after oxyfluorination were analyzed by XPS measurement. XPS spectra were obtained with X-ray photoelectron spectroscopy (XPS, Ulvac Phi Model 5500) by using MgK radiation. The binding energies of C1s, F1s and O1s XPS peaks for surface-fluorinated samples were determined to be relative to that of C1s electron of graphite, 284.4 eV without charging correction. The X-ray diffraction pattern analysis of the oxyfluorinated fiber was also performed by using a Shimadzu XD-610 and CuK $\alpha$  radiation ( $\lambda=1.5405$ ) operated at 20 mA and 40 kV. The diffractograms were recorded in the 2 $\theta$  range of 5–80° with 0.02° resolution.

## RESULTS AND DISCUSSION

The contact angles and surface free energies of oxyfluorinated carbon fibers are shown in Figs. 1 and 2 as a function of Oxygen



**Fig. 1. The contact angles of carbon fibers at 5 kPa of the reactant gas for 30 min as a function of Oxygen mole fraction (0 of Oxygen mole fraction means unmodified carbon fiber).**



**Fig. 2. The surface free energies of carbon fibers oxyfluorinated at 5 kPa of the reactant gas for 30 min as a function of Oxygen mole fraction (0 of Oxygen mole fraction means unmodified carbon fiber).**

mole fraction in the fluorine-oxygen mixtures. The oxyfluorination was carried out at total pressure of 5 kPa for 30 min. The water contact angles of unmodified carbon fiber (Oxygen mole fraction=0) were 113° but those of the oxyfluorinated fibers were under 80°, as shown in Fig. 1. The hydrophilicity of carbon fiber was particularly improved by oxyfluorination depending on Oxygen mole fraction. In particular, the contact angle of oxyfluorinated fiber was decreased to 45° at 0.5 of Oxygen mole fraction even if the contact angle of water increased again with the further increase of oxygen mole fraction. These results indicated that oxyfluorination method using fluorine-oxygen mixtures was more effective in developing hydrophilicity of carbon fiber than fluorination using fluorine gas or fluorine-nitrogen mixtures [Chong et al., 1992]. On the other hand, methylene iodide contact angles of carbon fiber hardly changed after oxyfluorination. Total surface free energies ( $\gamma^T$ ) calculated from the contact angles of oxyfluorinated carbon fiber were highly increased with the increase of polar surface free energies ( $\gamma^p$ ), as shown in Fig. 2. However the dispersive surface free energies ( $\gamma^d$ ) of oxyfluorinated fiber were lower than that of unmodified fiber because oxyfluorination resulted in a slight decrease in the dispersive component of the surface free energy. The dispersive contribution to the surface free energy was also relatively small. The total surface free energy of oxyfluorinated carbon fibers decreased with increasing Oxygen mole fraction over 0.5. The polar components of surface free energies were, however, still higher for all oxyfluorinated samples than that for the untreated carbon fiber. This would be because surface oxygen species are gradually replacing covalently bonded fluorine. From these results, carbon fibers were oxyfluorinated at 0.5 of Oxygen mole fraction as a function of the reactant gas for 30 min at room temperature.

The contact angles and surface free energies of oxyfluorinated

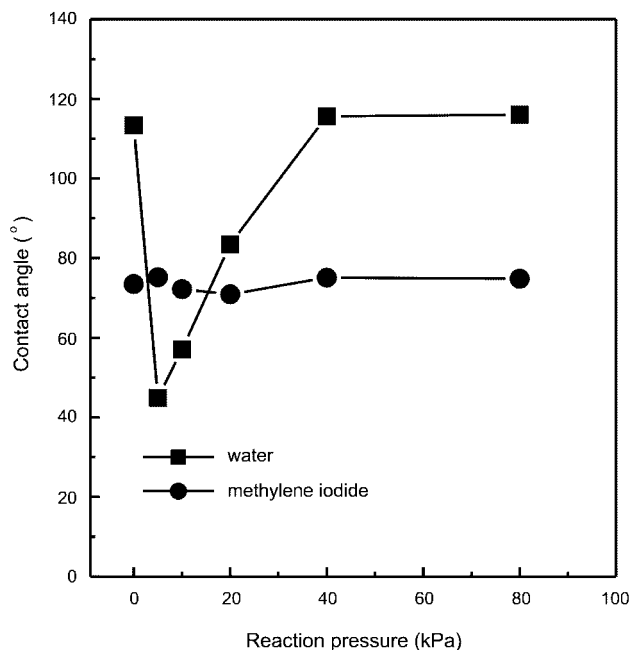


Fig. 3. The contact angles of carbon fibers oxyfluorinated at 0.5 of Oxygen mole fraction for 30 min at various the reactant gas (0 of Oxygen mole fraction means unmodified carbon fiber).

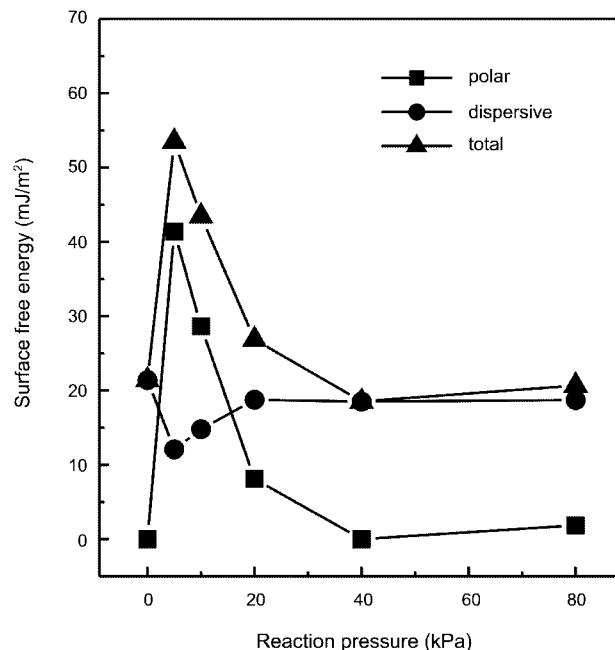


Fig. 4. The surface free energies of carbon fibers oxyfluorinated at 0.5 of Oxygen mole fraction for 30 min as a function of the reactant gas (0 of Oxygen mole fraction means unmodified carbon fiber).

carbon fibers are shown in Figs. 3 and 4 as a function of total pressure. The oxyfluorination was carried out at 0.5 of Oxygen mole fraction for 30 min. The contact angles of water on carbon fibers indicated that the oxyfluorination at a total pressure of 5 kPa increased the wettability of carbon fibers, but the wettability gradually decreased with the further increase of total pressure (Fig. 3). However, oxyfluorinated fiber showed nearly the same methylene iodide contact angle with unmodified fiber. In this case,  $\gamma^t$  decreased with the increase of the reactant gas the dependant with  $\gamma^p$  (Fig. 4), and  $\gamma^d$  showed reverse tendency to  $\gamma^p$ . On one hand, the polar component of surface free energy highly increased to 41.4 mN/m at 5 kPa, and then decreased to zero. On the other hand, the dispersion component considerably decreased at 5 kPa, and then gradually increased to 18 mN/m with increasing total pressure. In conclusion, it was

found that the polar surface free energy term,  $\gamma^p$  was more sensitive than dispersive surface free energy with oxyfluorination. From the results of contact angle and surface free energies, it was found that oxyfluorination is a very effective method in developing hydrophilicity on the surface of carbon fiber, and the best oxyfluorination conditions were 0.5 of Oxygen mole fraction at 5 kPa of reactant gas pressure for 30 min of fluorination time only at room temperature. The low total pressure and introduction of oxygen might explain the increased wettability. This behavior may be caused by formation of hydrophilic C-O and semi-covalent C-F bond. At higher total pressures, the oxyfluorinated carbon fibers demonstrated high contact angles of water, that is, high hydrophobicity as expected from explained XPS data latter.

Table 2. C1s, F1s, and O1s binding energies, relative amounts of C, F, and O in each spectrum before and after oxyfluorination

Spectra	Binding energy (eV); relative amount (%) <sup>a</sup>					Peak no. <sup>b</sup>	Assignment of the components
	Untreated	F <sub>2</sub> : O <sub>2</sub> =1 : 9	F <sub>2</sub> : O <sub>2</sub> =3 : 7	F <sub>2</sub> : O <sub>2</sub> =5 : 5	F <sub>2</sub> : O <sub>2</sub> =9 : 1		
C1s	284.24; 40	284.22; 46	284.22; 45	284.17; 40	284.23; 44	1	Graphite C
	285.22; 16	284.94; 17	284.93; 16	284.80; 16	284.98; 16	2	C-O-C, COH
	286.19; 31	285.97; 18	285.93; 14	285.92; 18	285.97; 17	3	C=O
	288.88; 13	287.42; 11	287.28; 16	287.43; 14	287.30; 12	4	O-C=O
		289.77; 8	289.80; 9	289.50; 12	289.46; 11	5	C-F
F1s	-	684.75; 40	684.86; 45	684.47; 53	684.87; 42	1	Semicovalent C-F
	-	686.19; 60	686.20; 55	685.60; 47	685.73; 58	2	Covalent C-F
O1s	531.82; 45	532.06; 71	531.93; 59	531.55; 27	532.15; 69	1	C=O
	533.09; 29	533.55; 22	533.41; 24	532.80; 47	533.59; 23	2	C-O
	534.25; 26	534.86; 7	534.85; 17	534.16; 26	534.95; 8	3	O-C=O

<sup>a</sup>Relative amount was calculated from the relative area ratio of the each peak.

<sup>b</sup>The peak numbers correspond to those in the Figs. 5, 6, and 7.

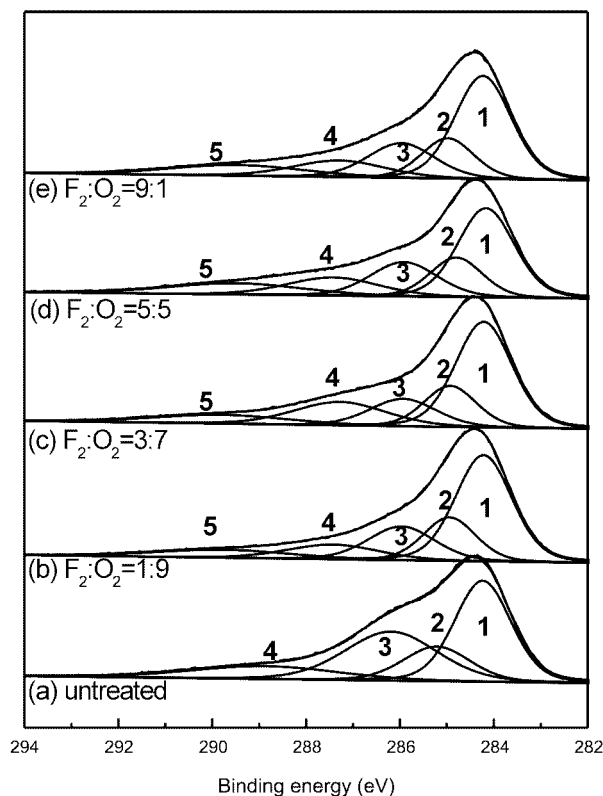


Fig. 5. C 1s spectra of unmodified and oxyfluorinated carbon fibers at 0.5 of Oxygen mole fraction for 30 min as a follow the reactant gas.

Here, it is necessary to confirm the surface functional group introduced with oxyfluorination of carbon fiber for understanding improvement of hydrophilicity. XPS analysis was performed on both the unmodified and oxyfluorinated carbon fibers with the various Oxygen mole fraction. The oxyfluorination was carried out at total pressure of 5 kPa for 30 min of fluorination time at various Oxygen mole fraction of 0.1, 0.5, 0.7 and 0.9. Figs. 5-7 show the XPS analysis of the samples. C1s, F1s and O1s binding energies, and relative amounts of C, F and O of carbon fiber before and after oxyfluorination are also summarized in Table 2.

Fig. 5 shows XPS C1s curve fit spectra for the samples. In the case of unmodified fibers (original carbon fibers, (a) in Fig. 5), four peaks appear at 284.24 eV (peak 1, graphite C, C=C bonding), 285.22 eV (peak 2, C-O-C, and C-OH bonding), 286.19 eV (peak 3, C=O bonding), and 288.88 eV (peak 4, O-C=O bonding). As one can see in Fig. 5, the C-F bonding is generated after oxyfluorination and additional peaks 5 appear at  $289.6 \pm 0.2$  eV [Tressaud et al., 1995]. Due to the presence of many defects at the surface of the fibers, fluorine can easily react with the unsaturated carbon atoms to form C-F bond [Mathur et al., 2000].

In the F 1s spectra (Fig. 6), semicovalent and covalent C-F groups appear at  $684.67 \pm 0.2$  eV (peak 1) corresponding to either fluorine atoms involved in the semicovalent C-F bonding or fluorine atoms attaching in the defects present at the surface and  $685.9 \pm 0.3$  eV (peak 2) corresponding to covalent C-F bonding. The contribution of semicovalent (peak 1) is increased at 0.5 of oxygen mole fraction (Fig. 6(D)), but it gradually decreases with increasing oxygen mole

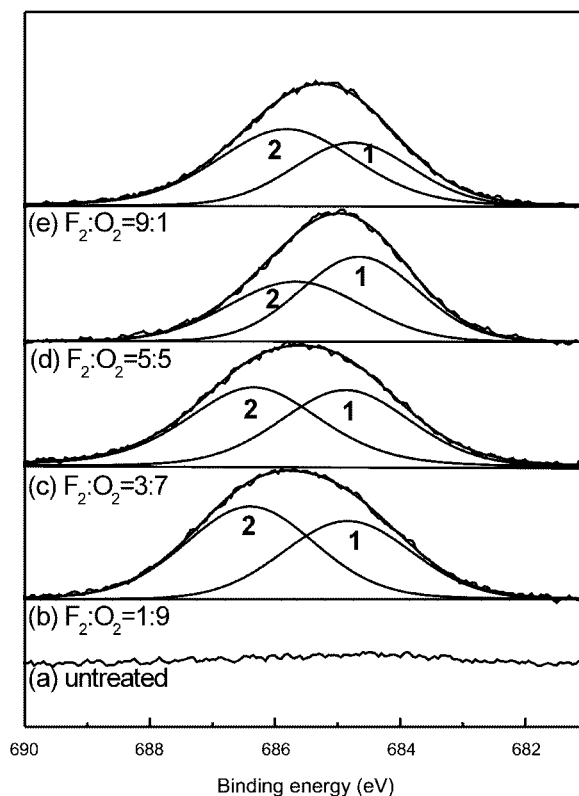


Fig. 6. F 1s spectra of unmodified and oxyfluorinated carbon fibers at 0.5 of Oxygen mole fraction for 30 min as a follow the reactant gas.

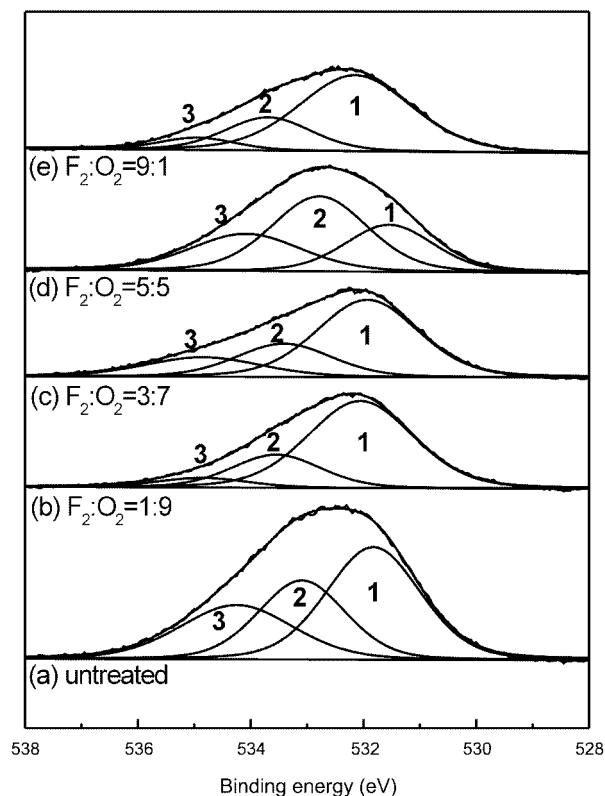


Fig. 7. O 1s spectra of unmodified and oxyfluorinated carbon fibers at 0.5 of Oxygen mole fraction for 30 min as a follow the reactant gas.

fraction. When Oxygen mole fraction is increased from 0.5 to 0.9, it is probable that attached fluorine atoms at the surface of the fibers reacted with other components shown in Table 2.

Fig. 7 shows the O 1s spectra fitted to three component peaks. Peak 1 ( $531.8 \pm 0.3$  eV) corresponds to C=O groups (ketone, lactone), peak 2 ( $533.2 \pm 0.4$  eV) to C-OH and/or C-O-C groups and peak 3 ( $534.5 \pm 0.4$  eV) to O-C=O group (carbonyl). The contribution of C=O groups (peak 1 and peak 3) is significantly decreased from 79% (unmodified fiber) to 53% after oxyfluorination at 0.5 of Oxygen mole fraction, but that of C-O bonding is considerably increased. After all, we should understand that C-O bonding at the surface of carbon fiber is more active for fluorine atom than C=O bonding. This result is consistent with oxidized carbon fiber reported by other researchers [Pittman et al., 1999]. From the results of XPS spectra, hydrophilicity of carbon fiber oxyfluorinated at 0.5 of mole fraction and 5 kPa of the reactant gas could be significantly improved by the formation of C-O bonding.

It is found that the crystal structure of carbon fibers (but not shown here) is not changed by the oxyfluorination of 0.5 of Oxygen mole fraction and 5 kPa of the reactant gas for 30 min according to the (002) diffraction line of carbon fiber. Therefore oxyfluorination for improving hydrophilicity at room temperature must be progressing only at the surface of the carbon fiber. Although the detailed characterization of the oxyfluorinated fiber is restrained, it is supposed that the surface of carbon fiber was etched by fluorine atom [Mathur et al., 2000].

## CONCLUSION

We investigated the hydrophilicity of oxyfluorinated carbon fiber as a new approach to carbon fiber surface treatment. It was found that through this treatment, wettability of the surface of surface modified carbon fibers increased drastically compared with that of raw carbon fiber. The contact angles of water on carbon fibers indicated that oxyfluorination at a total pressure of 5 kPa increased the wettability of carbon fibers, but the wettability gradually decreased with the further increase of total pressure. The total surface free energy of oxyfluorinated carbon fibers decreased with increasing Oxygen mole fraction over 0.5.

XPS analysis was also performed on both the unmodified and oxyfluorinated carbon fibers with the various Oxygen mole fraction. In the case of unmodified fibers (original carbon fibers, four peaks appear at 284.24 eV (graphite C, C=C bonding), 285.22 eV (C-O-C, and C-OH bonding), 286.19 eV (C=O bonding), and 288.88 eV (O-C=O bonding). The C-F bonding is generated after oxyfluorination and additional 5 peaks appear at  $289.6 \pm 0.2$  eV. In the F 1s spectra, semicovalent and covalent C-F groups appear at  $684.67 \pm 0.2$  eV corresponding to either fluorine atoms involved in the semicovalent C-F bonding or fluorine atoms attaching in the defects present at the surface and  $685.9 \pm 0.3$  eV corresponding to covalent C-F bonding. The contribution of semicovalent is increased at 0.5 of Oxygen mole fraction, but it gradually decreases with increasing Oxygen mole fraction. The O 1s spectra was fitted to three component peaks. Peak 1 ( $531.8 \pm 0.3$  eV) corresponds to C=O groups (ketone, lactone), peak 2 ( $533.2 \pm 0.4$  eV) to C-OH and/or C-O-C groups and peak 3 ( $534.5 \pm 0.4$  eV) to O-C=O group (carbonyl). We should understand that C-O bonding at the surface of carbon fiber is more

active for fluorine atoms than C=O bonding. From the results of XPS spectra, hydrophilicity of carbon fiber oxyfluorinated at 0.5 of mole fraction and 5 kPa of the reactant gas could be significantly improved by the formation of C-O bonding.

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## NOMENCLATURE

$\gamma^T$  : total surface tension  
 $\gamma^d$  : dispersive surface tension  
 $\gamma^p$  : polar surface tension

## REFERENCES

- Alexander, M. R. and Jones, F. R., "Effect of Electrolytic Oxidation upon the Surface Chemistry of Type A Carbon Fibres-Part II, Analysis of Derivatised Surface Functionalities by XPS, and TOF SIMS," *Carbon*, **33**, 569 (1995).
- Bogoeva-Gaceva, G., Mäder, E., Häußler, L. and Dekanski, A., "Characterization of the Surface and Interphase of Plasma-treated HM Carbon Fibres," *Composites Part A*, **28**, 445 (1997).
- Chong, Y. B. and Ohara, H., "Modification of Carbon Fiber Surfaces by Direct Fluorination," *J. Fluorine Chem.*, **57**, 169 (1992).
- Delamar, M., Desarmot, G., Fagebaume, O., Hitmi, R., Pinson, J. and Savent, J. M., "Modification of Carbon Fiber Surfaces by Electrochemical Reduction of Aryl diazonium Salts: Application to Carbon Epoxy Composites," *Carbon*, **35**, 801 (1997).
- Fukunaga, A., Ueda, S. and Nagumo, M., "Air-oxidation and Anodization of Pitch-based Carbon Fibers," *Carbon*, **37**, 1081 (1999).
- Fukunaga, A. and Ueda, S., "Anodic Surface Oxidation for Pitch-based Carbon Fibers and the Interfacial Bond Strengths in Epoxy Matrices," *Composites Sci. and Tech.*, **60**, 249 (2000).
- Gupta, V., Nakajima, T., Ohzawa, Y. and Iwata, H., "Electrochemical Characteristics and Structures of Surface-fluorinated Graphites with Different Particle Sizes for Lithium Ion Secondary Batteries," *J. Fluorine Chem.*, **112**, 233 (2001).
- Kharitonov, A. P., "Improved and Novel Surface Fluorinated Products," *J. Fluorine Chem.*, **104**, 97 (2000).
- Köster, K. F. and Schwartz, P., "Influence of Acetylene Plasma Treatment on the Torsional Fatigue of Carbon-fiber-reinforced Composite Strands," *Composites Sci. and Tech.*, **60**, 2005 (2000).
- Lee, W. H., Lee, J. G. and Peucroft, P. J., "XPS Study of Carbon Fiber Surfaces Treated by Thermal Oxidation in a Gas Mixture of O<sub>2</sub>/(O<sub>2</sub>+N<sub>2</sub>)," *Appl. Surf. Sci.*, **171**, 136 (2001).
- Mathur, R. B., Gupta, V., Bahl, O. P., Tressaud, A. and Flandrois, S., "Improvement in the Mechanical Properties of Polyacrylonitrile (PAN)-based Carbon Fibers after Fluorination," *Synthetic Metals*, **114**, 197 (2000).
- Montes-Moran, M. A., Martiez-Alonso, A., Tascon, J. M. D. and Young, R. J., "Effects of Plasma Oxidation on the Surface and Interfacial Properties of Ultra-high Modulus Carbon Fibres," *Composite: Part*

- A, **32**, 361 (2001).
- Nakajima, T., "Fluorine-containing Energy Conversion Materials," *J. Fluorine Chem.*, **105**, 229 (2000).
- Park, S. H. and Kim, S. D., "Functionalization of HDPE Powder by CF<sub>4</sub> Plasma Surface Treatment in a Fluidized Bed Reactor," *Korean J. Chem. Eng.*, **16**, 731 (1999).
- Pittman, C. U., Jiang, W., Yue, Z. R., Gardner, S., Wang, L., Toghiani, H. and Leon, C. A., "Surface Properties of Electrochemically Oxidized Carbon Fibers," *Carbon*, **37**, 1797 (1999).
- Rhee, B. S., Ryu, S. K., Joo, H. J. and Jeong, B., "Mechanical Properties of Carbon Fiber-Mesophase Pitch Composites," *HWAHAK KONGHAK*, **25**, 504 (1987).
- Schonherr, H., Hruska, Z. and Vancso, G. J., "Surface Characterization of Oxyfluorinated Isotactic Polypropylene Films: Scanning Force Microscopy with Chemically Modified Probes and Contact Angle Measurements," *Macromolecules*, **31**, 3679 (1998).
- Sea, B. K., Choo, S. Y., Lee, T. J., Morooka, S. and Song, S. K., "Tensile Strength and Morphological Investigation of SiC-coated Carbon Fibers," *Korean J. Chem. Eng.*, **12**, 416 (1995).
- Toit du, F. J. and Sanderson, R. D., "Surface Fluorination of Polypropylene; 1. Characterization of Surface Properties," *J. Fluorine Chem.*, **98**, 107 (1999).
- Tressaud, A., Gupta, V., Guimon, C. and Moguet, F., "Fluorine-intercalated Carbon Fibers: II: An X-ray Photoelectron Spectroscopy Study," *Mater. Sci. Eng. B*, **30**, 61 (1995).
- Tressaud, A., Shirasaki, T., Nanse, G. and Papirer, E., "Fluorinated Carbon Blacks: Influence of the Morphology of the Starting Material on the Fluorination Mechanism," *Carbon*, **40**, 217 (2002).
- Wu, Z., Pittman, Jr. C. U. and Gardner, S. D., "Nitric Acid Oxidation of Carbon Fibers and the Effects of Subsequent Treatment in Refluxing Aqueous NaOH," *Carbon*, **33**, 597 (1995).
- Yang, K. S., Lee, D. J., Ryu, S. K., Korai, Y., Kim, Y. J. and Mochida, I., "Isotropic Carbon and Graphite Fibers from Chemically Modified Coal-Tar Pitch," *Korean J. Chem. Eng.*, **16**, 518 (1999).