Influence of Oxyfluorination on Properties of Polyacrylonitrile (PAN)-Based Carbon Fibers

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Abstract

In this study, the oxyfluorination of PAN-based carbon fibers was undertaken at room temperature using fluorine-oxygen mixtures, and the influence of oxyfluorination on properties was investigated. The surface characteristics of the modified fiber were determined by using X-ray photoelectron spectroscopy (XPS) and dynamic contact angle analyzer. The oxyfluorination of carbon fibers was one of the more effective methods to increase surface wettability by the formation of semicovalent C-F bond and C-O bond depending on reaction conditions. 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. As increased oxyfluorination time and decreased its pressures, semi-covalent peak is increased at 0.5 of oxygen mole fraction. The total surface free energy of oxyfluorinated carbon fibers decreased with increasing oxygen mole fraction over 0.5. These results indicate that the surface of carbon fibers became much more hydrophilic after the short oxyfluorination. The surface free energy of oxyfluorinated carbon fibers progressively decreased after 10 min treatment. The polar components of surface free energies were however, significantly higher for all oxyfluorinated samples than that for the untreated carbon fiber.

Keywords : *carbon fibers, oxyfluorination, surface free energy, wettability, hydrophilicity*

1. Introduction

Carbon fibers are widely used as importance reinforcing materials such as carbon fibers-reinforced plastics, carbon-carbon composites and carbon fibers-reinforced cements. They combine a high stress factor and strength with a low density; which has led to their increasing use in high-performance construction materials. Considerable effort is being put into modifying the properties of these fibers [1, 2]. 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. Generally the oxidative methods for the modification of such non-polar carbon fiber surfaces include oxidation in various plasmas [3], oxidation in air [4], electrochemical oxidation in various electrolytes [5] and wet chemical methods such as immersing in phosphoric acid or boiling in nitric acid [6, 7]. An alternative technique to increase the surface polarity of carbon is mild fluorination using elemental fluorine [8]. Several studies on fluorinated carbon fibers have been published [7, 9-12]. In recent years, several studies on fluorine containing energy conversion materials have also been published [13, 14]. As an alternative technique, fluorine gas was used as a surface treatment agent for many kinds of organic and inorganic plastic materials because of its very high reactivity [8].

Tressaud and co-workers [15, 16] investigated the fluorination of carbon fibers in the presence of HF gas. They estimated the transport properties through electrical resistance measurements and the structure of fluorinated compounds by X-ray diffraction and electron photoelectrons by X-ray photoelectron spectroscopy. Nakajkima and co-workers [17] compared the stability of fluorine-intercalated graphite prepared from different hosts, namely, PAN- and pitch-based carbon fibers, and vapor-grown carbon fiber (VGCF). Nanse and co-workers [18-20] reported the results obtained by XPS investigation of a carbon black fluorinated with gaseous F diluted by N at room temperature.

Surface modification of carbon fibers by a fluorine-oxygen gas mixture is quite interesting for controlling the reaction rate and surface fluorine and oxygen species that govern the surface properties of carbon fiber. In this study, the surface properties of PAN-based carbon fibers at variable oxyfluorination condition such as surface treatment temperature and time, the atmosphere of fluorine and fluorine-oxygen mixtures were investigated using X-ray photoelectron spectroscopy (XPS) and dynamic contact angle analyzer.

2. Experimental

2.1. Oxyfluorination of PAN-based carbon fiber

The high tensile strength polyacrylonitrile (PAN)-based carbon fibers (FT300 6000-99) were obtained from Torayca Inc. and exposed to the fluorine-oxygen mixtures with changing the mole fraction of oxygen (0.1~0.9), oxyfluorination time (0~60 min) 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. The system was evacuated for about 2 h, and then mixed gas introduced into the reactor.

2.2. Chemical and physical characterization

The contact angles of water and diiodomethane on the surface of oxyfluorinated carbon fibers were measured by CAHN (DCA-315) dynamic contact angle analyzer. All contact angles reported here were the average values and they had well the reproducibility with errors below 3%. Experiments were performed in an air-conditioned room at 25°C. To check the reproducibility, all measurements were taken 12 times on fibers of the same samples and the average value was obtained by omitting the largest and smallest ones. The surface free energy of solid material was calculated by owens-wendt geometric mean method using contact angles of two liquid, polar and dispersion (nonpolar) components.

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, MgKα radiation). The XPS data were fitted using Gaussian-Lorentzian function. 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.
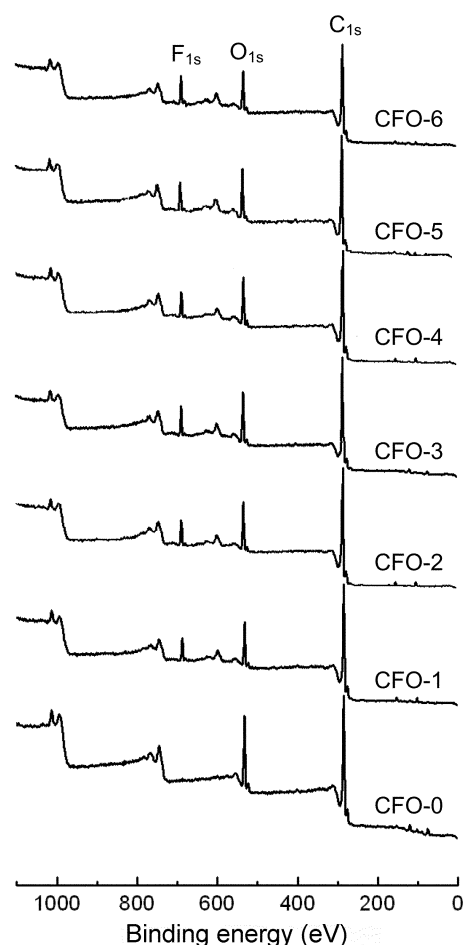
3. Results and Discussion

3.1. Surface composition and chemical bonds of oxyfluorinated samples

XPS analysis was preformed on both as-received (untreated) and selected oxyfluorinated carbon fibers. Experimental conditions for PAN-based carbon fibers are given in Table 1. XPS wide scan spectra of untreated and oxyfluorinated carbon fibers are shown in Fig. 1. The XPS spectra of untreated fibers show distinct C1s and O1s peaks with a

Table 1. Experimental conditions of PAN-based carbon fibers

	Experimental conditions		
	Total pressure (kPa)	F_2/O_2 mole ratio	Oxyfluorination time (min)
CFO-0		Untreated	
CFO-1	5	1:9	30
CFO-2	5	5:5	10
CFO-3	5	5:5	30
CFO-4	5	5:5	60
CFO-5	80	5:5	30
CFO-6	5	9:1	30

Fig. 1. XPS wide scan spectra of carbon fiber and oxyfluorinated carbon fiber. Sample number as given in Table 1.

week N1s peak, representing the major constituents of the carbon fibers investigated. No other major elements were detected from wide scan spectra at the surface of the untreated carbon fibers. Fig. 2-4 shows 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.

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

| Spectra	Assignment	Binding energy (eV) and relative amount (%)						
		CFO-0	CFO-1	CFO-2	CFO-3	CFO-4	CFO-5	CFO-6
C_{1s}	Graphitic C	284.24; 40	284.22; 46	284.30; 56	284.23; 44	284.28; 38	284.40; 45	284.23; 44
	C-O-C, COH	285.22; 16	284.94; 17		284.98; 16	285.61; 44	285.80; 39	284.98; 16
	C=O	286.19; 31	285.97; 18	285.74; 18	285.97; 17	288.17; 6	288.11; 7	285.97; 17
	O-C=O	288.88; 13	287.42; 11	287.46; 22	287.30; 12	289.65; 6	289.24; 4	287.30; 12
	C-F		289.77; 8	290.46; 4	289.46; 11	290.26; 6	290.37; 5	289.46; 11
F_{1s}	Semicovalent CF	–	684.75; 40	686.87; 83	684.87; 42	686.84; 85	686.70; 20	684.87; 42
	Covalent CF	–	686.19; 60	688.39; 18	685.73; 58	688.39; 15	688.31; 80	685.73; 58
O_{1s}	C=O	531.82	532.06	531.96	531.94	531.93	532.31	532.15
	COH	533.09	533.55	533.21	533.59	533.34	533.73	533.59
C_{1s}	Graphitic C	284.29; 42	284.39; 55	284.30; 56	284.34; 51	284.30; 61	284.38; 38	284.34; 49
	C-O-C, COH	285.85; 34	285.91; 24	285.74; 18	285.92; 22	285.82; 12	285.62; 45	285.84; 29
	C=O	287.96; 24	287.25; 15	287.46; 22	287.63; 20	287.46; 23	288.27; 12	287.80; 11
	O-C=O		290.47; 6	290.46; 4	290.47; 7	290.65; 4	290.59; 5	289.39; 11
F_{1s}	Semicovalent CF	–	684.89; 48	686.87; 83	685.71; 72	686.84; 85	686.69; 20	685.30; 54
	Covalent CF	–	686.39; 52	688.39; 18	686.51; 28	688.39; 15	688.30; 80	686.17; 46
O_{1s}	C=O	531.82	532.37	531.96	532.21	531.93	532.31	532.35
	COH	533.09	533.66	533.21	533.50	533.34	533.73	533.99
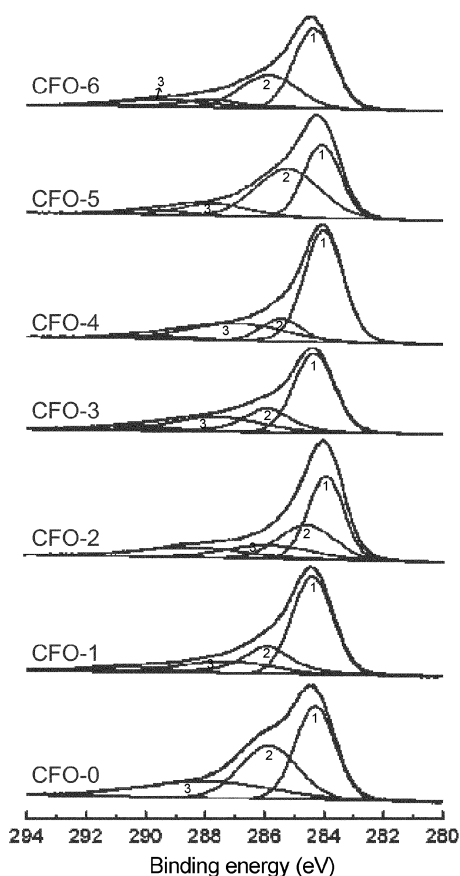
Fig. 2. X-ray photoelectron C1s spectra of untreated and oxyfluorinated PAN-based carbon fibers. Sample number as given in Table 1.

Fig. 2 shows XPS C1s curve fit spectra for the samples. In the case of untreated fibers (original carbon fibers, (a) in Fig. 2), three peaks appear at 284.29 eV (peak 1, graphite C, C=C bonding), 285.85 eV (peak 2, C-O-C, and C-OH bonding), and 287.96 eV (peak 3, O-C=O bonding). As shown in Fig. 2, the C-F bonding is generated after oxyfluorination and additional peaks 4 appear at 290.5 (peak 4, CF) [16]. Due to the presence of many defects at the surface of the fibers, fluorine can easily react with the unsaturated carbon atoms to form covalent bond [9]. The contribution of peak 1 is considerably decreased in CFO-5 sample oxyfluorinated at 80 kPa as compared to the other samples oxyfluorinated at 5 kPa.

The F1s spectra are appeared in Fig. 3. Semicovalent and covalent C-F groups appear at 684.9±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 686.3±0.3 eV (peak 2) corresponding to covalent C-F bonding. The contribution of peak (covalent C-F, CF_2) is increased with increasing total pressure. The contribution of semicovalent (peak 1) is increased at 0.5 of oxygen mole fraction, but it gradually decreases with increasing oxygen mole 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. As increased oxyfluorination time and decreased its pressures, semicovalent (peak 1) is increased at 0.5 of oxygen mole fraction.

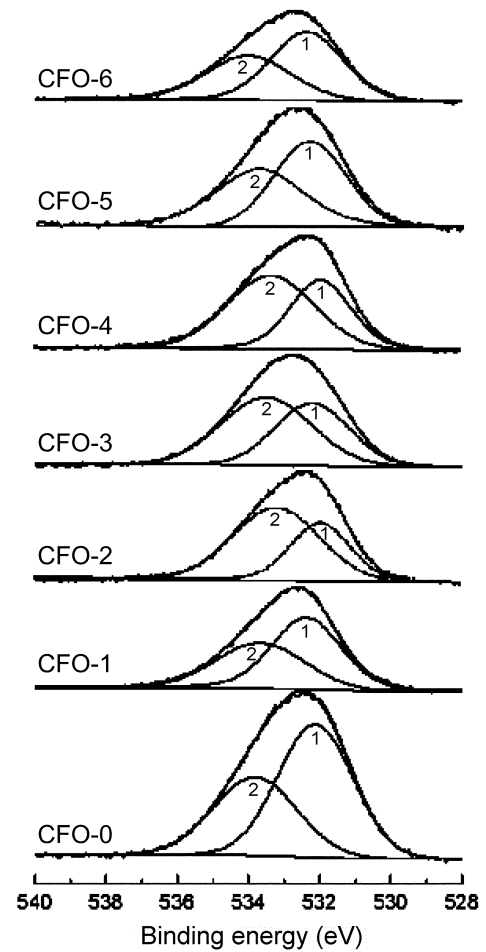Fig. 4 shows the O 1s spectra fitted to two component
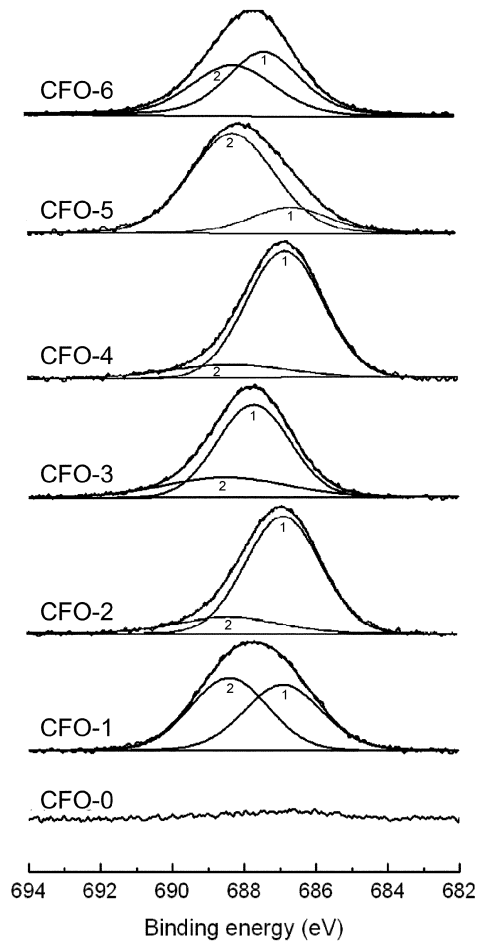
Fig. 3. X-ray photoelectron F1s spectra of untreated and oxyfluorinated PAN-based carbon fibers. Sample number as given in Table 1.

Fig. 4. X-ray photoelectron O1s spectra of untreated and oxyfluorinated PAN-based carbon fibers. Sample number as given in Table 1.

peaks; peak 1 (531.93-532.31 eV) corresponds to C=O groups (ketone, lactone, carbonyl) and peak 2 (533.34-533.73 eV) to C-OH and/or C-O-C groups. The contribution of peak 1 is significantly decreased from 61% (untreated fiber) to 43% after oxyfluorination at 0.5 of oxygen mole fraction, but that of peak 2 is considerably increased. This result is consistent with oxidized carbon fiber reported by Pittman and co-workers [21, 22]. In the CFO-2 sample oxyfluorinated for 10min, area of peak 1 was more decreased than those of others. This result indicates that fluorine and oxygen are easily introduced into the sample even at a low pressure and short time at room temperature.

### 3.2. Surface of properties of oxyfluorinated samples

The contact angles of water and diiodomethane were measured and surface free energies of oxyfluorinated carbon fibers are shown in Figs. 5 and 6 as function of oxygen mole fraction and oxyfluorination time. The water contact angles of untreated carbon fiber (CFO-0) were 113° but those of the oxyfluorinated fibers except CFO-5 sample (oxyfluorinated
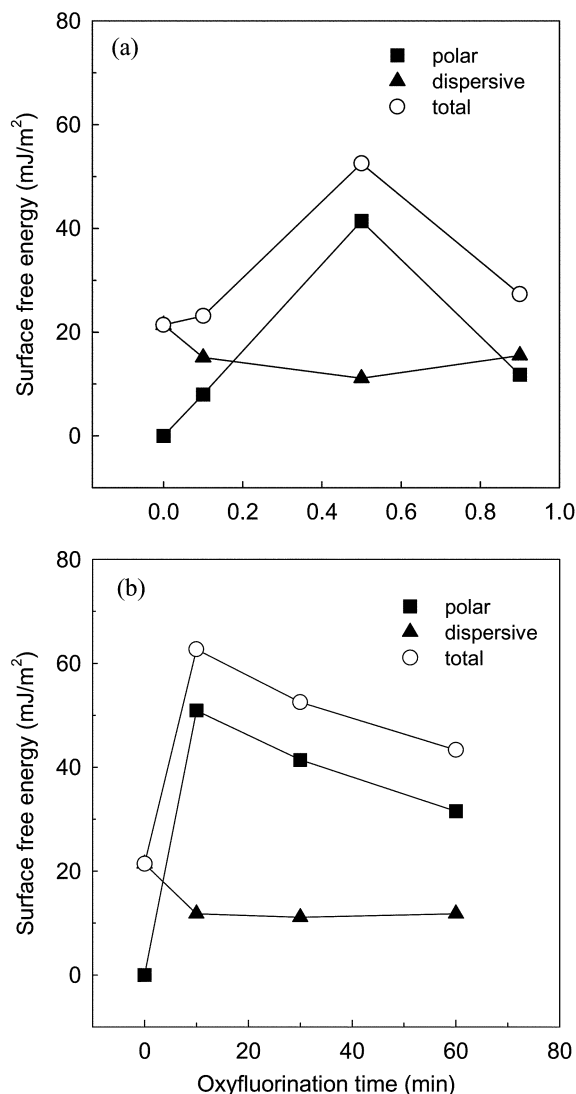
at 80 kPa) were under 80° as shown in Fig. 5. The wettability of carbon fiber was particularly improved by oxyfluorination depending on oxygen mole fraction. In particular, the contact angle of oxyfluorinated fiber was decreased to 45° at 0.5 of oxygen mole fraction even if the contact angle of water increased again with the further increase of oxygen mole fraction. The contact angles of water on carbon fibers indicate that the oxyfluorination at a total pressure of 80 kPa decreases the wettability of carbon fibers. The wettability of carbon fiber decreases with increasing total pressure and oxyfluorination time. In particular, short oxyfluorination (5-10 min) results in the realization of very high wettability, i.e. hydrophilic surface, but the contact angles of water remarkably increase again as the oxyfluorination time increased. This result is in agreement with those obtained for the oxyfluorination of polypropylene [2]. On the other hand, diiodomethane contact angles of carbon fiber hardly changed after oxyfluorination.

Total surface free energies (γ^T) calculated from the contact angles of oxyfluorinated carbon fiber were highly increased
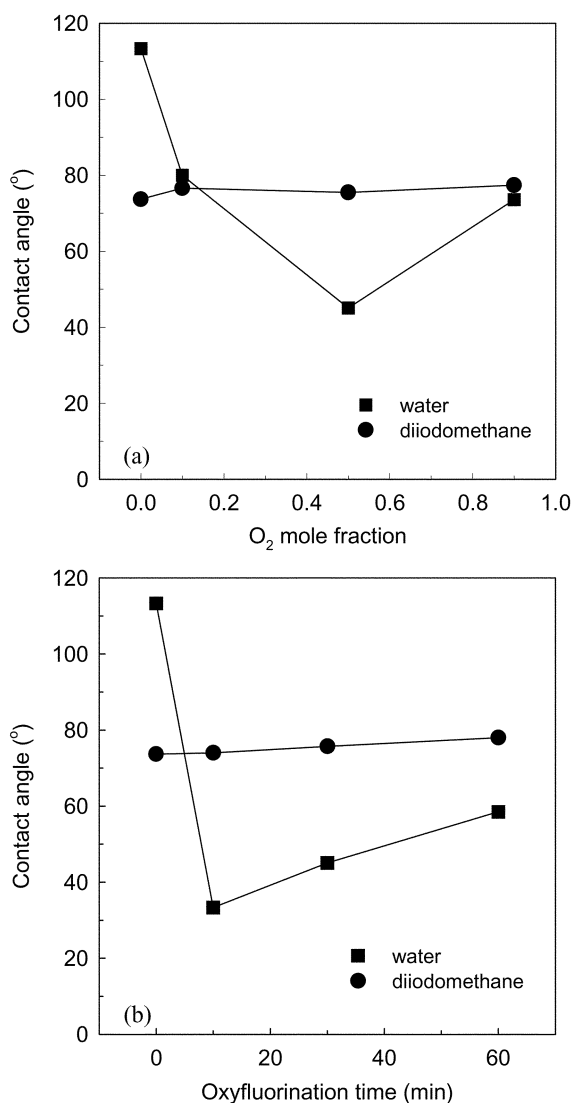
Fig. 5. The contact angles of PAN-based carbon fibers as (a) O_2 mole fraction and (b) oxyfluorination time. Sample number as given in Table 1.

Fig. 6. The surface free energies of PAN-based carbon as (a) O_2 mole fraction and (b) oxyfluorination time. Sample number as given in Table 1.

with the increase of polar surface free energies (γ^p), as shown in Fig. 6 and Table 3. However, the dispersive surface free energies (γ^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.

Table 3. Surface free energies and polarity of oxyfluorinated PAN-based carbon fibers as a function of oxyfluorination time

Oxyfluorination time (min)	γ^p (mJ/m^2)	γ^d (mJ/m^2)	γ (mJ/m^2)	$X^P = \gamma^p/\gamma$
CFO-0	0.0	21.4	21.4	0.00
CFO-1	11.8	15.5	27.3	0.43
CFO-2	50.9	11.8	62.7	0.81
CFO-3	41.4	11.1	52.5	0.79
CFO-4	31.5	11.8	43.3	0.73
CFO-5	0.0	17.5	17.5	0.00
CFO-6	8.0	15.1	23.1	0.35

In conclusion, it was found that the polar surface free energy term, polar surface free energies were 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 wettability 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.

4. Conclusion

We investigated the wettability 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 except CFO-5 sample. As the oxyfluorination time increased at a total pressure of 5 kPa, both the fluorine: carbon ratios and oxygen: carbon ratios increased. The contribution of semi-covalent C-F bond to F1s spectra is considerably decreased in sample CFO-5 oxyfluorinated at 80 kPa compared to the other samples oxyfluorinated at 5 kPa. The contribution of the covalent C-F bond is increased with the total pressure. As the total pressure of fluorine-oxygen mixture was increased, the contact angle of water remarkably decreased at first and increased again until its value was slightly higher than that of the as-received 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. These results indicate that the surface of carbon fibers became much more hydrophilic after the short oxyfluorination. The surface free energy of oxyfluorinated carbon fibers progressively decreased after 10 min treatment. The polar components of surface free energies were, however, significantly higher for all oxyfluorinated samples than that for the untreated carbon fiber. From this result, fluorine and oxygen are easily introduced into the sample even at a low pressure and short time at room temperature. And then the hydrophilicity of carbon fibers oxyfluorinated could be improved.

Acknowledgements

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